Composites in the Alumina-Zirconia system: an engineering approach for an effective tailoring of microstructural features and performances

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Abstract

The aim of this PhD study is the development of composites in the alumina-zirconia system through a powder engineering approach which allows tailoring the compositional and microstructural features, and, as a consequence, the properties of the final materials.

The experimental activities refer to two different projects. The first, named MITOR project, was devoted to the elaboration and mechanical characterization of macro-porous Alumina-Zirconia composites. It dealt with the development of a new method for the elaboration of composite cellular ceramics and with the investigation of the role of zirconia and its toughening mechanisms in porous materials, thus filling a gap in the scientific literature.

The latter, a European Project named Longlife, was dedicated to the preparation and characterization of zirconia (stabilized with ceria)-based composites for dental and spine implants. The major aim was to overcome the drawbacks proper of yttria-zirconia-based materials, concerning their stability in moisture atmosphere as well as their low toughness. Ceria-zirconia-based composites should benefit from phase transformation toughening still keeping high strength. In addition, they should not suffering of surface degradation in presence of water. So, materials characterized by high strength, high toughness with a perfect reliability and a lifetime longer than 60 years were investigated.

The first chapter collects a literature overview of the most relevant zirconia-containing materials, either dense and macro-porous, with particularly emphasis on the transformation toughening proper of such materials and its effects on the mechanical properties and stability. It is described the role of the elaboration route used to prepare the composite powders and the role of some parameters (such as nature of the dopant, microstructural features and phase composition) on the final properties. A brief introduction of the mechanical models, particularly the Gibson-Ashby model, and of the influence of the total porosity and pore size on the mechanical behavior of porous ceramics is also illustrated.

The second chapter deals with the set-up of the elaboration process of composite powders through the surface modification of commercial powders with inorganic precursors of the secondary phases. This innovative approach insures a high degree of control of the size and distribution of the second-phase grains on the surface of the parent material. Alumina-based composite powders containing 10 vol% of un-stabilized zirconia as well as tri-phasic zirconia-based composite powders containing 8 vol% of alumina and 8 vol% of an aluminate phase, were developed and characterized in terms of phase evolution and thermal behaviour. In addition, the adopted elaboration route allowed tailoring the ceria amount inside the zirconia grains: four different zirconia stabilization degree were thus investigated.

It was shown that the deep knowledge of all the involved mechanisms (such as raw powders dispersion, pH suspension, powder thermal treatments) is crucial for achieving a full control of the powders features and, consequentlty, of the final microstructures.
The third chapter is related to the MITOR project and deals with the development of macro-porous alumina-zirconia bodies through a modified gel-casting method in which a sacrificial phase was used as pore former. The selected pore former agent allows tailoring the porosity features, such as the amount of porosity, the pores shape and size distribution. Bodies with porosity amounts ranging from about 60% to 80 vol% were produced and characterized in terms of their microstructures and mechanical properties. Their properties were compared with those obtained on pure alumina components produced by the same way.

The compressive strength decreased with decreasing the relative density and, from a compositional point of view, the porous composites showed higher strength values as compared to the pure alumina ones. The well-known zirconia toughening mechanisms (transformation and microcracking toughening mechanisms) were investigated, revealing a poor influence on the mechanical properties. The improvement of the compressive strength in the composite materials can be reasonably due to their finer microstructure, being characterized by smaller grains and pores.

The last part of this thesis, related to the Longlife project, describes the development of dense Ce-TZP tri-phasic composites by slip casting and pressureless sintering.

Here, the main results of a full characterization in terms of phase composition, microstructure, mechanical (hardness, fracture strength and toughness) as well as physical properties (aging behaviour, transformability, optical properties) are presented.

The adopted surface modification technique of a commercial Ce-TZP powder was successful in developing composites having highly homogeneous and complex microstructures characterized by a very good distribution of the secondary phases (round-shaped alumina and elongated aluminate grains) inside a fine zirconia matrix.

A strong influence of the composition and sintering cycle on the microstructure and, consequently, on the mechanical properties was revealed. In particular, two completely different mechanical behaviors were observed: in some composites (when the strontium-aluminate phase is present), the strength was transformation driven and the t-m transformation phase took place well before failure. Instead, when a magnesium-aluminate is present, the tetragonal-monoclinic phase transformation took place only around the fracture surface where weak transformation bands can be observed.

Two very promising composites with high fracture strength, of about 900 MPa, and high crack resistance were found. Furthermore, the investigated composites showed high transformability and no low temperature degradation in moisture atmosphere in the time-scale of medical applications.

It was shown that these properties are strongly affected by the zirconia stabilization degree: it is necessary to carefully investigate the relationship between the final properties and the composition/microstructure architecture in order to reach the desired properties.
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Preface

The aim of this PhD study is the development of composites in the alumina-zirconia system through a powder engineering approach which allows tailoring the compositional and microstructural features, and, as a consequence, the properties of the final materials.

The experimental activities carried out during this PhD work refer to two different projects: the first, named MITOR project was carried out under the supervision of Professor Jean-Marc Tulliani of Politecnico di Torino; the latter is a European Project named Longlife, coordinated by Professor Jérôme Chevalier of INSA Lyon.

The MITOR project, titled “Development of new cellular materials by gel-casting technique: optimisation of production process and functional simulation of the microstructure” was devoted to the elaboration and mechanical characterization of macro-porous Alumina-Zirconia composites. It was carried out in collaboration with Professor Lorna Gibson of Massachusetts Institute of Technology, expert in mechanical testing and modelling of cellular materials.

Since materials containing tailored porosity exhibit unique properties and features, in the last decades an increasing number of applications that require porous ceramics have appeared, especially for environments where high temperatures, extensive wear and corrosive media are involved.

The desired properties can be achieved only by the development of a specific structure with controlled volume fraction, size, type and geometry of pores. These features can be strictly controlled by combining gel casting method with sacrificial template techniques in which the pore forming agent is added in a suitable volume fraction into the ceramic slurry.

Concerning the composition, thanks to the high strength provides by the alumina matrix and the transformation toughening effect exerstes by the zirconia particles, the Zirconia Toughened Alumina (ZTA) composites exhibit excellent mechanical properties. Most of the current applications of ZTA materials are based on dense, fully sintered materials and few works have been reported in the scientific literature on porous ZTA composites.

Therefore, the aims of the MITOR project were: i) developing new methods for the elaboration of composite cellular ceramics, with tailored microstructural features and phase composition and ii) deepening the role of zirconia and its toughening mechanisms in porous materials.

The second part of activities refers to the European Project Longlife, “Advanced multifunctional zirconia ceramics for long-lasting implants”, devoted to the preparation and characterization of Zirconia-based composites for dental and spine implants.

Zirconia ceramics are the only oxide technical ceramics able to be used as structural bio-ceramics, withstanding very high loads for long duration. Biomedical grade zirconia was developed in the 1990s to overcome the problem of alumina brittleness; particularly yttria-stabilized zirconia (Y-TZP) became a popular alternative to alumina because of higher fracture toughness, due to the stress-induced phase transformation, and high strength.
Its major application concerns femoral heads and knee replacement in orthopaedics field. Nevertheless, despite its success, the propensity of Y-TZP materials to Low Temperature Degradation (LTD) in moisture atmosphere was detrimental for the in vivo applications.

In 2001, hundreds of failures of Y-TZP heads were reported within a very short period with a negative impact for the use of zirconia in orthopaedics. At the same time, ceramics are becoming important restorative materials in dentistry and nowadays many efforts are directed towards metal-free dental prosthetic restorations. In fact, oral implant made of metal sometimes suffer lack of osseointegration and/or must be replaced because bacterial infection or allergic reactions.

Furthermore, there is a high attractiveness for a lumbar disc prosthesis that restores some mobility between two vertebrae by replacing the damaged disc. To date, such implants are developed with metals leading to wear debris and critical ion release.

It is a challenge to develop new zirconia based ceramics that can benefit from phase transformation toughening, still keeping high strength and without suffering surface degradation in presence of water, with a perfect reliability and a lifetime longer than 60 years.

These are the ambitious goals of the Longlife project, achievable by combining the development of new zirconia-based ceramics materials with new surfaces able to promote osseointegration of the implants and to limit the risk of bacterial infection.

In the framework of the Longlife project, this PhD work deals with the development of new compositions of zirconia-based materials having complex microstructures in which the formation of both round- and elongated-shaped reinforcing particles has been in-situ induced.

The MITOR and Longlife projects, above described, share a common aspect which is the set-up of new processes for the development of (nano)composite structures having tailored compositional and microstructural features, toward the achievement of increased physical and mechanical properties. Precisely, in both projects a nanopowder engineering approach was followed: it can be defined as the design, preparation and control of a composite powder, in which chemical composition, phase nature, distribution and size of the matrix and the second phases are optimized in view of the following processing steps and of the final applications. This approach will allow overcoming the limited availability of proper raw materials and better controlling the microstructural evolution and grain growth during sintering. In recent papers, biphasic nanocomposites have been elaborated by using processing routes starting from powder mixing or by nanocomposite powders obtained by coprecipitation of complex compositions. However, many drawbacks can be associated to the above routes, for instance in terms of microstructural homogeneity, purity, process reproducibility and costs. An innovative procedure, called powder-alkoxide mixture, have been recently proposed based on surface modification of commercial ceramic powders by alkoxide precursors of the second phase. However, more economic and effective products can be obtained by using inorganic salt aqueous solutions as precursors of the nano-reinforcements.

The aim of this research is to apply this innovative route, based on the surface modification of a commercial powder with inorganic precursors of the secondary phases, to develop both zirconia and alumina-based composites for applications as long-lasting components for biomedical devices or for other harsh working conditions, in terms of mechanical loads and/or high operative temperatures.

On the basis of these general considerations, an important part of this PhD work deals with the set-up of the elaboration process: many efforts have been devoted in the understanding of the influence of the process parameters on the powder features.

This manuscript has been organized as follows:

- A first bibliographic chapter in which the state of the art of the zirconia-based materials as well as porous ZTA systems is reported;
- A second, experimental chapter, devoted to illustrate the set-up of the synthesis process, used to develop both alumina-based and zirconia-based composites powders. In this part, results of the chemical-physical characterization of the powders are described and discussed;
- The third chapter focus on the elaboration and characterization of Alumina-Zirconia macroporous materials. Gel casting coupled with sacrificial template technique was used and the correlation between the micro/macrostructural features and the mechanical properties are discussed;
- The fourth chapter describes the elaboration and characterization of zirconia-based multi-phase composites prepared by slip casting and pressureless sintering. Microstructure, aging behaviour, optical and mechanical properties (in terms of hardness, strength and toughness) of such composites are reported and discussed. The relationship between phase composition/microstructure and the material performance is highlighted, allowing the identification of the optimal material in view of the final biomedical application.
Chapter 1

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The purpose of this bibliographic chapter is to report the state of the art of the alumina- and zirconia-based systems in the literature in order to define the appropriate context of this PhD work. In the first part, a brief description of the transformation toughening proper of zirconia materials will be given with particular emphasis on its effects on the mechanical properties and stability of such ceramics. For a deeper understanding, it is here described the role of some parameters, such as nature of the dopant, microstructural features and phase composition, on the final properties. It is provided a literature overview of the most relevant zirconia-containing materials, either dense and macroporous.

The second part provides a comparative description among the main elaboration routes used to prepare composite powders with the aim of highlighting their influence on the microstructure and consequently on the mechanical properties. The need of carefully tailoring the microstructure and the phase composition of ceramic composites through innovative elaboration processes will be underlined.

Finally, the third part focus on the development of porous zirconia composites, by describing the role of the fabrication process on microstructure and properties. A brief introduction of the mechanical models, particularly the Gibson-Ashby model, and of the influence of the total porosity and pore size on the mechanical behavior of porous ceramics will be also illustrated.
1. Bibliography

1.1 An overview on zirconia-based materials

Zirconia has been one of the most important ceramic materials for well over a century but the discovery of transformation toughening in 1975 heralded new visions for new high-performance applications of zirconia, ranging from bearing and wear applications to thermal barrier coatings to, most recently, biomedical applications\(^1\).

Comprehensive reviews of the crystallography and phase transformation proper of zirconia can be found in Green et al.\(^2\) and Chevalier et al.\(^3,4\)

In order to understand the reason of its impressive combination of mechanical properties, the phase diagram has to be considered. Here, the main features are reported\(^3,4\).

In pure zirconia from low to high temperature, the stable phases are the monoclinic (up to 1170 °C), the tetragonal (from 1170 to 2370 °C) and the cubic phase (above 2370 °C and up to the melting point at 2680 °C).

As illustrated in Figure 1.1, the cubic structure is a calcium fluorite-type structure where the zirconium ions occupy the summits of the cube and the center of the faces, while oxygen ions are located in the tetrahedral sites. Compared to the cubic structure, the tetragonal one presents an elongated c-axis, so that it can be described as a distorted calcium fluorite structure. It is still unclear whether the monoclinic structure is a homogeneous single phase or forms a series of incommensurate solid solutions. However, in this structure, the Zr atoms are in sevenfold coordination with the oxygen ions sublattice.

![Diagram showing the polymorphs of zirconia](Image)

Fig. 1.1: The polymorphs of zirconia: a) cubic, b) tetragonal and c) monoclinic structures.

(Green spheres: zirconia ions, red spheres: oxygen ions)\(^5\)

The lattice transformations are martensitic, meaning that: i) are diffusionless (i.e. involving only coordinated shifts in lattice positions versus transport of atoms), ii) occur athermally, implying the need for a temperature change over a range rather than at a specific temperature and iii) involve a shape deformation\(^5\).

Volume changes on cooling associated with these transformations inevitably provoke a cracking of dense, pure zirconia bodies, making them unsuitable for applications requiring an intact solid structure. In particular, a very large volume increase, estimated of about 5\(^%\)\(^5\), occurs during the tetragonal to monoclinic (t-m) transformation.
In order to avoid this transformation-induced cracking it is possible either sintering below 1170 °C (the material remains monoclinic during the whole sintering cycle, which leads to untransformable, low strength and low tough ceramic) or retaining the tetragonal or the cubic phases at room temperature by alloying with aliovalent cations.

The latter approach is the basis of the use of zirconia as a technical ceramic, and was first described by Ruff and Ebert\(^6\) almost a century ago.

At the same time, if the tetragonal phase is metastable, it is able to transform to monoclinic, if either mechanical or chemical energy is provided, giving rise to a phase transformation toughening\(^1\), as illustrated in Figure 1.2. The presence of tensile stresses in the vicinity of a crack allows the metastable tetragonal phase to transform to the monoclinic phase, leading to the formation of a transformation zone. The transformation induces compressive stresses that hinders the crack propagation. Additional contributions to toughness may result from microcracking associated with accommodation of the transformation shape strain and from crack deflection within the transformation zone ahead of the crack\(^7\).

![Figure 1.2: Concept of phase transformation toughening](image)

The first thermodynamic model of t–m transformation in zirconia was proposed by Lange \textit{et al.}\(^8\) considering a rather idealized case of a spherical tetragonal particle. The change of total free energy (\(\Delta G_{t-m}\)) as a result of the transformation is given by the following equation:

\[
\Delta G_{t-m} = \Delta G_c + \Delta U_{SE} + \Delta U_S
\]

where \(\Delta G_c\) (<0 at low temperature) is the chemical free energy (dependent on temperature and composition), \(\Delta U_{SE}\) (>0) is the strain energy associated with the transformed particles (dependent on the surrounding matrix, the size and shape of the particle, and the presence of stresses), and \(\Delta U_S\) (>0) the change in energy associated with the surface of the particle (creation of new interfaces and microcracking).

The balance between \(\Delta U_S\) and \(\Delta G_c\) explains why it is possible to retain tetragonal pure zirconia powders at room temperature (\(\Delta U_{SE}\) is zero), up to grain sizes around 24 nm\(^9,10\).
Since it is almost impossible retain such low grain size and avoid internal residual stresses, it is possible to stabilize the tetragonal phase only with:

- the help of stabilizing oxides that increase $\Delta G_c$ (or decrease $\Delta G_s$) and/or
- the existence of additional compressive stresses that decrease $\Delta U_{SE}$.

Since $\Delta U_{SE}$ is directly related to the surrounding matrix modulus, the matrix of a stiffer material (such as alumina) increases $\Delta U_{SE}$ thus stabilizing the tetragonal phase. At the same time, it is influenced by applied or internal stresses: tensile hydrostatic stresses will act to reduce $\Delta U_{SE}$, thus destabilizing the tetragonal phase.

In addition, since $\Delta U_{SE}$ and $\Delta U_s$ are not the same inside the bulk and on its surface, a different driving force for the transformation has to be considered. This discrepancy is highlighted by the fact that the critical size for the transformation is often reported on the order of a micrometer in the bulk and around a nanometer at the surface.

Following this model, zirconia ceramics may conveniently be classified into three major types according to their microstructure, as illustrated in Figure 1.3:

- PSZ (Partially Stabilized Zirconia) composed of nanometric precipitates of tetragonal or monoclinic phase embedded in a cubic matrix; generally obtained with the addition of lime or magnesia;
- TZP (Tetragonal Zirconia Polycrystals), often considered monoliths of the tetragonal phase. The most investigated are those stabilized with yttria or ceria. Moreover, composites based on TZP have been also developed and investigated, such as TZP/Alumina, TZP/Spinel;
- ZTA (Zirconia Toughened Alumina) in which tetragonal zirconia particles are embedded in a stiffer alumina matrix.

![Fig. 1.3: Schematic representation of the microstructures of the main zirconia ceramics: a) PSZ (i.e. 8 mol% MgO), b) TZP (i.e. 3 mol% Y$_2$O$_3$, 12 mol% CeO$_2$) and c) ZTA.](image)

Since the t-m phase transformation, so important for the improvement of the mechanical properties, can not occur if the tetragonal phase is stable, but takes place only in its metastability range, the classical phase equilibrium diagram has to be associated to the metastable one, that provides the t-m transformation temperatures ($T_{t-m}$) for each composition of the tetragonal grains.

As example, the zirconia-yttria phase diagram (continuous lines) and the metastable one (dotted lines) are illustrated in Figure 1.4.
An overview on zirconia-based materials

Above $T_{0}^{t-m}$, the tetragonal phase is stable; below $T_{0}^{t-m}$, the stable phase is the monoclinic one but the metastable tetragonal phase can be retained as well. Such $T_{0}^{t-m}$ temperatures give a clear indication of the stability of the tetragonal phase as a function of the thermal history followed during processing: sintering at high temperatures for long time results in a higher $T_{0}^{t-m}$ temperature, giving rise to a lower (meta)stability of the t-phase at room temperature.

The role of temperature can be understood within a thermodynamic framework following the work of Becher and Swain. They expressed the total unit volume free energy change, $\Delta F_{0}$, for the transformation as:

$$\Delta F_{0} = \Delta F_{CH} + \Delta U_e + \Delta U_s - \Delta U_I$$

where $\Delta F_{CH}$ is the chemical free energy change, $\Delta U_e$ the strain energy change, $\Delta U_s$ the surface energy change and $\Delta U_I$ the interaction term due to stress application.

$\Delta U_s$ can be considered negligible while $\Delta F_{CH}$ can be expressed as a function of the transformation entropy change, $\Delta S^{t-m}$, and temperature:

$$\Delta F_{CH} = \Delta S^{t-m} \cdot (T_0 - T)$$

where $T$ is the test temperature and $T_{0}$ the transformation temperature for an unconstrained tetragonal phase particle.

The term $\Delta U_e$ can also be stated as a function of the transformation entropy change and the martensitic temperature ($M_s$) since metastable tetragonal particles embedded within a matrix are stabilized by both matrix constraint and strain energy. Constrained, metastable particles will transform at the martensitic start temperature $M_s < T_{0}$.

Dopants (such as $Y_2O_3$) act to decrease both $M_s$ and $T_{0}$, thus creating an energy change term, $\Delta U_{se}$, equal to

$$\Delta S^{t-m} \cdot (T_0 - M_s)$$
Thus, without an applied stress, the total unit volume free energy change for transformation can be stated as:

$$
\Delta F_0 = \Delta S^{t-m} \left[ (T_0 - T) - (T_0 - M_s) \right] = \Delta S^{t-m} \cdot (M_s - T)
$$

The monoclinic phase will start to form and it will be in equilibrium with the tetragonal phase when T is decreased and just equals M_s (being $\Delta F_0 = 0$). Cooling to M_s is sufficient to initiate the transformation, and no external stress is required. However, even if T>M_s the transformation can be initiated if the stress applied, $\Delta U_I$, is sufficiently large to reduce $\Delta F_0$ to zero. The expression for $\Delta F_0$ becomes:

$$
\Delta F_0 = \Delta S^{t-m} \cdot (M_s - T) - \Delta U_I
$$

By expressing the term $\Delta U_I$ as a function of the applied stress $\sigma_a$ and the transformation dilatation strain $\varepsilon^T$ ($\Delta U_I = \sigma_a \cdot \varepsilon^T$), the following expression can be obtained:

$$
\Delta F_0 = \Delta S^{t-m} \cdot (M_s - T) - \sigma_a \cdot \varepsilon^T
$$

when $\Delta F_0$ equals to zero the transformation is initiated and $\sigma_a$ can be expressed as the critical transformation stress, $\sigma_{c-t-m}$. Thus, $\sigma_{c-t-m}$ can be stated as:

$$
\sigma_{c-t-m} = \frac{\Delta S^{t-m} \cdot (M_s - T)}{\varepsilon^T}
$$

As a consequence, the critical transformation stress increases as T is increased above M_s, for a given material, and increases as M_s decreases, for a given temperature test. In addition, the crucial role of local residual stresses as well as applied stresses on the phase transformation is highlighted.

### 1.1.1 Mechanics of transformation toughening

From a generic point of view, the transformation toughening contribution ($\Delta K^t$) can be defined as:

$$
K_c = K_0 + \Delta K^t
$$

where $K_0$ is the fracture resistance inherent to the matrix without transformation toughening.

Three principal shielding mechanisms have been identified inside $\Delta K^t$ \cite{13,14,15}: transformation toughening $\Delta K_{CT}$, transformation induced microcrack toughening $\Delta K_{CM}$ and crack deflection $\Delta K_{CD}$.

The extent of the contribution from each mechanism depends on the scale, morphology, dispersion and volume fraction of the transforming tetragonal zirconia \cite{16}.

The simplest and most used toughening mechanism concept was developed by McMeeking and Evans \cite{17} at the beginning of the 1980s.
It stated that the stress-induced transformation leads to a shielding $K_{ish}$ of the applied stress intensity factor $K_I$, thus reducing the real stress intensity factor at the crack tip, $K_{itip}$, according to

$$K_{itip} = K_I - K_{ish}$$

with

$$K_{ish} = \frac{\eta \cdot E \cdot \epsilon_T \cdot V_f \cdot h^{1/2}}{1 - \nu}$$

where $\eta$ is a factor depending on the zone shape at the crack tip and on the nature of the stress field in that zone, $E$ is the elastic modulus of the material, $\epsilon_T$ the dilatational strain, $V_f$ the transformed volume fraction of particles, $h$ the width of the transformation zone from the crack surface and $\nu$ the Poisson ratio.

Since the width of the transformation zone ($h$) is directly related to $K_I$ according to the equation:

$$h = \frac{\sqrt{3} \cdot (1 + \nu)^2}{12\pi} \left( \frac{K_I}{\sigma^c_{t-m}} \right)^2$$

in which $\sigma^c_{t-m}$ is the critical transformation stress, also $K_{ish}$ directly relates to $K_I$ by a coefficient named $C_{ish}$, $K_{ish} = C_{ish} \cdot K_I$ where $C_{ish}$ is expressed as:

$$C_{ish} = \frac{0.214 \cdot E \cdot V_f \cdot \epsilon_T \cdot (1 + \nu)}{(1 - \nu) \cdot \sigma^c_{t-m}} \left( \frac{\sqrt{3}}{12\pi} \right)$$

The higher the applied stress intensity factor, the larger the transformation zone and the larger the shielding effect.

In addition, the toughness capability of a given zirconia is directly dependent on the critical local stress leading to phase transformation, $\sigma^c_{t-m}$. It depends on the magnitude of the undercooling below the $T_{0-t-m}$ temperature: large undercooling will result in a high propensity toward the phase transformation and thus, in a low $\sigma^c_{t-m}$ and large transformation toughening.

As a consequence of the above equations, toughness continuously increases with crack length (scaling proportional to $\sqrt{h}$) until $h$ is fully developed and the toughness reaches a plateau.

Under these circumstances, the critical stress intensity is reached and the cracks start to propagate in an unstable manner, until fracture.

This is the so-called R-curve behavior shown in Figure 1.5 for various ceramic materials.
Nevertheless, it was shown that for ZrO₂-based ceramic systems there is an inverse relationship between strength and toughness: for a given flaw size, also the Griffith equation has to be taken into account.

In agreement with the Heuer description\textsuperscript{18}, the fracture strength $\sigma_f$ can be approximated as:

$$\sigma_f = \frac{(K_{\text{Griffith}} + \Delta K)}{Y(c_0 + \Delta c_f)^{1.5}}$$

where $\Delta K$ is the toughening increment as a function of the crack extension (R-curve), $\Delta c_f$ the stable crack extension prior to failure, $c_0$ the initial flaw size and $Y$ a flaw geometry constant.

Since $\Delta K$ is proportional to $\sqrt{h}$ while $\Delta c_f$ scales directly with $h$, a maximum of the strength with increasing toughness is achieved as shown in Figure 1.6.

The maximum indicates a transition from flaw-size control of strength to transformation-limited strength.
Consequently, as highlighted by Swain and Rose\textsuperscript{19}, the limitation of strength can be due to: a) the flaw size at low toughness (if the transformation toughening is low) or b) the critical stress to induce the t-m transformation at higher toughness values.
In the former case, the material is sensitive to processing flaws: in order to increase the fracture strength, it is necessary to decrease the flaw size.
Instead, in the latter case, the material is flaw and damage tolerant: in order to decrease the critical stress to induce the phase transformation, parameters such as the grain size, amount of the stabilizing oxides and compressive residual stresses have to be taken into account.

1.1.2 Stabilization versus aging

As above discussed, one way to retain the tetragonal phase at room temperature requires the use of stabilizing oxides.
They should be characterized by a large solubility in zirconia and by the ability to form fluorite-type phases over large temperature and compositional ranges. Alkaline earth oxides for PSZ and Y$_2$O$_3$ and CeO$_2$ for TZP are the most commercially used stabilizers.

Many researchers argued that stabilization is a direct consequence of the presence of oxygen vacancies introduced by aliovalent dopant\textsuperscript{20,21,22}. However, in order to explain the solubility at different temperatures, the features of the alloying elements, such as ion size, have also to be studied. Li and coworkers\textsuperscript{20,23,24} examined the effect of trivalent and tetravalent dopant ions on the local environment of zirconium ions by X-Ray absorption spectroscopy, including undersized (Fe$^{3+}$, Ga$^{3+}$, Ge$^{4+}$) as well as oversized (Y$^{3+}$, Gd$^{3+}$, Ce$^{4+}$) ions.
A comprehensive comparison among the several dopants has been reported by Chevalier et al.\textsuperscript{4}.

In the case of trivalent dopants, oxygen vacancies are generated for charge compensation: the vacancies are associated with the Zr cations in the case of oversized dopants, and with the two dopant cations in the case of undersized dopants. Both configurations favor 7-fold coordinated oxygen ions around the Zr cations and stabilize the tetragonal or even the cubic phases. However, the different availability of oxygen vacancies to Zr is responsible for the more effective stabilization of oversized trivalent dopants (the stabilization of tetragonal zirconia with oversized trivalent cations is twice as compared to undersized trivalent cations).
Therefore, the doping by trivalent oversized cations, such as Y$^{3+}$, is the most efficient in relieving the oxygen overcrowding, via both oxygen vacancies generation and dilatation of the cation network. Instead, in the case of tetravalent ions, the stabilizing effect cannot be ascribed to the generation of oxygen vacancies, but they operate as cation network stabilizers. In particular way, they act on the c and a lattice parameters, modifying the tetragonality of zirconia.
The oversized cations, because of their larger ionic size, decrease the tetragonality, inducing a more symmetric 8-fold coordination and giving rise to a random substitutional solid solution.
On the contrary, the undersized species are arranged in ordered domains, thus increasing the tetragonality.
The stabilizer effect by larger ions is due to a decreased strain energy and oxygen overcrowding around Zr$^{4+}$. The smaller ions induce a stabilizing effect due to cation ordering effect. Thus, the stabilization ability of ions follows the above trend:

trivalent oversized $>$ trivalent undersized $>$ tetravalent oversized $>$ tetravalent undersized.

For this reason, the most attractive and commercialized zirconia compositions for transformation toughening are those with $3 \text{ mol}\% \text{ of } Y_2O_3$ (typically referred as 3Y-TZP). They show exceptional mechanical properties with fracture strength of about 1300 MPa$^{25}$. Despite their excellent mechanical properties, a major drawback is present, due to the propensity to Low-Temperature Degradation (LTD) or aging in moist atmosphere.

Stress-induced transformation and aging are two alternative ways by which the metastable tetragonal phase can transform to monoclinic. Unfortunately, the aging phenomenon causes a loss of strength and generation of microcracking in presence of water in a narrow but important temperature range, typically from room temperature up to around 400 °C. This was partly responsible for the failure episode in 2001-2002 in orthopedics, when hundreds of 3Y-TZP femoral heads failed after 1-2 years in-vivo application.

It is known that LTD depends on the nature of the stabilizing oxide, on its concentration as well as on the zirconia grain size$^4$, as illustrated in Figure 1.7 where the aging behavior of several TZP and ZTA composites is compared.

As shown in the above Figure, 3Y-TZP material is the most sensitive to aging, followed by the Alumina Toughened Zirconia composite. On the other hand, aging does not occur in the timeframe of biomedical application in Ce-TZP and it is almost absent in Mg-PSZ and ZTA composites.
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In order to understand these different behaviors, the LTD mechanisms in moisture have to be investigated. To date, the involved mechanisms are not completely known: the three most important models stated in literature are reported below.

- Lange et al.\textsuperscript{27} propose, based on some TEM observations, that water reacts with Y\textsubscript{2}O\textsubscript{3} to form clusters rich in Y(OH)\textsubscript{3}, this leads to a depletion of the stabilizer in the surrounding zirconia grains which are then free to transform to monoclinic.

- According to Yoshimura et al.\textsuperscript{28} water vapor attacks the Zr-O bond, breaking it and leading to a stress accumulation due to the movement of OH\textsuperscript{−}; this, in turn, generates lattice defects acting as nucleating agents for the subsequent t–m transformation. The mechanism is illustrated in Figure 1.8.

- Chevalier et al.\textsuperscript{4} proposes that O\textsuperscript{2−} originating from the dissociation of water is responsible for the filling of oxygen vacancies (and thereby for the destabilization of the tetragonal phase), through the following steps:

  - chemical adsorption of H\textsubscript{2}O on ZrO\textsubscript{2} surface;
  - reaction of H\textsubscript{2}O with O\textsuperscript{2−} on the ZrO\textsubscript{2} surface to form hydroxyl ions OH\textsuperscript{−};
  - penetration of OH\textsuperscript{−} into the inner part by grain boundary diffusion;
  - filling of oxygen vacancies within the grains by OH\textsuperscript{−} ions, and therefore formation of proton defects;
  - occurrence of a t–m transformation when the oxygen vacancy concentration is reduced to the extent that the tetragonal phase is no longer stable.

![Fig. 1.8: Proposed degradation process of Y-TZP by the OH\textsuperscript{−} trigger mechanism\textsuperscript{28,29}](image)

The mechanisms by which the filling of oxygen vacancies results in destabilization of the tetragonal phase are still uncertain. On one hand, the decrease of oxygen vacancies content by itself causes destabilization; on the other hand, the filling of oxygen vacancies may be associated to lattice parameters changes, giving rise to stresses in the grains.
According to Chevalier et al.⁴, both phenomena account for destabilization, even if the relative importance of each of them still remains to be investigated.

However, there is evidence that aging starts in isolated grains on the surface of the material, then the transformation proceeds from a grain to the neighbor ones and it continues in the bulk of zirconia. Its kinetic is well fitted with the standard Mehl-Avrami-Johnson (MAJ) equations for a nucleation and growth process.³⁰

As consequence, aging causes a roughening of the material and microcracking generation that increases the failure probability.

In Figure 1.9 a schematic explanation of the aging mechanism and the neighbor to neighbor transformation is shown.

Fig. 1.9: Nucleation and growth at the microscale: simultaneous apparition of new monoclinic nuclei (grey grains) and extension of the existing ones. For a given surface monoclinic content, microcracks (in light blue) are formed and through them water can penetrate to the bulk, thus protruding the transformed zones. (The arrows indicate the nature of the stress)⁴

It is clear that the use of trivalent dopant cations, such as Y³⁺, favors the aging phenomenon.

However, as stated in literature⁴,³⁰,³¹, aging can be controlled: density, grain size as well the homogeneity of the phase distribution and the residual stress state on the surface, are of primary importance.

The presence of low density, especially the presence of open porosity, offers to water molecules an easy access to the bulk of the material.

The beneficial effect of reducing grain size on the aging is well recognized also if not well understood. Some researchers, focusing on a purely thermodynamic approach, identify a critical zirconia size, of about 5-10 nm for pure zirconia powders, below which the tetragonal phase is stable.³²

However, the role of residual stresses, the effect of stabilizers have also to be considered in order to estimate the critical grain size. At the same time, reducing the grain size allows decreasing the toughness and the slow crack propagation threshold (because of less efficient transformation toughening) and to an increase of grain boundaries, considered as preferential nucleation sites.³¹

Regarding residual stresses, compressive stresses due to machining delay the transformation phase and aging but the surface state is not suitable for wear applications. A fine polishing is required leading an acceptable roughness but removing compressive stresses³⁰. In addition, tensile stresses may appear along the residual scratches so machining has to be carefully controlled.
To summarize, all these aspects can slow down LTD but it can never be completely suppressed in 3Y-TZP, it is a “question of time”. However, methods to improve LTD resistance and to follow up its kinetics are today available. In response to these problems, both alternative dopants (such as ceria in Ce-TZP ceramics) and ZTA composites have been developed, both attracting a significant interest, especially for biomedical applications.

1.1.3 Ce-TZP Ceramics

Ceria-stabilized zirconia is currently one of the mostly developed ceramic materials in biomedical applications. As shown by the ceria-zirconia phase diagram illustrated in Figure 1.10, the region of (meta)stability of the tetragonal phase, highlighting by the $T_0(t/m)$ line, is wider with respect to the yttria-zirconia phase diagram (Figure 1.4).

![Fig. 1.10: Zirconia-ceria phase diagram](image)

A typical Ce-TZP composition, capable of $t$-$m$ transformation, contains 8 mol% of CeO$_2$; above 12 mol% the system is not transformable and the $T_0(t/m)$ line falls to zero at about 16 mol% of CeO$_2$.

The mostly used compositions for biomedical applications contain ceria in the range 10-12 mol% (typically referred as 10Ce-TZP and 12Ce-TZP, respectively); according to this diagram, the 10Ce-TZP is fully tetragonal at the sintering temperature and on cooling becomes metastable with respect to the formation of monoclinic at a $T_0(t/m)$ temperature of about 400 °C.

The amount of the stabilizing oxides as well as the grain size play a crucial role on the mechanical properties, as reported by Tsukuma et al. The main results regarding the monoclinic fraction on fractured surface, strength and toughness are reported in Figure 1.11.
As results, the amount of monoclinic phase formed by stress-induced transformation increased with decreasing CeO$_2$ content and with increasing grain size, since both lead to higher martensitic transformation temperature, which corresponds to a reduced stability of the tetragonal phase.

Due to the high transformability, a significant non-linear, permanent (sometimes referred as plastic) deformation was observed prior to failure: Ce-TZP ceramics show the most pronounced pseudo-plastic behavior among ceramic materials and to certain extent can bend before fracturing.

The mechanical properties, such as hardness, strength and toughness, were understood on the basis of the correlation with its high transformability. Consequently, the hardness was observed to increase and the fracture toughness to decrease as the ceria amount increases.

Instead, the optimum fracture strength was observed for ceramics containing about 10-12 mol% of ceria; out of this range, the strength decreased. On one hand, for lower ceria amount the material is too unstable and the strength is limited by the low critical stress to induce transformation. On the other hand, for higher ceria amount, the transformation is hindered and the strength is mainly limited by the critical flaw size.

In addition, as the grain size decreases, the maximum of the strength can be reached at lower ceria amounts as reported in Figure 1.12.
The influence of grain size on the martensitic temperature and on transformation toughening was investigated also by Becher and Swain\textsuperscript{11} (Figure 1.13), reporting a decrease of the critical stress to induce transformation as the grain size increases.

![Fig. 1.13: a) Martensitic start temperature and b) the transformation toughening contribution (ΔK) as a function of grain size of a 12Ce-TZP material\textsuperscript{11}](Image)

Even if the relationship between strength and grain size is still under discussion, it is well known that a microstructure refinement is needed in order to improve mechanical properties.

Regarding the LTD behavior, being the stabilizer a tetravalent ion (Ce\textsuperscript{4+}), Ce-TZP ceramics exhibit substantially reduced susceptibility to aging as compared to Y-TZP. However, a certain amount of aging degradation also occurs in these materials, probably due to native oxygen vacancies present for thermodynamic equilibrium at the sintering temperature and retained at room temperature. Anyway, the concentration of these native vacancies is much lower, being determined by the oxygen vacancy formation energy, instead of the concentration of charge compensating vacancies in the trivalent-stabilized zirconia.

Another possibility is the presence of a finite concentration of Ce\textsuperscript{3+} ions inside the zirconia lattice, so that LTD cannot be completely ruled out in these materials. In fact, as reported in literature\textsuperscript{31,36,37}, Ce\textsuperscript{4+} can be reduced to Ce\textsuperscript{3+} in a relatively easy way, even in air at room temperature.

Sergo and coworkers\textsuperscript{37} suggested that under hydrostatic tension, the chemical reduction from Ce\textsuperscript{4+} to Ce\textsuperscript{3+} is promoted, thus destabilizing the tetragonal phase since both the solubility of the Ce\textsuperscript{3+} is lower than that of Ce\textsuperscript{4+} and the oxygen vacancies formation is promoted.

Therefore, according to Sergo et al., even if a water-vapor mediated mechanism cannot be ruled out, the ageing is stress-assisted. It occurs when tetragonal zirconia is itself under significant tensile stresses, still without the presence of moisture. This condition can be reached inside a deformation band: far away from it, the residual tensile stress in the tetragonal phase is relatively small (about 100 MPa, in the case of 8.5Ce-TZP containing 15 vol% of alumina).

By contrast, as the t-m transformation proceeds, the tensile stress in the remaining tetragonal zirconia within the deformation bands increases, reaching considerable values.

A schematic representation of how a partial t-m transformation increases the tensile stress in the remaining tetragonal grains is illustrated in Figure 1.14.
1. Bibliography

(a) The whole microstructure of the sample is composed by t-ZrO$_2$ with the top surface exposed to water (liquid or vapor).

(b) One grain transforms to monoclinic; on the top surface, it is free to expand, provoking an uplift of the surface itself. On the left, right and below, the newly formed m-grain is constrained by the surrounding untransformed material. Since this grain is limited in its expansion, it implies that it is in a large compression, whereas its push against the surrounding materials gives origin to a small tensile stress, +σ$_1$.

(c) When more grains transform to monoclinic, they are less constrained and the compressive stress diminishes to −σ$_2$, whereas they put in larger tensile stress, +σ$_2$, the remaining t-ZrO$_2$.

Fig. 1.14: Schematic representation of how a partial t-m transformation increases the tensile stress in the remaining tetragonal grains$^{31}$

As experimentally proved, no transformation to the monoclinic phase, even after 100 days of test, was observed far from the deformation band, while an increase of the monoclinic concentration with time was revealed within the deformation band. In addition, this increase was observed to be parabolic with time, suggesting a bulk diffusional process of the oxygen vacancies driven by the tensile stress gradient between the center of the deformation band and the external surface as well as the undeformed surrounding material.

As a consequence, the rate of aging is greatly different among different sample zones (it is localized inside the deformation bands) and there is little or no grain size dependence.

In order to estimate the amount of the reduced cerium, the magnitude of the residual stress gradient and its relationship with the chemical potential was investigated and described by Sergo et al.$^{18}$.

The presence of a higher concentration of Ce$^{3+}$ ions in the deformation band with respect to other undeformed regions, in which Ce$^{4+}$ is the predominant oxidation state, was also revealed by XPS spectra on alumina/Ce-TZP composites tested in 4-point bending at room temperature.

As the tests were interrupted before failure, some pale yellow bands appeared on the tensile side. After 4-5 weeks the bands became darker, suggesting the cerium oxidation as confirmed by XPS measurements.
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These tests indicated that the transformation to monoclinic zirconia induces residual stresses that provide a chemical potential gradient within the material that motivates oxygen diffusion and thus the reduction from $\text{Ce}^{4+}$ to $\text{Ce}^{3+}$.

In any case, drawbacks related to the cerium reduction can be limited by controlling, for instance, the reduction conditions (such as time, temperature and atmosphere) thus to limit the reduction phenomenon only to the material surface. In fact, a reduction at low temperature leads to a more stable tetragonal phase as reported by Zhu$^{39}$: due to the presence of oxygen vacancies and the bigger ionic radius of $\text{Ce}^{3+}$, crystallographic changes occur giving rise to compressive stress that improves the strength and hardness.

In the PhD thesis of Courtois$^{34}$, an increase of hardness of 12Ce-TZP materials from 8.25 to 10.20 GPa was reported when a sintering under Argon atmosphere was carried out.

On the ground of this information, one strategy to limit long-term aging in Ce-TZP is to incorporate a second phase such that, after fabrication, the residual stress in the tetragonal phase is compressive. However, a compromise has to be reached since compressive residual stresses can hinder the transformation phase with negative effect on the mechanical properties.

In fact, on one side, Ce-TZP ceramics exhibit superior toughness and reduced aging with respect to 3Y-TZP; on the other side, they present the major drawback of lower strength, typically 600 MPa, as compared to $>1000$ MPa for 3Y-TZP. This aspect is strongly related to the difficulty of producing dense Ce-TZP with grain size as small as that of 3Y-TZP ($<0.5$ µm).

Due to the stability problems related to cerium reduction, the innovating sintering techniques, such as spark plasma sintering or hot isostatic pressing are hardly applicable to reduce grain size.

An additional phase, such as alumina, in a zirconia matrix can also be useful for applications in dentistry: from an aesthetic point of view, it can decrease the yellow component proper of Ce-TZP ceramics$^{40}$.

Thus, Ce-TZP composites are promising alternative both to refine microstructure and improve the strength and are attracting, nowadays, a lot of interest among the scientific community. Chemical stabilizers, stresses, second phase amount and grain size are interlinked and affect one another in a complex way the mechanical properties. All these parameters have to be well investigated and optimized in view of the final application.

Among the several oxides, alumina is certainly the most used inside a zirconia matrix. The first investigation belong to Sato et al.$^{41}$ in 1989, proving (as expected by the rule of mixture) an increase of the hardness and of the Young modulus of the alumina/Ce-TZP composites with respect to pure Ce-TZP ceramics.

In the following years several Authors developed alumina/Ce-TZP composites characterized by a zirconia grain size of about 1 µm$^{42,43,44}$. The best results were reached by Nawa et al.$^{45,46}$ when in 1997 developed an intra-granular microstructure in which several 10-100 nm sized $\text{Al}_2\text{O}_3$ particles were trapped into zirconia grains.
Firstly, the influence of the second phase amount on mechanical properties was investigated, as shown in Figure 1.15. As expected, hardness, elastic modulus and fracture strength increase as the alumina content increases. At the same time, a decrease of the fracture toughness, in line with the decrease of transformability, was observed with increasing alumina content.

![Graphs showing mechanical properties](image)

Fig. 1.15: a) Vickers hardness, b) fracture strength, c) fracture toughness and d) volume fraction of the monoclinic phase on fractured and polished surface of a 12Ce-TZP/alumina composites as a function of Al₂O₃ content.
Secondly, the role of the stabilizing oxides was carefully investigated: the addition of a small amount of TiO$_2$ (0.05 mol%) on 10Ce-TZP/30vol% Al$_2$O$_3$ composite allowed to reach both high strength (950 MPa) and high toughness (9.8 MPaVm by SEVNB method).

The fracture strength as a function of the ceria (a) and titania (b) amount, as reported by Nawa et al.\textsuperscript{45}, are illustrated in Figure 1.16.

These results revealed that a small amount of TiO$_2$ improves the phase stability of the tetragonal phase: being the Ti$^{4+}$ radius smaller than those of Ce$^{4+}$ and Zr$^{4+}$, titanium ions can be easily dissolved into the zirconia tetragonal lattice. In addition, they increase the grain boundaries mobility, allowing the development of an intra-granular microstructure.

Thanks to the strict control of the microstructure and composition, the mechanical properties were optimized, giving rise to the patent US 7928028 and a commercial product named NANOZR (Panasonic Electric Works, Japan\textsuperscript{47}).

The NANAZOR microstructure is depicted in Figure 1.17: thanks to the integration of Al$_2$O$_3$ and Ce-TZP particles on a scale of few nanometers in grains, bending strength and fracture toughness of 1290 MPa and 8.62 MPaVm (by following the standard ISO 6872), respectively, were achieved.
More recently, a new type of zirconia matrix composite based on a Ce-TZP/magnesium spinel system was successfully developed\textsuperscript{48}. The composition with 10Ce-TZP/16 vol\% of MgAl\textsubscript{2}O\textsubscript{4} allowed the combination of high strength (about 900 MPa) and toughness (15 MPa\textcdot$m$ by double torsion). Ce-TZP and spinel grain size of about 0.5 and 0.2 µm were respectively obtained. According to the Authors, the grain size reduction due to inter- and intragranular dispersion of the nano-scale spinel yields to an increase of the critical stress to induce transformation, still maintaining a high level of transformability. Its microstructure is illustrated in Figure 1.18.

In addition, the material resulted stable in the presence of water in the time-scale of medical applications in agreement with the standard ISO 13356. This composite was the object of a recent patent, referred as EP 2377506 A1.

Since, as above discussed, the presence of a second phase inevitably affects the transformation toughening reducing the level of transformability, a second strategy was explored. In order to increase the toughness by additional bridging/crack deflection mechanisms, the role of elongated-shape grains was studied.
The first investigations on Ce-TZP reinforced by \textit{in situ} formed strontium hexaaluminate (SrAl$_{12}$O$_{19}$, referred often as SA$_6$) were carried out by Cutler \textit{et al.} \textsuperscript{49,50}.

Both good toughness and strength values were achieved. Particularly, they developed three-phases zirconia-based composites having a composition of 12Ce-TZP/Al$_2$O$_3$/SrAl$_{12}$O$_{19}$ where the alumina was added in the range 15-30 vol\% and the aluminate phase was obtained by adding SrZrO$_3$, in the range 0.5-8 wt\%, according to the following reaction:

\[
\text{SrZrO}_3 + 6\text{Al}_2\text{O}_3 \rightarrow \text{SrAl}_{12}\text{O}_{19} + \text{ZrO}_2
\]

A zirconia matrix having Ce-TZP grain size of 1-3 \(\mu\text{m}\), equiaxed Al$_2$O$_3$ grains of 0.1-1 \(\mu\text{m}\) and SrAl$_{12}$O$_{19}$ platelets of 1-3 \(\mu\text{m}\) in length was obtained, as shown in Figure 1.19.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image1}
\caption{SEM micrographs of: a) 12Ce-TZP/15 vol\%Al$_2$O$_3$/2.0 wt\% SrZrO$_3$ and b) 12Ce-TZP/30 vol\%Al$_2$O$_3$/SrAl$_{12}$O$_{19}$.\textsuperscript{49,50}}
\end{figure}

Depending on the composition, fracture strength in the range 500-700 MPa, fracture toughness of 10-15 MPa\(\text{m}^\text{\textfrac{1}{2}}\) (by double cantilever beam) and hardness values of 10-14 GPa were obtained.

In particular, the hardness and strength increased within the alumina content, whereas the toughness showed the opposite trend.

The fracture toughness as a function of the SrZrO$_3$ addition and the strength-toughness relationships for the several studied compositions, are reported in Figure 1.20.
The above Figures clearly show the improvement of both toughness and strength of the tri-phasic composites with respect to Ce-TZP and Ce-TZP/Al₂O₃ materials. However, the three-phases composites were characterized by a lower level of transformability as compared to Ce-TZP ceramics. According to the Authors, mechanisms of crack branching and bridging can be supposed to be responsible of the toughness improvement.

In the following years, several papers reported the use of elongated grains inside zirconia-based materials: Ce-TZP composites reinforced by LaNbO₄, barium and lanthanum hexaaluminate were reported by Maschio et al.⁵¹, Ori et al.⁵², Miura et al.⁵³ and Tsukuma et al.⁵⁴. More complex quasi-ternary aluminates, such as BaMnAl₁₁O₁₈ and CeMnAl₁₁O₁₉ were investigated as well ⁵⁵,⁵⁶.

In the latter case, the hexaaluminate phase was obtained by simply adding MnO and Al₂O₃ to 12Ce-TZP powders. Thus, the formation of CeMnAl₁₁O₁₉ occurred by depletion of CeO₂ from the tetragonal matrix during sintering. The electron microprobe revealed a composition of the aluminate phase equal to CeMn₀.₉₃Al₁₁O₁₈₊ₓ, indicating a slight deviation from stoichiometry (Ln²⁺M²⁺Al₁₁O₁₉ where Ln is a lanthanide element and M a divalent cation).

In addition, a decrease of the amount of CeO₂ stabilizers in zirconia grains from 12 to 10.9 mol% and a cerium reduction from Ce⁴⁺ to Ce³⁺ were revealed.

The observed microstructure confirmed the formation of grains having magnetoplumbite structure proper of CeMnAl₁₁O₁₉ as illustrated in Figure 1.21.
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Regarding the mechanical properties, a weak improvement of fracture strength and toughness was observed as reported in Figure 1.22.

![Fig. 1.21: Microstructures of 1.5 wt% MnO doped Ce-TZP/10 wt% Al₂O₃ composite at different magnifications.](image1)

<table>
<thead>
<tr>
<th>Material</th>
<th>Fracture strength* (MPa)</th>
<th>Fracture toughness† (MPa·m⁰.⁵)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce-TZP</td>
<td>273 ± 6</td>
<td>6.5 ± 0.1</td>
</tr>
<tr>
<td>Ce-TZP/Al₂O₃</td>
<td>632 ± 34</td>
<td>6.0 ± 0.2</td>
</tr>
<tr>
<td>Ce-TZP/Al₂O₃/MnO</td>
<td>648 ± 29</td>
<td>8.5 ± 0.2</td>
</tr>
</tbody>
</table>

*Measured in four-point bending. †Short-rod measurements.

Anyway, to date, toughening mechanisms of crack bridging were always supposed even if not clearly identified. Available data give some evidence that toughening characteristics of Ce-TZP reinforced *in situ* by hexaaluminate are strongly dependent on the type and amount of the hexaaluminate.

In order to investigate the influence of the aluminate structure, in a recent work, Kern⁵⁷ compared the mechanical properties of a 12Ce-TZP composite reinforced by: *i)* β-aluminate (LaAl₁₁O₁₈ referred as LA₆) and *ii)* magnetoplumbite (SrAl₁₁O₁₉ referred as SA₆) phase.

Magnetoplumbite and β-alumina type structures are strongly correlated: both belong to the same space group and are built of spinel blocks and intermediate layers. They are different in the c/a ratio of the unit cell parameters: c/a in the range of 3.91-3.97 are proper of magnetoplumbite structures while higher c/a are related to the β-alumina structure. Generally, this depends on the ionic radius: large cations (as Ba²⁺) give rise to the latter structure while small cations (as Ca²⁺) give rise to the former one. In addition, they differ in the intermediate layer: in β-alumina it is only filled with the alkaline-earth ion and one oxygen ion. On the other hand, in the magnetoplumbite this layer is filled with alkaline-earth ion, one aluminum ion and three oxygen ions ⁵⁸.

From a microstructural point of view, Kern⁵⁷ observed a slightly higher aspect ratio and a broader size distribution of LA₆ compared to SA₆ grains, while the size of 12Ce-TZP grains was similar in both composites (1-1.5 µm). Both the materials showed high fracture resistance (in the range 7.5-9 MPaVm) and attractive strength (in the range 550-750 MPa), strongly dependent on the sintering temperature.
Anyway, 12Ce-TZP/30 vol% LA6 composites showed always higher strength and lower fracture resistance as compared to 12Ce-TZP/30 vol% SA6 composites.

A different crack propagation behavior was observed: 12Ce-TZP/30 vol% SA6 composites showed strong crack deflection at grain boundaries with cracks that propagated around SA6 grains. Moreover, a strong transformation toughening and a moderate crack tip toughness were revealed in this type of composites.

On the contrary, in the 12Ce-TZP/30 vol% LA6 composites the cracks propagated through the reinforcement; cracks running along or onto LA6 grains were stopped after a short distance and reinitiated in the vicinity. The crack tip toughness was high but the efficiency of the transformation toughening was very low.

Figure 1.23 highlights the different crack propagation behaviors between the two investigated composites.

![Crack propagation through 12Ce-TZP/30 vol% SA6 (left) and 12Ce-TZP/30 vol% LA6 (right) composites](image)

The results above discussed pointed out the role of the aluminate type and structure on the toughening mechanisms but further efforts are needed to deepen its relationship with transformation toughening proper of Ce-TZP ceramics.

### 1.1.4 Zirconia-Toughened-Alumina composites

In order to overcome the aging problems proper of Y-TZP ceramics and improve toughness and reliability, two main strategies were developed.

The first strategy, previously discussed, is related to the development of Ce-TZP based composites. The second one, described in this paragraph, is related to the development of ZTA composites.

The stability of the zirconia tetragonal phase at room temperature in ZTA composites is controlled by the possible addition of dopants but also by particle size, morphology and location (inter-or intra-granular) as well as by the presence of a stiff alumina matrix that hinders the transformation (by increasing ΔU_{SI}).
In addition, tensile residual stresses in metastable zirconia particles, due to the thermal expansion mismatch between the tetragonal zirconia and the alumina phases, can improve both the amount of transformed volume fraction and the size of transformation zone around the crack path, thus contributing to toughening and strengthening effects in ZTA composites. On the other hand, compressive residual stresses stored in the alumina matrix can greatly enhance the wear behavior of the material as compared to monolithic alumina.

In order to retain transformable tetragonal phase at room temperature, zirconia grain size must be between two critical values: the highest is the size for spontaneous transformation to the m-phase during cooling, and the lowest is the size for which the t-m transformation is hindered (even under stress). Both critical sizes depend on the stiffness of the matrix, the amount and composition of zirconia particles. The smaller the particle size, the higher the difficulties in nucleating the transformation. Also the effects of surface, strain energy and chemical free energy driving force have to be taken into account.

Concerning the aging behavior, if the zirconia phase is not microstructurally continuous (i.e., below the percolation limit), there is not a continuous pathway for diffusion of the moisture species into the ceramic so that the degradation is limited at the surface. Transformation to monoclinic was found to occur once the percolation threshold is exceeded, estimated to about 16 vol% for a random distributions of spheres. Thanks to all these features, aging can be almost suppressed in ZTA composite containing fine and well-dispersed zirconia particles below the percolation threshold.

Optimal mechanical properties were obtained with 10 vol% intergranular zirconia particles: threshold and fracture toughness of 4.0 and 5.9 MPaVm were respectively found. Thanks to a very fine microstructure with submicrometer alumina grains and nano-sized zirconia particles (Figure 1.24), high portion of metastable tetragonal phase is still retained at room temperature, allowing the transformation toughening mechanism.

![SEM micrographs of Al₂O₃-10 vol% ZrO₂ developed by De Aza et al.: alumina (the darker phase) and zirconia (the brighter phase) grains](image)

Fig. 1.24: SEM micrographs of Al₂O₃-10 vol% ZrO₂ developed by De Aza et al.: alumina (the darker phase) and zirconia (the brighter phase) grains
The attractiveness of ZTA composites is traduced by their industrial use for biomedical products. CeramTec (Plochingen, Germany) has already developed the BIOLOX Delta composites which consists of 80 vol% of aluminum oxide, providing hardness and wear resistance, 17 vol% of zirconium oxide, for improved toughness, and 3 vol% of strontium aluminate platelets to improve crack resistance. Y$_2$O$_3$ and Cr$_2$O$_3$ were also added to the raw materials in quantities of 0.6 and 0.3 wt%, respectively. The former was added in order to increase zirconia stability, the latter to increase the hardness and wear resistance.

In addition, especially in the case of yttria and chromia co-doping, the hydrothermal degradation is reduced because of the strong interaction between the chromia and zirconia phase, which prevent the diffusion of oxygen$^{62}$. The chemical composition and microstructure were optimized to achieve a ceramic material having strength of about 1200 MPa, fracture toughness of 6.5 MPa$\sqrt{m}$ and Vickers hardness of 1800 Hv$^{10}$. The corresponding microstructure is reported in Figure 1.25 where well-dispersed zirconia (white grains) and strontium aluminate (gray elongated grains) particles are embedded into alumina matrix (dark grains).

![Fig. 1.25: SEM micrograph of Biolox Delta composite$^{64}$](image)

Aging tests showed a slower increase of the monoclinic phase content on the surface of the composite with respect to the conventional monolithic zirconia materials. In spite of this, aging phenomena can still occur since the stabilization is partly achieved by yttria addition$^{65}$. Thus, further optimization can still be done.

For this purpose, CeO$_2$ was used as stabilizing oxide for zirconia in ZTA ceramics. The mechanical behavior of ZTA composites, having different Ce-TZP amount, was investigated by Yang et al.$^{66}$ revealing high strength (757-1091 MPa) and fracture toughness (6.9-9.7 MPa$\sqrt{m}$). Instead, in order to improve the fracture toughness, La$_2$O$_3$ was added to zirconia-toughened-alumina in order to form in-situ LaAl$_{12}$O$_{18}$ rodlike particles by Guo et al.$^{67}$. Depending on the aluminate content and the sintering temperature, fracture toughness and strength in the range of 5-7 MPa$\sqrt{m}$ and 400-550 MPa, respectively, were obtained.
Finally, CeMgAl\textsubscript{11}O\textsubscript{19} platelets, previously obtained by coprecipitation method, were added to ZTA by Magnani and Brillante\textsuperscript{68}, thus achieving fracture toughness in the range 5.8-8.1 MPa\textsubscript{m}.

Despite the platelets toughening through crack deflection mechanism, a less effective transformation toughening was revealed. The corresponding microstructure and crack propagation in platelets are shown in Figure 1.26.

![Microstructure and crack propagation in CeMgAl\textsubscript{11}O\textsubscript{19}-doped ZTA](image)

**Fig. 1.26:** Microstructure and crack propagation in CeMgAl\textsubscript{11}O\textsubscript{19}-doped ZTA (white grains: zirconia; black rounded-shape grains: alumina; black elongated-shape grains: CeMgAl\textsubscript{11}O\textsubscript{19})\textsuperscript{68}

Although the above description was focused on dense materials, in principle the well-known toughening mechanisms could be also effective in porous materials.

Porous ceramics are required where high temperature, wear and corrosive media are involved (i.e., filtration of molten metals, support for catalytic reaction) but recently, the use of porous ZTA ceramics as bone grafts for load-bearing applications has been envisaged\textsuperscript{69}. In fact, the achieved compressive strength of 20–27 MPa (with respect to 15 MPa of pure alumina) with a porosity of 77 vol\% could potentially meet the mechanical requirement for load-bearing applications because it is comparable to that of the cancellous bone.

In addition, the surface bioactivity of the porous ZTA ceramics can be usefully improved through a surface hydroxylation treatment, as reported by He et al.\textsuperscript{69}.

Few works concerning porous alumina-zirconia composites are present in literature without deepen the toughening mechanisms\textsuperscript{70–76}.

Among them, Pabst et al.\textsuperscript{70} and Živcová-Vlčková et al.\textsuperscript{72} developed porous alumina-zirconia composites by starch consolidation method. The bulk density, porosity, pore size and pore distribution were investigated. All these features were primarily influenced by the adopted processing route, the amount of pore forming agents as well as by the firing temperature.

However, Pabst et al.\textsuperscript{70} reported a slight decrease of the mean pore size and a change in pore shape (from convex to concave) as the zirconia amount of the ZTA composites increased. The monoclinic zirconia content detected by XRD analysis was almost the same in all the studied compositions.

Concerning the mechanical properties, they reported, as expected, a dependence of the Young’s moduli on both porosity and composition as shown in Figure 1.27.
1. Bibliography

Fig. 1.27: Effective tensile modulus as a function of the zirconia volume (on the left) and the porosity fraction (on the right); experimental data (square/triangle) compared to theoretical models (dash and solid lines)70

The mechanical properties of porous ZTA foams were deeper investigated by Vogt et al.71: alumina and alumina-zirconia (molar ratio of 70:30 referred as AZ73) were produced by replica method followed by a vacuum infiltration process and a pre-sintering cycle. In this way, the hollow struts of the ceramic skeleton can be filled up, thus improving the compression strength. Vogt and coworkers reported almost the same strength for alumina and ZTA foams before infiltration whereas an improvement of the ZTA strength of more than 300% (depending on the ppi, pores per inch, of the PU sponge used) with respect to the alumina foams was observed after infiltration.

In Figure 1.28 the compressive strength of alumina (on the left) and ZTA (on the right) foams, before and after infiltration, is reported.

Fig. 1.28: Compressive strength and weight gain before and after vacuum infiltration of alumina (on the left) and ZTA (on the right) foams sintered at 1400 °C 71

Since the infiltration step led to a better degree of the struts densification, according to the Authors, the improvement of the mechanical properties of the ZTA foams was explained by the stress-induced phase transformation.
The same conclusions were drawn by Yu et al.\textsuperscript{70} who observed, for a given porosity of about 76%, a compressive strength of 3.80 MPa in ZTA composites (having 15 vol\% of ZrO\textsubscript{2}), compared to 3.20 MPa in alumina foams. As expected, the strength was found to decrease as the porosity increases but ZTA composites showed always higher values with respect to the pure alumina.

For 83\% of porosity, the former was characterized by a strength equal to 2.07 MPa whereas a strength of 1.78 MPa was observed in the latter one. According to the Authors, the addition of ZrO\textsubscript{2} particles into Al\textsubscript{2}O\textsubscript{3} matrix contributes to the improvement of mechanical properties of the foam because of the t-m phase transformation of the ZrO\textsubscript{2} particles.

The enhancement of the mechanical properties of porous ZTA was also reported by Shen et al.\textsuperscript{74}. He studied the thermal shock resistance of such composites as a function of the porosity and the critical difference temperature: despite the results of Vogt et al.\textsuperscript{71}, Shen and coworkers\textsuperscript{74} attributed the improvement of the strength of porous ZTA to the pores in the specimens which relax the thermal shock stress and arrest the propagation of microcracks effectively, rather than to the phase transformation of ZrO\textsubscript{2}.

This conclusion was confirmed by XRD analyses of the specimens in which no monoclinic phase due to transformation was observed after different thermal shock.

The above results clearly show that there is still a gap in the scientific literature on porous ZTA materials, particularly on the mechanical characterization. The well-known toughening mechanisms of zirconia grains inside the alumina matrix in dense specimens are still uncertain in the corresponding porous materials.
1.2 Elaboration of composite powder: effect of the processing route on microstructure

In the previous section, the role of the microstructural features on the mechanical properties of composite ceramics was highlighted. As the resultant properties are a fundamental consequence of the microstructural features, in the same way the latter are a fundamental consequence of the starting material characteristics and the fabrication process and parameters. Thus, in order to obtain the desired mechanical properties, each step of the fabrication process, from synthesis to sintering, has to be carefully set up. In this section the attention will be mainly focused on the first step, the elaboration process, and its effects on microstructure.

In the case of zirconia and alumina-based composites, several elaboration techniques have been exploited, from the traditional milling–mixing to wet chemical routes (such as alkoxide-based route, sol–gel, co-precipitation).

As stated in literature, the former is the most applied method in which the powders are mainly mixed in form of oxides to produce bi and three-phasic composite materials.

When powder mixing route is performed, i) the characteristic of the starting powders and ii) the dispersion and stabilization of the mixed suspension are crucial points in order to reach a homogenous microstructure.

Concerning the characteristics of the starting powder, the size and the size distribution, the shape and morphology, the agglomeration degree, the phase composition and the surface properties have to be considered. In fact, a wide size distribution on one hand leads to a higher packing density in the green bodies. On the other hand, the control of the microstructural development during sintering could be difficult because the larger grains can coarsen, including the smaller ones.

At the same time, the particle size influences the final grains size and the densification rate. Due to the higher specific surface, the densification rate increases as the particle size decreases.

In addition, if the powder is characterized by a certain agglomeration degree, the packing in the green density will be heterogeneous, giving rise to differential sintering rates and to heterogeneous microstructures.

A further key role is played by the mixed suspension: it is well-recognized that microstructural defects, aggregates or uneven phase distribution of the second phase in the ceramic matrix can arise from a non-optimized or unstable mixed suspension. Thus, the dispersion degree (and eventually the nature of dispersant selected), the homogeneity and the rheological properties of the suspension have to be carefully studied. Furthermore, when powder mixtures contain a relevant nanoscale fraction, additional complications can arise. This implies, in fact, the use of high shear forces during dispersion, necessary to homogeneously distribute the nanoscale fraction. Separation by selective agglomeration or sedimentation during the shaping process can also occur affecting the final microstructure.
Elaboration of composite powder: effect on the processing route on microstructure

As examples, the microstructure of some zirconia-alumina composites obtained by powder mixing are reported in Figure 1.29.

![Microstructure images](image)

Fig. 1.29: Microstructure of: a) 12Ce-TZP/30 vol%\(\text{Al}_2\text{O}_3\)\(^{57}\); b) 12Ce-TZP/15 vol%\(\text{Al}_2\text{O}_3\)\(^{49}\) and c) \(\text{Al}_2\text{O}_3/50\) wt%\(\text{ZrO}_2\)\(^{68}\) obtained by powder mixing

With the aim of avoiding aggregates and improving the control of the size and distribution of the secondary phase, several wet chemical routes were exploited in the last years. Among them sol-gel and co-precipitation are the most known.

In the sol-gel method, inorganic salts or metal-organic compounds are used for the sol preparation. Then, by hydrolysis and condensation reactions, the sol is converted into a gel that has to be dried, to eliminate the exceeding liquid phase. This route allows obtaining complex shape, directly from the gel state, to control the homogeneity of chemical composition and to lower the processing temperatures. However, the used chemical products are expensive and often sensitive to moisture. Moreover, in order to avoid component segregation in the case of more than one metal cation, the hydrolysis and condensation reactions have to be carefully controlled: suitable pH solution, temperature and reactant concentration have to be set up.

An example of ZTA composites developed through sol-gel process was reported by Jayaseelan et al.\(^{80}\). The process involves the following steps: preparation of stable (hydrus) boehmite and oxalate (zirconyl oxalate, cerium zirconyl oxalate and yttrium zirconyl oxalate, for yielding unstabilized, ceria or yttria-stabilized zirconia, respectively) sols; mixing the sols in proper ratio to obtain the final precursor of the desired composition; stabilizing the mixed sol thus to form a gel; drying the gel. Then, the amorphous precursors were calcined at different temperatures in order to investigate the effect of the calcination treatment on phase composition and density.

The SEM micrographs (Figure 1.30) revealed a homogeneous microstructure in which most of the zirconia grains were located at the junctions of the alumina grains and grain boundaries.
Kakihana et al.\(^8\) demonstrated that stable suspensions of alumina powder and zirconium(IV) propoxide can be achieved by adding small quantities of glacial acetic acid. In the precipitation technique, the solubility of the desired cations dissolved in an aqueous solution is exceeded by evaporation of the liquid or by adding a chemical reactant. Thus, the precipitation of metal hydroxides is promoted. On one hand, the modification of pH and temperature of the solution allows controlling nucleation and growth mechanisms and consequently the particles morphology. On the other hand, a common problem for co-precipitation is the achievement of a suitable condition for the simultaneous precipitation of all the species present in solution.

Three different processing routes, precisely gel precipitation (GPT), precipitation (PPT) and washed precipitation (WPT) were adopted by Rana et al.\(^8\) to prepare \(\text{Al}_2\text{O}_3\)-\(\text{ZrO}_2\) composites starting from zirconium and aluminum chloride. In all the three routes, the precipitation was affected by the addition of ammonia: pH in the range of 6-6.5 (gelation point) was maintained for the GPT route whereas for the other two routes the pH was in the range 8.7-9.1.

Once the precipitation occurs, in the PPT route the supernatant liquid was drained off, while in the WPT one the precipitates were washed with hot water and alcohol. Instead, in the GPT method the concentration of the starting solution is increased until the gel becomes fully viscous. Then, all the three types of hydrated samples were dried and calcined. The processing route was found to have an effect on the crystallization behavior as well on particle size and sinterability. While GPT and PPT powders crystallize at 350 °C, no crystallization was observed in WPT powders till 650 °C. In addition, at about 950 °C both monoclinic and tetragonal zirconia phases are present in the GPT and PPT powders while only tetragonal zirconia phase was revealed in the WPT powders. The low crystallization temperature of the GPT and PPT powders can be probably due to the presence of chloride ions, while finer WPT crystallite size can help to retain the tetragonal zirconia even at high temperature. Thus, washing of precipitated powders prior to calcination, allows shifting the crystallization at higher temperature and producing very fine powders. As a consequence, WPT powders give rise to compacts with good green density as well as higher sintering density. WPT sample sintered at 1550 °C reached the maximum Vickers hardness and bending strength values.
Elaboration of composite powder: effect on the processing route on microstructure

In Figure 1.31, the particle size distribution and the relative density, as a function of the sintering temperature, of the alumina-zirconia bodies obtained by the three precipitation methods are reported.

![Graph showing particle size distribution and relative density](image)

**Fig. 1.31:** Particle size distribution (on the left) and relative density, as a function of the sintering temperature (on the right), for the three applied methods (GPT, PPT and WPT) \(^{86}\)

A wet chemical route was also used by Balmer et al.\(^ {89}\) to develop ZrO\(_2\)/Al\(_2\)O\(_3\) nanocomposites having platelike grains. According to the Authors, the scale and development of the lamellar microstructure can be controlled by setting-up the composition and heat treatment conditions.

The composites were prepared starting from an aqueous solution containing aluminum nitrate hydrate and zirconium acetate. Then, to avoid the selective crystallization of the aluminum nitrate during solvent removal, the solution was atomized onto a Teflon-coated aluminum substrate at 250 °C. An amorphous powder was thus obtained and then submitted to thermal treatments.

At temperatures below 1100 °C the tetragonal zirconia and \(\gamma\)-alumina phases with a grain size ranging between 40-100 nm were found. At 1200 °C large (2-4 \(\mu m\)) and thin platelike alumina grains, containing nanometer zirconia inclusions, were formed inside the zirconia matrix (Figure 1.32).

The electron diffraction revealed that the plates are \(\alpha\)-Al\(_2\)O\(_3\) and only occasionally had \(\beta\)-Al\(_2\)O\(_3\) structure due to Na contamination.

According to the Authors, the lamellar morphology is a consequence of the strain energy and diffusional phenomena associated with the \(\gamma\rightarrow\alpha\) phase transformation.

![Microstructure images](image)

**Fig. 1.32:** Microstructure of ZrO\(_2\)/10 mol%Al\(_2\)O\(_3\) (on the left) and ZrO\(_2\)/40 mol%Al\(_2\)O\(_3\) obtained via the solution precursor method \(^ {89}\)
An innovative precipitation method for the preparation of ZTA composites was recently reported by Liu et al.\textsuperscript{90}: alumina-zirconia composites with various zirconia contents were fabricated via cyclic solution infiltration of pre-sintered alumina preforms with zirconium oxychloride solution, followed by immersion in ammonia solution to induce precipitation. Infiltration treated samples were then dried in an oven for 24 h and then the infiltration step was repeated for 1-5 times. The influence of the drying temperature and the number of infiltration cycles on the phase evolution, microstructure and mechanical properties was investigated. Lower drying temperature (40 °C) results in a smaller free volume available for infiltration and a wider pore size distribution, while higher temperature (100 °C) leads to a narrow pore size distribution. Homogeneous microstructures with fine sized zirconia grains (100-200 nm) distributed mainly at the grain boundaries of alumina (having grain size of about 1 μm) matrix were obtained after sintering at 1500 °C. The zirconia amount is directly dependent on the number of infiltration cycles. As the infiltration treatment was repeated, the alumina grain size did not significantly change, whereas an increase of the zirconia grain size was revealed since coalescence of two nearby zirconia grains occurs. SEM images revealed a good distribution of the zirconia grains along the infiltration depth. Regarding the mechanical properties, the Vickers hardness was dependent on the drying temperature and infiltration cycles since they affect the zirconia content and grain size. The microstructures of the ZTA composites as a function of the infiltration cycles are reported in Figure 1.33.

![Microstructures of ZTA composites after 1 (left), 3 (center) and 5 (right) infiltration cycles](image)

Fig. 1.33: Microstructures of ZTA composites after 1 (left), 3 (center) and 5 (right) infiltration cycles\textsuperscript{90}

To summarize, the traditional powder mixing is a simple procedure but often lead to inhomogeneity of the final microstructure. On the other hand, the chemical routes allow a better control of the microstructure but they can be really complex to manage.

For these reasons, innovative procedures consisting in the surface modification of commercial powders with the secondary phase precursors have been exploited in the last years. They can be considered as a compromise between the powder mixing technique and the chemical ones and allow a deeper control of the final microstructure.

Among them, Schehl et al.\textsuperscript{78} developed a modified colloidal method for the production of alumina composites. Briefly, this method consist in grafting alumina commercial powders by using organic precursors (metal-alkoxides) of the secondary phases. Through an organic media (typically ethanol), the addition of metal alkoxides causes a substitution reaction between the metal alkoxide and the hydroxy groups on the particles surface as illustrated in Figure 1.34.
The modified powder is then dried under magnetic stirring at 70 °C and thermally treated so as to obtain a composite powder.

\[ \text{Surface Reaction} \]

\[ \text{O-H} + M(\text{OR})_n \rightarrow \text{O-M(OR)}_{n+m} + m \text{ROH} \]

\[ \text{H-O} \]

\[ \text{Dispersed particle in ethanol absolute} \]

Fig. 1.34: Substitutional reaction between the metal alkoxide and the hydroxy groups on the particles surface

Zircona, YAG and mullite as secondary phases were investigated: fine and homogeneous microstructure with well-distributed nanoparticles of the secondary phase in the alumina matrix were obtained as illustrated in Figure 1.35.

Fig. 1.35: SEM micrographs of: a) Al\textsubscript{2}O\textsubscript{3}/5 wt%ZrO\textsubscript{2}, b) Al\textsubscript{2}O\textsubscript{3}/2 wt%Y\textsubscript{2}O\textsubscript{3} and c) Al\textsubscript{2}O\textsubscript{3}/ 1.81 wt%ZrO\textsubscript{2}/0.88 wt% SiO\textsubscript{2} processed by colloidal route \textsuperscript{78}

The effect of the processing route on microstructure and slow crack propagation was investigated by De Aza \textit{et al.}\textsuperscript{60,61} on ZTA composites by comparing mechanical mixing and the previously described modified colloidal method.

The ZTA composites obtained by the colloidal processing route were characterized by a fine and homogeneous microstructure with ZrO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3} particles having mean size of 0.4 and 1.2 µm, respectively and a minimum number of microstructural flaws (Figure 1.36).

On the other hand, the composites obtained by the conventional powder-mixing technique showed larger zirconia and alumina grains of 0.7 and 1.7 µm, respectively. In addition, in these composites a wider grain size distribution and some agglomerates were observed (Figure 1.36).
Thanks to the finer microstructure proper of the composites processed by colloidal route, they showed better mechanical properties, particularly higher stress-intensity factor for crack-growth and slower transformation rate in autoclave, as illustrated in Figure 1.37.

Despite the method investigated by Schehl et al.\textsuperscript{78}, based on organic precursors, also inorganic precursors of the secondary phases were used to modify the surface of commercial alumina particles\textsuperscript{92}.

The effect of the processing route on the microstructure and mechanical properties of Al\textsubscript{2}O\textsubscript{3}/5 vol\%ZrO\textsubscript{2} (referred as AZ5) composites prepared both by powder mixing and wet chemical methods was recently investigated by Kern and Palmero\textsuperscript{93}.

The results revealed that when the powder mixing technique is carefully set up, AZ5 composites show finer alumina and zirconia grain size, higher strength and hardness, lower toughness and transformability with respect to those obtained from zirconia coated alumina.
The microstructure of the AZ5 composites sintered at 1500 °C for 1 h obtained by the two processing routes are compared in Figure 1.38.

![Microstructure of AZ5 bodies sintered at 1500 °C for 1 h obtained from zirconia coated alumina (on the left) and powder mixing (on the right)](image)

Even if in most cases the modified colloidal route was exploited for the production of alumina-based composites, also ceria-stabilized zirconia/alumina composites were developed by Yuan et al. 94. Precisely, they used inorganic precursors of the secondary phase to modify the surface of commercial monoclinic zirconia particles: a water solution of cerium and aluminum nitrates was added to the isopropanol suspension of zirconia powder in order to obtain 12Ce-TZP/2 wt% Al2O3 composites. The as-obtained suspension was mixed for 48 h on a multidirectional mixer, then the water and alcohol were removed from the suspension by means of a rotating evaporator at 95 °C, thus promoting the formation of ceria.

The dried powder was subsequently calcined in air at 800 °C for 1 h in order to obtain the Al2O3-doped CeO2-coated ZrO2 nanopowder. The calcined powder was shaped into small cylinders by cold isostatic pressing and sintered in a furnace in air for 1 h at 1450 °C.

The diffraction patterns of the polished sintered ceramic revealed that all CeO2 had dissolved in the ZrO2 with the formation of stabilized tetragonal zirconia and only a relatively small amount of monoclinic zirconia was found.

The microstructure of the as-obtained composites was compared with those of Ce-TZP ceramics (without the alumina phase) available in the market and prepared by co-precipitation method. In the former Ce-TZP ceramics, a broad grain size and ceria content distribution, with a fraction of highly transformable tetragonal zirconia grains, were obtained. Sub-micron Al2O3 particles were mainly located in the triple points of the zirconia matrix.

However, a small amount of submicron pores was also observed. Instead, the co-precipitated powders resulted in a material with a narrow grain size and ceria distribution. The comparison between the two microstructures is reported in Figure 1.39.
The hardness and density of the alumina and ceria-coated ZrO2 ceramics was lower than that of the co-precipitated powder-based ceramic, whereas the fracture toughness of the former was significantly higher.

According to the Authors, the higher toughness of the ceria-coated powder based ceramic can be attributed to an increase in transformability of the tetragonal zirconia grains and to the larger grain size. However, the role of the different compositions has to be also taken into account.

The above results clearly highlight the improvement of the microstructural features that can be achieved by the modified colloidal methods. However, to the best of our knowledge, these innovative routes have been exploited only for the elaboration of bi-phasic materials characterized by round-shaped grains.

In fact, when a secondary phase having elongated morphologies is required, it is often previously produced by solid state reaction or co-precipitation method and then added to the other mixture components, as in the case of lanthanum aluminate or CeMgAl11O19 exploited by Miura et al.53 and Magnani and Brillante68, respectively.

On the other hand, the aluminate phase can be obtained in situ through the reaction of metal precursor (metal zirconate, oxide, niobate) and alumina, as in the case of SrAl12O19 produced by Cutler et al.49 and Liu et al.95.

In the former case, the reaction between SrZrO3 and Al2O3 takes place whereas in the latter SrAl12O19 was obtained through the reaction of Al2O3 and Sr2Nb2O7.
1.3 Role of the processing route on microstructure and properties of macroporous ceramics

Macroporous materials are used in various forms and composition in everyday life, from polymer foams for packaging, aluminum light-weight structures in buildings and airplane, to porous ceramic for water purification.

Particularly, porous ceramics are required where high temperatures, extensive wear and corrosive media are involved. Filtration of molten metals, high-temperature thermal insulation, support for catalytic reactions, filtration of hot corrosive gases or of particulates from exhaust diesel are some example of applications in which porous ceramics have been employed.6-98

More recent applications include electrodes and supports for batteries and solid oxide fuel cells, scaffolds for bone replacement and tissue engineering, chemical sensors and solar radiation conversion.99

The properties required for each specific application are strictly controlled by composition and microstructure: changes in open and closed porosity, pore size distribution as well as pore morphology strongly affect the material’s properties. In order to tailor all of these microstructural features, the processing route used for the production of the porous materials has to be carefully selected. Also surface finishing and flaw population in the ceramic material are dependent on the adopted processing route.

The processing routes can be schematically classified into replica, sacrificial template and direct foaming methods, as illustrated by Studart et al.100 in Figure 1.40.

Fig. 1.40: Scheme of the possible processing routes used for the production of porous ceramics.100
1. Bibliography

The processing-microstructure-properties relationship for each of the main processing route was also investigated by Studart and coworkers who summarized it in the following Figures 1.41-1.42.

Fig. 1.41: Typical porosity and average pore size achieved via the replica, sacrificial template and direct foaming processing routes

Fig. 1.42: Relative compressive strength as a function of the relative density of macroporous ceramics produced via replica, sacrificial template and direct foaming methods
Role of the processing route on microstructure and properties of macroporous ceramics

The replica technique is considered as the first method used for the production of porous ceramics; it was developed in the 1960s by Schwartzwalder and Somers. It consists in the impregnation of a flexible polymer sponge with a ceramic slurry, in the removal of excess slip by squeezing or centrifuging followed by drying (a burn-out step to eliminate the polymer template) and high-temperature sintering.

Macroporous ceramics exhibiting the same morphology as the original porous material are in this way obtained.

The replica technique is today extensively used in industry to prepare ceramic filters for molten metal filtration since it is a flexible and simple method, applicable to any ceramic material that can be dispersed into a suspension. Predominantly open porous structures, with open porosity level within the range 40-95% and highly interconnected pores with sizes between 200 μm and 3 mm can be produced with this method (Figure 1.41). A disadvantage of the replica technique is that, during heating, the expansion and gas evolution of the polymer lead to significant stresses that can damage the ceramic coating producing macroscopic flaws into the struts. As a consequence, these materials are characterized by weak mechanical properties (Figure 1.42). In order to avoid this shortcoming, the wetting of the suspension on the sponge can be improved with the help of additives or a second impregnation can be performed.

The sacrificial template technique consists on the preparation of a composite comprising the ceramic matrix and a dispersed sacrificial phase homogeneously distributed through the matrix that will be extracted to generate pores (Figure 1.40). Starch, wax, polymeric beads (PMMA, PE), carbon black, sawdust, have all been used as pore formers. In the case of natural and synthetic organics, the extraction step (generally, a thermal treatment at temperatures between 200 and 600 °C for a long time) leads to the development of a large amount of gas that can damage the ceramic structure. In order to avoid it, the ceramic structure can be consolidated with the help of setting agents or binders.

One of the main advantages of the sacrificial template method in comparison with the other fabrication routes is the possibility to deliberately tailor the porosity, pore size distribution, and pore morphology of the final ceramic component through the appropriate choice of the sacrificial material. Figure 1.41 shows that the range of porosity and pore sizes that can be achieved is very broad (20-90% and 1-700 μm, respectively), as they only depend on the volume fraction and size of the sacrificial template used. The materials obtained by sacrificial method show higher mechanical strength with respect to that of porous materials produced via positive replica, since the former does not lead to flaws in the struts (Figure 1.42).

Finally, in direct foaming methods, porous materials are produced by incorporating air into a suspension which then needs to be set in order to maintain the porous morphology. The blowing agent can be a volatile liquid or solid or a gas that can be developed in situ by chemical reaction. The total porosity is related to the amount of gas incorporated into suspension whereas the pore size is determined by the stability of the wet foam.
Therefore, the crucial point is the approach used to stabilize the air bubbles: stabilization with surfactants and particles are the most used approaches.

Direct foaming allows manufacturing of both closed and open-cell foams: as shown in Figure 1.41 porosity and pore size in the range 40-93% and 10-300 μm respectively, can be achieved.

The as-obtained materials, generally, exhibit remarkable mechanical properties since dense ceramic struts with a limited amount of defects are produced.

Particularly when highly porous ceramic with small pores are required, the gel casting technique can be combined with all the three examined methods. Gel casting is a well-established colloidal process in which a macromolecular network (formed by the action of temperature or/and chemical cross-linking reaction) is created to hold the ceramic particles together. High strength and complex shape green bodies are the two main advantages of the gel casting method.

Organic monomers (i.e. acrylamide and urea-formaldehyde) are widely used even if alternative natural gelling agents (like agar, gelatin, egg white, glucose) have been extensively tested in these last years\textsuperscript{106}. In addition, the combination of gel casting and freeze-drying technologies allows the fabrication of porous ceramic with unidirectional pore channels, as reported by Huang et al.\textsuperscript{107}.

To conclude, advance in fabrication technique now offers the possibility to manufacture cellular materials possessing structure and properties required for a specific application but the adopted processing route should be carefully selected.

1.3.1 Mechanical models and behavior of porous ceramics

The mechanical properties of cellular solids are strongly affected by their microstructural features, such as the relative density, the cell morphology, the pore size distribution and the nature of the ceramic material. Among them, the most studied factor is the relative density, $\rho^*/\rho_s$, defined as the ratio between the density of the cellular solid ($\rho^*$) and that of the solid from which it is made ($\rho_s$); it is equivalent to the volume fraction of the solid.

From an empirical point of view, the physical properties ($A$), including hardness, strength, Young’s modulus, thermal conductivity and diffusivity, can be correlated to the porosity ($\rho$) by the following exponential relationship\textsuperscript{96}:

$$A = A_0 \cdot \exp(-b_\alpha \cdot \rho)$$

where $A_0$ is the value of the property at zero porosity and $b_\alpha$ is a measure of the rate of decrease in $A$ with increasing the porosity $\rho$ and it is related to the pore characteristics.

Thus, Rice\textsuperscript{96} associated the effective properties of porous media with pore shape and packing arrangement by noting that these geometric features are related to the minimum solid area (MSA) that transfers load. However, the above equation holds for low and intermediate porosity ranges, roughly from 0 to 30-40 vol% of porosity\textsuperscript{108,109}: when the porosity exceeds this limit, the material property $A$ may decrease faster with increasing porosity than would be predicted by the above
equation. It is therefore extremely important to identify consistent predictive models that can reliably assess the consequences of all the microstructural features (such as shape, dimension and distribution of cavities and pores) on the mechanical behavior of the real components.

The mechanical response of cellular solids has been modeled by representing the cellular structure in several ways. Initial models analyzed a unit cell such as a hexagon in two dimensions or a 12-14-faced polyhedron in three dimensions\textsuperscript{110}. The geometry of the unit cell makes the analysis tractable but may not give an exact representation of the real material.

A simpler approach was developed by Gibson and Ashby\textsuperscript{111} who underlined the dependence of the foam properties on the relative density and the solid properties requiring experiments to determine the constants related to the cell geometry.

A third different approach, aimed to design a model able to reply as accurately as possible the microstructure of porous materials, is based on digital image based finite element modeling (DIB-FEA)\textsuperscript{112}. The general idea is that of building up a finite element model that includes all the relevant microstructural features starting directly from real micrographs of its cross-sections, and carrying out structural and functional analyses on the designed model.

Gibson and Ashby\textsuperscript{111}, in particular, have given the most important contribution to the construction of the theoretical basis for calculating the stress and strain fields inside cellular solids.

The main general assumption is that of a uniform spatial distribution of cavities and pores: the real material is modeled as a repetitive spatial structure of elementary cells having cubic geometry.

On the basis of the interconnections among the pores, two structures were described: open-cell foams if the solid is present only at the edge of the polyhedron, while closed-cell foams have solid membranes over the faces of the polyhedron.

The cubic unite cell for both the structures are shown in Figure 1.43.

![Fig. 1.43: Cubic model of unit cell for a) closed-cell and b) open-cell foams](image)

As a consequence of the adopted model, two parameters have to be taken into account: the cell edge length ($l$) and the cell wall thickness ($t$). Both of them are related to the relative density by the following relationship:

$$\frac{\rho^*}{\rho_s} \propto \left(\frac{t}{l}\right)^2$$

where the proportional constant depends on the details of the cell shape.
In addition, for the closed-cell structure, the parameters $t_e$, the cell edge thickness, $t_f$, the face thickness, $\phi$, the fraction of the solid contained in the cell edge and ($1- \phi$), the solid fraction contained in the face, have to be considered.

The mechanical behavior of a brittle foam under compression is shown in Figure 1.44. It is characterized by three regimes: (a) a linear elastic region at low stresses (generally for strain $<5\%$), (b) a collapse plateau in which the stress is constant while the sample starts crushing and (c) a final regime of densification corresponding to the collapse of the cells.

(a) The linear elasticity is controlled by the cell wall bending and according to the Hooke law, the slope of the stress-strain curve is the Young’s modulus of the porous ceramic, $E^*$. It is related to the relative density by the following equation:

$$\frac{E^*}{E_s} = C_1 \left( \frac{\rho_s^*}{\rho_s} \right)^2$$

where the constant $C$ depends on the details of the cell shape and it is generally equal to 1 or 0.3 in the case of porous materials prepared through replica technique.

For close-cell components, cell face stretching must be considered in addition to the cell wall bending: when the cell edges bend contracting, the cell faces stretch and the elastic modulus depends also on the wall stiffness. Therefore, the expression for the Young modulus becomes:

$$\frac{E^*}{E_s} = C_1 \phi^3 \left( \frac{\rho_s^*}{\rho_s} \right)^2 + C_1 (1-\phi) \frac{\rho_s^*}{\rho_s}$$

where, once again, $C_1$ and $C_1^*$ are constant generally equal to 1.

(b) In the second regime, a progressive cell collapse by cell wall fracture takes place. It is characterized by a plateau at brittle collapse stress, $\sigma_{cr}^*$, defined as

$$\frac{\sigma_{cr}^*}{\sigma_{bc}} = C_6 \left( \frac{\rho_s^*}{\rho_s} \right)^{3/2}$$

Fig. 1.44: A typical compressive stress-strain curve for a brittle foam material

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where \( \alpha_s \) represents the modulus of rupture of the cell-wall material and \( C_6 \) is a constant related to the cell shape, equal of about 0.2 according to the fit of experimental data.

Once again, the role of the solid face have to be added in the closed cell foams and the above equation is corrected as:

\[
\frac{\sigma^*_{cr}}{\sigma_{fs}} = C_6 \left( \frac{\rho_s^*}{\rho_s} \right)^{1/2} + C_6^* (1 - \phi) \frac{\rho^*}{\rho_s},
\]

where the constant \( C_6^* \) is generally equal to 1. As the fraction of solid in the cell faces increases, the dependence of the strength on density should move from a power of 1.5 to a linear one.

The mechanisms of the cell edge bending and brittle crushing of the first and second regime are shown in Figure 1.45.

(c) Finally, when the cells have almost completely collapsed, opposing cell walls touch and further strain compresses the solid itself, giving rise to the final region of rapidly increasing stress.

The Gibson Ashby model can only be applied when the shape and distribution of cavities is regular all over the total volume and it is based on the assumption that the modulus of rupture of the strut is constant. Indeed, when micro or macroscopic flaws are present in the struts (such as pores, cracks or triangular voids), the modulus of rupture can drastically decrease \(^{113} \). Therefore, when the Gibson Ashby assumptions are not verified the results obtained can provide only averaged values for the parameters of interest.

Sammis and Ashby\(^ {114} \) demonstrated that brittle solids containing closed pores fail in compression by a progressive micro-fracture and that the pore dimensions influence the crack development.

Materials having smaller pores present cracks at higher stress. It is hypothesized that, firstly, the micro-crack initiation takes place at the end of the elastic behavior and then the propagation phase occurs through a competition between micro and macro-cracking propagation.

The micro-cracking initiation is more influenced by the total porosity rather than the pore dimension while, logically, the nucleation and the growth of the cracks depend on the microstructure of the porous materials, such as the number of pores and their arrangement and distribution.
A recent study performed by Meille et al.\textsuperscript{115} highlights the influence of the total porosity on the mechanical behavior of porous alumina under compression. They noted that for a relative porosity below 50\%, the load-displacement curves in compression show the typical brittle behavior with propagation of some long cracks parallel to the loading direction. Instead, for a relative porosity above 50\%, the behavior of the materials is that of a cellular ceramics, with a fracture of the solid walls between the pores and a progressive damage accumulation. These two failure modes are explained considering the solid wall size and the distance between two neighbor pores: if the total porosity increases, the solid wall size decreases and two pores can be directly linked with a progressive collapse of the material.

Following Meille’s assumption, the transition between a brittle and cellular-like fracture occurs when the mean distance between particles equals the crack length.

Also the influence of the microstructure of the porous materials, such as the pore size, shape and distribution, on the mechanical behavior was extensively studied in literature\textsuperscript{115-117}. In particular, Tang and coworkers\textsuperscript{118} studied these aspects through a new numerical code (MFPA, Material Failure Process Analysis): the specimen is modeled as a two-dimensional solid and the numerical tool is used to simulate the failure process of specimens containing holes. The influence of the pore diameters and the arrangement of the pore distribution were deeply investigated as shown in Figures 1.46-1.47.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{crack_growth.png}
\caption{Cracks growth from a multi-holes distribution arranged in a) diagonal, b) vertical and c) horizontal lines\textsuperscript{118}}
\end{figure}
Role of the processing route on microstructure and properties of macroporous ceramics

The Figure 1.47 demonstrates a decrease of the compressive strength as the pore diameter increases, while the influence of the pore arrangement on the cracks formation and propagation is illustrated in Figure 1.46. In the case of holes arranged in diagonal lines, cracks propagate with higher rate at lower strengths.

Tang’s results can be summarized considering that in the case of randomly arranged pores having different diameters, cracks involve only some pores, particularly, the largest ones, closer to boundary and those arranged in diagonal lines. Therefore, homogeneous microstructures with regular distribution of pores imply higher maximum strength.

Finally, the influence of the pore shape on the mechanical properties was investigated by Herakovich and Baxter\textsuperscript{119} and Brown et al.\textsuperscript{120}.

Brown et al. expressed the stress-porosity relation taking into account the parameter $\alpha$, closely related to the pore morphology as illustrated by the following equation:

$$\sigma = \sigma_{\text{max}} \left[ 1 - \left( \sum_i \alpha_i p_i \right) \right]$$

where $\sigma_{\text{max}}$ is the strength of the dense sample and $p_i$ is the porosity of the $i$th type of pores.

According to the calculated values of $\alpha$, of different pore shape and orientation, porous materials with cylindrical pores show higher strength than those with spherical pores for a given porosity, as recently confirmed by Feng et al.\textsuperscript{121}.
1. Bibliography

1.4 Conclusions

In this chapter the state of the art of the zirconia-based systems has been discussed, by keeping in mind that this PhD work involved both the elaboration of macroporous (in the frame of the MITOR project) and dense (in the frame of Longlife project) materials.

After a brief description of the transformation toughening proper of zirconia materials and its consequences on the mechanical properties of such ceramics, the role of some parameters (such as nature of the dopant, microstructure features and phase composition) on the final properties has been described.

Due to aging phenomena in moisture atmosphere proper of Y-TZP materials, the necessity to develop new ceramic composites for biomedical application has been depicted. Among them, Ce-TZP and ZTA ceramics offer the main advantages, coupling biocompatibility, stability and good mechanical properties.

The overview of the most relevant Ce-TZP and ZTA composites present in the literature has revealed the necessity of developing new composites with complex microstructure in order to further improve both toughness and strength of such ceramics. This goal can be achieved only by a careful tailoring of the phase composition and microstructure that is possible through innovative elaboration processes. Thus, powder mixing, sol-gel, co-precipitation techniques as well as new surface-modification routes were investigated, showing their influence on the microstructure and mechanical properties of composite ceramics.

Finally, in view of the development of porous alumina-zirconia composites, the role of the fabrication process on microstructure and properties of such materials has been described.

A brief introduction of the mechanical models, particularly the Gibson-Ashby one, and of the influence of the total porosity and pore size on the mechanical behavior of porous ceramics has been also illustrated.

The overview of the porous ZTA ceramics has revealed a gap in the scientific literature: few papers related to porous zirconia-containing composites have been reported and the toughening mechanisms, well-known in the corresponding dense materials, have not yet been deeply investigated.

Starting from this background information, the aim of this study is on one side the development of dense Ce-TZP composites having complex microstructure and on the other side the development of porous ZTA composites.

Consequently, in the former case, the improvement of mechanical properties and stability of the ceramics currently used in the biomedical field will be the main goal.

Instead, in the latter one, the main aim will be the investigation of the toughening mechanisms in porous materials.

In both cases, the surface modification approach has been exploited in order to develop composite ceramics having tailored compositional and microstructural features.
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2. Elaboration of composite powders by the surface modification route

Chapter 2

Elaboration of composite powders by the surface modification route

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In this chapter, an innovative procedure to prepare oxide composite powders, consisting on the surface modification of matrix powders by inorganic precursors of the second-phases, is described. Two kinds of materials are prepared by using this method, the former are alumina-based composites, the latter zirconia-based ones. As already described in the Preface, the experimental activities carried out during this PhD Thesis refer to two different projects.

The first part of activities is related to the MITOR project, under the supervision of Professor Jean-Marc Tulliani (titled “Development of new cellular materials by gel-casting technique: optimisation of production process and functional simulation of the microstructure”) and devoted to the elaboration and mechanical characterization of macro-porous Alumina-Zirconia composites.

The second kind of activities refer to a European Project, named Longlife (“Advanced multifunctional zirconia ceramics for long-lasting implants”), coordinated by Professor Jérôme Chevalier of INSA of Lyon, devoted to the preparation and characterization of zirconia-based composites for dental and spine implants.

The common point of these two projects is the development of (nano)composite ceramic powders, having tailored compositional and microstructural features, through the surface modification approach. This method insures a high degree of control of size and distribution of the second-phase grains on the surface of the parent material.

So, in this chapter the method is first generally described (section 2.1). Then, its application to Alumina-based (section 2.2) and to Zirconia-based composites (section 2.3) is separately described and discussed.
2. Elaboration of composite powders by surface modification route

2.1 Elaboration of composite powders by the surface modification route

Figure 2.1 shows the typical flow chart of the adopted procedure: first, the selected commercial powder (α-Al₂O₃ or Ceria-stabilized ZrO₂) was dispersed in distilled water in order to reach a fine and narrow particle size distribution.

Then, the inorganic precursors of the second/third phases (preferred as chlorides or nitrates) were dissolved in water, and this doping solution was drop-wise added to the ceramic slurry.

After homogenisation under magnetic stirring for 2 h, the suspension was dried, inducing the precipitation of the precursors onto the commercial particles surface, by liquid evaporation.

After drying, the obtained product was submitted to thermal treatment to promote the second/third phases crystallization, yielding the desired final composition.

![Flow chart of the adopted procedure for the composite powder elaboration](dispersion_of_commercial_starting_powders.png)

Each of the elaboration steps is crucial to control the powder features:

- The dispersion of the starting powder is needed in order to break the particle agglomerates and to reach a very close contact between the dopant and matrix particles, thus assuring the homogeneous precipitation of second-phase grains on the particle surfaces;

- The control of the pH and dilution of the modified suspension is essential to obtain a stable suspension and to avoid flocculation and heterogeneity. It is well-known that the concentration, the suspension pH, the ionic strength influence the stability of a ceramic powder slurry\(^1\). The same time, the pH of the suspension should carefully selected and controlled to avoid the precipitation of secondary phases. Furthermore, a very acid working pH can induce the corrosion of equipment steel parts. Consequently, for all these reasons, the doping solution pH is controlled and suitably modified, to achieve the best condition for each composition;
In order to obtain an homogeneous distribution of the second/third precursors onto the commercial particles surface, a fast drying step is preferred. In fact, this avoids the segregation of the second-phase, which can occur during a slow drying in an oven. Therefore, the suspensions were spray dried: thanks to the small volume of the droplets and the high surface area, the water evaporation of the atomized suspension occurs in a very short time;

- The powder thermal treatment is needed to decompose the synthesis by-products (mainly chlorides and nitrates) and to promote the second/third phases crystallization.
  Moreover, the thermal treatment can influence the phase evolution, playing a role on the final phases development as well as on their distribution and size.
  The best thermal pre-treatment for each composition was set up on the ground of thermogravimetric data, as shown in the following sections.

### 2.2 Alumina-based composite powders: elaboration and characterization

Alumina-10 vol% Zirconia composite powders (hereafter referred as AZ10) were prepared according to the method described in the previous section.

The zirconia content in the composite material was chosen on the ground of the previous investigations on dense Zirconia Toughened Alumina (ZTA) specimens, showing the best mechanical properties (in term of the fracture threshold, \( K_{1c} \)) for this zirconia content\(^3\),\(^4\).

A commercial \( \alpha \)-alumina powder (TM-DAR TAIMICRON, supplied by Taimei Chemicals Co., Japan) was selected to develop the above composition.

The main features of the powder, as provided by the supplier\(^5\), are reported in Table 2.1.

#### Table 2.1: Technical data of TM-DAR TAIMICRON alumina powder\(^5\)

<table>
<thead>
<tr>
<th>Item</th>
<th>Analysis results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystalline phase</td>
<td>Alpha</td>
</tr>
<tr>
<td>B.E.T. Specific surface area (m(^2)/g)</td>
<td>14.5</td>
</tr>
<tr>
<td>Primary particle size (by SEM) (µm)</td>
<td>0.10</td>
</tr>
<tr>
<td>Purity (by ICP-AES)</td>
<td>99.99%</td>
</tr>
<tr>
<td>Impurities (ppm) (by ICP-AES)</td>
<td>Si (10) Fe (8) Na (8)</td>
</tr>
</tbody>
</table>
2. Elaboration of composite powders by surface modification route

Figure 2.2 collects SEM micrograph (on the left) and the XRD pattern (on the right) of the as-received powder.

The SEM and XRD analyses confirmed that the starting powder was a well-crystallized α-alumina phase with ultra-fine size of primary particles, even if a certain degree of agglomeration can be observed.

In fact, by laser-granulometry analysis, an average agglomerate size of 30 µm was determined. So, an alumina powder suspension, at a solid loading of 30 vol%, was dispersed in distilled water under magnetic stirring for 5 days. A natural pH value of about 6.5 was recorded.

Particle size distribution, determined by laser-granulometry, revealed a good dispersion degree as shown in Figure 2.3 where the volume cumulative distributions as a function of the agglomerate size of as-received and dispersed alumina powder are compared.

An average particle size of 0.45 µm was reached after dispersion.
Zirconium chloride (3M ZrCl$_4$ >99% purity, supplied by Fluka) was selected as zirconium precursor for obtaining AZ10 composite powder. A $\alpha$-Al$_2$O$_3$ to ZrCl$_4$ weight ratio of 1:0.636 was employed, assuming that zirconia is fully tetragonal in the final composites. Since Zr$^{4+}$ ions show a strong hydrolysis, when ZrCl$_4$ was dissolved in distilled water and then drop-wise added to the alumina slurry, the suspension pH decreased to <1. Thus, for avoiding the possible corrosion of the spray dryer steel parts (such as the screws and the metallic flanges) and partial dissolution of alumina, the suspension pH has to be risen. However, a basic solution, such as aqueous ammonia, can not be added since the precipitation of Zr(OH)$_4$, that starts at a pH value of about 3, could be induced$^6$.

Therefore, the suspension pH was modified by adding the tribasic ammonium citrate (molar ratio ammonium citrate: ZrCl$_4$ of 2:1) that, acting as chelating agent, allows the increase of the pH avoiding the Zr(OH)$_4$ precipitation. In this way, a pH value of about 4.5 was reached. This modified suspension, containing alumina powder and the solution of zirconium tetrachloride and tribasic ammonium citrate, was diluted to 4 wt% and then spray dried.

The as-dried powder was submitted to XRD analyses: as shown in Figure 2.4, $\alpha$-Al$_2$O$_3$ and ammonium chloride were detected. A broad peak at low angle, characteristic of an amorphous phase, was also revealed.

![Fig. 2.4: XRD pattern of the as-dried AZ10 powder
($\alpha$=alpha alumina, JCPDS no. 10-0173, $^*$ = NH$_4$Cl JCPDS no. 07-0007)](image)

The thermal behaviour of the powder was investigated by TG-DTA analyses. The corresponding TG-DTA curves are reported in Figure 2.5: a total mass loss of about 24%, due to by-products thermal decomposition, was completely recorded at 600 °C.

The first two endothermic peaks, at 115 and 220 °C are related to the dehydration process, suggesting that two types of water molecules are bonded to the complexes, by adsorption or coordination. In the range between 300-500 °C several overlapped phenomena, such as decarboxylation, carbon burning, chloride release, occur.
2. Elaboration of composite powders by surface modification route

In particular, at about 290 °C, the decarboxylation takes place and continues up to 380 °C and at about 483 °C the complete destruction of the organic skeleton and final chlorine release occur. Finally, around 600 °C the zirconia crystallization into tetragonal phase starts as stated in literature.

![Fig. 2.5: DTA (solid line) and TGA (dashed line) curves of the as spray-dried AZ10 powder](image)

Therefore, for inducing the by-products decomposition and the zirconia crystallization, a thermal treatment at 600 °C for 1 h was carried out. The corresponding XRD pattern (Figure 2.6) showed the presence of α-alumina and tetragonal zirconia phase.

![Fig. 2.6: XRD pattern of AZ10 powder calcined at 600 °C for 1 h](image)

(α=alpha alumina, JCPDS no. 10-0173, T=tetragonal ZrO₂, JCPDS no. 80-0965)
The precise follow up of the zirconia crystallisation at the surface of alpha-alumina grains during thermal treatment was reported by Naglieri et al.\(^8\). TEM and XRD analyses allowed to state that the zirconia starts to crystallize into the amorphous film by homogeneous nucleation, which can be induced by the similarity between the amorphous phase and tetragonal phase. The crystallization mechanism can be summarized as follows: a) at low temperature, a fast nucleation from the amorphous layer occurs as the organic by-products start to decompose, while crystal growth is negligible, being the atomic diffusion hindered; b) at higher temperature, the nucleation rate decreases, while diffusion becomes more effective and the growth of the existing nuclei is predominant.

Although no stabilizer of the tetragonal zirconia phase was added, it was retained at room temperature thanks to the presence of very small crystals with lower surface energy, as suggested by Garvie\(^9\).

These results highlight the key role of the thermal pre-treatment in the tailoring of the phase distribution and size in the alumina–zirconia composite powder and consequently on the sintered bodies.

Treatments at low temperature promote the formation of small zirconia crystals but very long times are needed to achieve a fully crystallization. At the same time, the amorphous layer tends to drain into discrete pockets among the alumina grains, dragging the zirconia crystals (Figure 2.7 a-b). Such gathering of zirconia nanocrystals could promote their coalescence and growth during sintering, hindering a successful control of the nanostructure.

Instead, a treatment at higher temperature for a short time promotes a fast disappearance of the amorphous phase layer and the crystallization of larger zirconia grains (Figure 2.7 c).

Fig. 2.7: TEM images of AZ10 powders after thermal treatment at: a) 500 °C-1 h, b) 500 °C-10 h and c) 1000 °C-1 h. The arrow indicates the zirconia nuclei drained into discrete pockets\(^8\)
2. Elaboration of composite powders by the surface modification route

2.3 Zirconia-based composite powders: elaboration and characterization

The microstructural and compositional design of the zirconia-based composites, to be used for dental and spine implants, was carried out in the frame of Longlife project.

First, it was decided to use a ceria-stabilized zirconia powder as a matrix material, because it presents a better aging behaviour as compared to yttria-stabilized zirconia benchmark material\textsuperscript{10,11}.

Secondly, the selection of second and third phases was carried out by considering the biocompatibility of many oxide phases\textsuperscript{12}.

Third, the specific role of second-phase particles, having different morphologies, on the mechanical properties of the composites was a further selection criterion. It was decided to add both rounded-shaped and elongated second phase particles, the former for retaining the zirconia grain growth during sintering, the latter for further increasing the fracture toughness of the ceramics. The retention of zirconia grain size during sintering allows retaining the tetragonal phase at room temperature\textsuperscript{13,14}, increasing the hardness, flexural strength as well as the aging behaviour. For this purpose, \(\alpha\)-\(\text{Al}_2\text{O}_3\) was selected.

Instead, the use of elongated morphologies allows increasing the toughness by additional bridging/crack-deflection mechanisms\textsuperscript{15-17}. For this purpose, two different aluminates were selected: \(\text{CeMgAl}_{11}\text{O}_{19}\) and \(\text{SrAl}_{12}\text{O}_{19}\).

Figure 2.8 schematically illustrates the Longlife approach in terms of zirconia matrix selection, nanoparticles and platelets addition, and the effect on aging, toughness and strength.

![Figure 2.8: Longlife approach: the red full line and the respective microstructure represent the final objective, which combines the addition of a secondary phases in the form of particles and platelets to improve fracture strength and toughness. The blue and the yellow full lines represent strength-toughness relations for pure Y-TZP and Ce-TZP.](image-url)
Zirconia-based composite powders: elaboration and characterization

On the basis of the estimated percolation volume fraction of 16% for a monosize spherically shaped particles, the volume amount of the round-shaped and elongated second phase particles was set at 8 vol% respectively.

For the sake of clarity, the tri-phasic composites will be labelled as (details of samples designation are collected in the Appendix):

- \( \text{ZA}_8 \text{Sr}_8 (\text{84 vol%Ce-TZP/8 vol%Al}_2\text{O}_3/8 \text{vol%SrAl}_{12}\text{O}_{19}) \)
- \( \text{ZA}_8 \text{Mg}_8 (\text{84 vol%Ce-TZP/8 vol%Al}_2\text{O}_3/8 \text{vol%CeMgAl}_{11}\text{O}_{19}) \)

In the following, the step-by-step elaboration of the zirconia-based three-phases composites is described.

**Characterization of the ceria-stabilized \( \text{ZrO}_2 \) matrix powders**

The ceria-stabilized zirconia raw powder was supplied by Daiichi Kigenso (Kagaku Kogio Co. ltd, Japan). It contains 10mol% of ceria inside zirconia, and it is hereafter referred as 10Ce-TZP. Other information supplied by the producer are collected in Table 2.2.

<table>
<thead>
<tr>
<th>Item</th>
<th>Analysis results</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{ZrO}_2 (+\text{HfO}_2) )</td>
<td>86.39 wt%</td>
</tr>
<tr>
<td>( \text{CeO}_2 )</td>
<td>13.37 wt%</td>
</tr>
<tr>
<td>( \text{Al}_2\text{O}_3 )</td>
<td>0.23 wt%</td>
</tr>
<tr>
<td>S.S.A.</td>
<td>14.3 m(^2)/g</td>
</tr>
<tr>
<td>Average particle size</td>
<td>0.5-1.0 ( \mu \text{m} )</td>
</tr>
<tr>
<td>(by laser diffraction method)</td>
<td></td>
</tr>
<tr>
<td>Green density</td>
<td>2.91 g/cm(^3)</td>
</tr>
<tr>
<td>Sintered density (1450 °C-2 h)</td>
<td>6.02 g/cm(^3)</td>
</tr>
</tbody>
</table>

Since, as shown in Table 2.2, the supplier does not specify the amount of Hafnia in the starting zirconia powder, the as-received powder was submitted to ICP-AES analysis: the hafnium oxide content in the raw material resulted lower than 1 wt%.

Then, the powder was submitted to DTA-TG analysis, carried out up to 1400 °C (heating and cooling rate of 5°C/min, under static air): the thermal curves (not shown) did not reveal any peak imputable to phase transformation and/or to crystallization phenomena, and no appreciable mass change was observed.

The XRD pattern of the as-received powder is reported in Figure 2.9 in which the peaks of both monoclinic and tetragonal zirconia phases have been indexed. A monoclinic volume fraction, \( V_{m} \), of about 68% was determined by applying the Toraya equation (as detailed in the Appendix).
2. Elaboration of composite powders by surface modification route

In order to study the phase evolution, the powder was calcined between 600 °C and 1500 °C, for different soaking times, and submitted again to XRD analysis. Some of the indexed XRD patterns are collected in Figure 2.10.

Fig. 2.9: XRD pattern of the as-received 10Ce-TZP powder

(M= monoclinic zirconia phase JCPDS no. 74-0815 and T= tetragonal zirconia phase JCPDS no. 82-1398)

Fig. 2.10: XRD patterns of the as-received and calcined 10Ce-TZP powder

(M= monoclinic zirconia phase JCPDS no. 74-0815 and T= tetragonal zirconia phase JCPDS no. 82-1398)
By applying the Toraya and Scherrer\textsuperscript{19} equations, the monoclinic volume fraction and the crystallites size evolution as a function of the calcination treatments were estimated. The corresponding results are reported in Figure 2.11.

![Graph showing the evolution of monoclinic volume fraction and mean crystallite size as a function of pre-treatment temperature and time for 10Ce-TZP powder.]

**Fig. 2.11: Evolution of the monoclinic volume fraction (bottom) and mean crystallite sizes (top) as a function of the pre-treatment temperature and time of the 10Ce-TZP powder.**

The monoclinic volume fraction (Figure 2.11 bottom) progressively decreases by increasing the calcination temperature, reaching a minimum at about 950 °C (with 1 h of holding time) and then increases again by increasing the heating temperature. A starting mean crystallite size, of about 25 nm was found, which remained almost constant up to about 950 °C. For higher temperatures, it started to increase, reaching values of about 50 nm after calcination at 1500 °C (Figure 2.10 top). In the temperature range from 900 to 950 °C, the lowest values for both monoclinic fraction and crystallite size are obtained.

The SEM observations and granulometric analysis carried out on the as-received 10Ce-TZP powder showed the presence of aggregates/agglomerates whose mean size was about 1 µm (see values in Table 2.3). Since an average particle size of 0.5-0.9 µm was declared by the producer (as shown in Table 2.2), it was necessary to disperse the powder.

The experimental conditions were set on the ground of the Zeta potential curves of zirconia and ceria-stabilized zirconia powders, as given in literature\textsuperscript{21,22}. The isoelectric point (i.e.p.) was localized in the pH range of 7-8, which is quite close to the natural pH of a 10Ce-TZP aqueous suspension (6.5 for 8 vol% 10Ce-TZP aqueous suspension).
2. Elaboration of composite powders by surface modification route

Thus, in order to obtain a surface charge density sufficiently high to induce a strongly repulsive double-layer force, the dispersions were prepared under both acidic conditions (at pH of about 3) and basic conditions (at pH of about 10). In addition, some tests were also performed at the natural pH of the powder, but adding suitable amounts of a dispersant.

The dispersibility of the as-received 10Ce-TZP powder was investigated by using the ball milling technique (stricto-sensu, it is a dispersion of the agglomerates). Zirconia spheres (2.0 mm in diameter, supplied by Tosoh Corporation) were employed and a laser-granulometry was used to check the degree of dispersion as a function of the milling time.

- Dispersion under acidic and basic conditions

The study of the dispersibility of the as-received 10Ce-TZP powder in acidic and basic conditions was carried out by using a solid loading of 8 vol% and a powder-to-spheres weight ratio of 1:10.

The acidic conditions (at a pH of 3) were reached by adding diluted hydrochloric acid, while basic conditions (at a pH of 10) were reached adding diluted ammonia. Thus, a decrease and an increase, respectively, of the natural pH (of about 6.5) of an aqueous 10Ce-TZP suspension was obtained.

As soon as the hydrochloric acid and ammonia were respectively added, a relevant increase of the suspension flowability was observed.

A good dispersion of the powder was reached after 16 hours of ball-milling under acidic conditions while 41 hours were necessary under basic conditions, as reported in Figure 2.12.

In addition, in Table 2.3 the diameters corresponding to 10%, 50% and 90% (referred hereafter as $d_{10}$, $d_{50}$ and $d_{90}$ values) of the particle size distributions are collected.

It should be pointed out that the suspension pH was almost constant at a value of about 3 or 10 respectively, during the dispersion tests.

![Cumulative frequency vs Agglomerate size](image)

**Fig. 2.12:** Volume cumulative distributions as a function of the agglomerate size of as-received (black-square curve), dispersed under acidic condition (red-rhombus curve) and basic condition (blue-triangle curve) 10Ce-TZP powders
Zirconia-based composite powders: elaboration and characterization

Table 2.3: Comparison of the values of \(d_{10}\), \(d_{50}\) and \(d_{90}\) of the particle size distributions of as-received and dispersed under basic and acidic conditions 10Ce-TZP powders

<table>
<thead>
<tr>
<th></th>
<th>(d_{10}) (µm)</th>
<th>(d_{50}) (µm)</th>
<th>(d_{90}) (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-received 10Ce-TZP</td>
<td>0.5</td>
<td>1.1</td>
<td>2.3</td>
</tr>
<tr>
<td>16h-ball milled 10Ce-TZP under acidic conditions</td>
<td>n.d.*</td>
<td>0.5</td>
<td>0.8</td>
</tr>
<tr>
<td>41h-ball milled 10Ce-TZP under basic conditions</td>
<td>n.d.*</td>
<td>0.4</td>
<td>0.6</td>
</tr>
</tbody>
</table>

n.d. (<0.31 µm), non-detected by the instrument, as detailed in the Appendix

- **Dispersion in the presence of a dispersant**

On the ground of literature\(^{21,22,23}\) the effect of two dispersants, namely Darvan C and Duramax D-3005, were investigated. Some technical information on both dispersants, as given by the Suppliers, are reported in Tables 2.4 and 2.5, respectively.

Darvan C is supplied by R.T. Vanderbilt Company, Inc., Norwalk, CT (USA) and it is an ammonium polymetacrylate. Its role is to improve particles dispersion by increasing the strength of the anionic charge on the particles surface, thus involving reciprocal repulsion.

Table 2.4: Technical data sheet of Vanderbilt Darvan C\(^{24}\)

<table>
<thead>
<tr>
<th>Item</th>
<th>Analysis results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight:</td>
<td>10000-16000 Da</td>
</tr>
<tr>
<td>Physical form:</td>
<td>Liquid</td>
</tr>
<tr>
<td>Appearance:</td>
<td>Clear to slightly opalescent amber fluid</td>
</tr>
<tr>
<td>Density at 25 °C:</td>
<td>1.11 mg/m³</td>
</tr>
<tr>
<td>Percent solids:</td>
<td>25%</td>
</tr>
<tr>
<td>pH:</td>
<td>7.5 to 9</td>
</tr>
<tr>
<td>Viscosity at 25 °C:</td>
<td>75 cps</td>
</tr>
<tr>
<td>Solubility:</td>
<td>Completely soluble in water systems</td>
</tr>
</tbody>
</table>

Duramax D-3005 is supplied by Rohm and Haas Company, Philadelphia, PA (USA); it is an ammonium salt of a polyelectrolyte. The recommended amount of Duramax D-3005 to be added is a function of the powder specific surface area: for zirconia powders, the supplier suggests about 2.2 mg/m\(^2\).

Being the specific surface area of 10Ce-TZP 14.3 m\(^2\)/g (see data in Table 2.2), the recommended amount of Duramax D-3005 was estimated to be about 3 wt% with respect to the powder weight.
2. Elaboration of composite powders by surface modification route

Table 2.5: Technical data sheet of Rohm and Haas Duramax D-3005

<table>
<thead>
<tr>
<th>Item</th>
<th>Analysis results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight:</td>
<td>2400 Da</td>
</tr>
<tr>
<td>Total solids:</td>
<td>35 %</td>
</tr>
<tr>
<td>Appearance:</td>
<td>Pale yellow liquid</td>
</tr>
<tr>
<td>Density at 23 °C:</td>
<td>1.16 g/ml</td>
</tr>
<tr>
<td>Viscosity:</td>
<td>&lt;100 cP</td>
</tr>
<tr>
<td>pH:</td>
<td>6.0-7.0</td>
</tr>
</tbody>
</table>

The study of the dispersibility of the 10Ce-TZP powder in the presence of the dispersants Darvan C or Duramax D-3005, was carried out by using a solid loading of 8 vol% and a powder-to-spheres weight ratio of 1:10. 3 wt% of both dispersants was added to powder aqueous suspensions, thus inducing an increase of the pH from about 6.5 to about 8.

Also in this case, as soon as the dispersant was added, a clear increase of the suspension flowability was observed. Once again, the pH remained constant during the whole dispersion process.

A good powder dispersion was reached after 30 h of ball-milling when Darvan C was added, while 16 h of ball milling was necessary to reach almost the same dispersion degree in the presence of Duramax D-3005.

The agglomerate size distributions and the corresponding d values are reported in Figure 2.13 and in Table 2.6, respectively.

![Fig. 2.13: Volume cumulative distributions as a function of the agglomerate size of as-received (black-square curve) and dispersed in the presence of 3 wt% of Duramax D-3005 (red-rhombus curve) and Darvan C (blue-triangle curve) 10Ce-TZP powders](image)
The results show that the 10Ce-TZP powder can reach a good dispersion degree in a wide pH range (under acidic and basic conditions) and in the presence of the dispersants Duramax D-3005 and Darvan C. However, taking into account the required time, the best dispersion conditions were obtained under acidic conditions and in the presence of the dispersant Duramax D-3005, since in both case 16 h were sufficient to reach a good dispersion degree.

Nevertheless, since the elaboration process involves the use of acidic salts (nitrate or chloride) 10Ce-TZP powder was dispersed under acidic conditions. In addition, under these conditions (pH=3), the hydroxide precipitation can be avoided (see paragraphs 2.3.1 and 2.3.2).

However, according to literature\textsuperscript{22}, acidic solutions can solubilize the cerium oxide in a certain extent inducing an undesired depletion of ceria from the zirconia lattice.

So, in order to limit as much as possible the above drawback, it was decided to compare the behaviour of the as-received 10Ce-TZP with that of calcined powders, characterized by a higher fraction of tetragonal phase, attesting a more effective stabilization from the cerium oxide.

On the ground of the results collected in Figure 2.11, two calcination treatments were selected, precisely at 900°C and 950 °C for 1 h. At these temperatures, a relatively low fraction of monoclinic phase was found by XRD analyses and a still very fine crystallite size of the zirconia phase was determined.

Powders are hereafter referred as 10Ce-TZP\textsuperscript{900-1h} and 10Ce-TZP\textsuperscript{950-1h} as detailed in the Appendix.

Such powders were thus dispersed under acidic conditions (solid loading of 8 vol%, powder-tospheres ratio of 1:10), reaching again a good degree of de-agglomeration after 16 hours.

The corresponding d\textsubscript{10}, d\textsubscript{50} and d\textsubscript{90} values were very close to the ones obtained for the dispersed un-calcined 10Ce-TZP powder (see values in Table 2.3).

Some SEM micrographs of the dispersed 10Ce-TZP powders, un-calcined, calcined at 900 °C/1h and at 950 °C/1h, are reported in Figure 2.14.

The three powders are characterized by similar microstructural features, showing agglomerates of 200-800 nm in size, in which primary particles of about 50 nm can be identified, in agreement with the particle size declared by the supplier (see values in Table 2.2).
2. Elaboration of composite powders by surface modification route

Fig. 2.14: SEM micrographs of the dispersed powders (under acidic conditions): (a) un-calcined, (b) calcined at 900 °C for 1 h and (c) at 950 °C for 1 h, 10Ce-TZP powders

In order to verify the possible solubilisation of cerium in the acidic dispersion conditions, the three dispersed suspensions were then submitted to ICP-AES analysis. So, after dispersion, zirconia powders were separated from the supernatant liquid phase by centrifugation. The results showed that, if cerium was present in the mother liquor, its concentration was lower than the instrumental detection limit.

Since very similar behaviours, regarding the dispersibility, particle size and phase composition, were found for the three dispersed powders, the composite materials elaboration was carried out only on the un-calcined 10Ce-TZP powder.

In the next paragraphs, the set-up of the elaboration process for the two different zirconia based composites (ZA₈Sr₈ and ZA₈Mg₈) is described.
2.3.1 Elaboration and characterization of ZA₈Sr₈ powder

In order to obtain α-Al₂O₃ and SrAl₁₂O₁₉ second phases, Al(NO₃)₃·9H₂O (≥ 98% purity, supplied by Sigma Aldrich) and Sr(NO₃)₂ (≥ 99.0% purity, supplied by Sigma Aldrich) were selected as precursors. A 10Ce-TZP to aluminum nitrate weight ratio of 1:0.449 was employed to obtain in the final composite 8 vol% of Al₂O₃.

A 10Ce-TZP to aluminum and strontium nitrate weight ratio of 1:0.389 and 1:0.018, respectively, were employed to obtain in the final composite 8 vol% of SrAl₁₂O₁₉. The nitrates were dissolved in distilled water and then drop-wise added to the dispersed zirconia suspension. A final suspension dilution of 10 wt%, with respect to the solid content, was reached by adding distilled water.

Moreover, in order to keep the pH suspension stable (pH=3) and to avoid hydroxide precipitation, the pH was periodically checked and, when needed, few drops of diluted HCl were added. Precisely, as experimentally determined, aluminum hydroxide starts to precipitate at pH of 4.5, whereas strontium hydroxide does not precipitate even at basic pH values. This modified suspension, containing zirconia powder and the solution of aluminum and strontium nitrates, was kept under magnetic stirring for 2 h to assure homogeneity.

Finally, it was spray-dried, setting the inlet temperature at 140 °C (more details about the spray-drying conditions are reported in the Appendix).

The as spray-dried XRD pattern revealed the presence of monoclinic zirconia, in a content equal to 75 vol%, and tetragonal zirconia phases as shown in Figure 2.15.

![XRD pattern](image)

**Fig. 2.15: XRD pattern of the as spray-dried ZA₈Sr₈ powder**

(M= monoclinic zirconia phase JCPDS no. 74-0815 and T= tetragonal zirconia phase JCPDS no. 82-1398)
In some cases also cerium nitrate was added to the zirconia slurry with the aim to modify the cerium content of the starting zirconia powders, in order to evaluate the effect of the stabilizer oxide on the physical and mechanical properties of the composites.

In this way it was possible to produce composites containing a precise ceria content inside the zirconia lattice, ranging from 10 to 11.5 mol%.

Ammonium cerium (IV) nitrate, supplied by Sigma Aldrich (\((\text{NH}_4)_2[\text{Ce(NO}_3]_6\), \(\geq 98.5\%\) purity), was selected as cerium precursor. It was dissolved in distilled water and added, in a proper amount, to the zirconia suspension, assuming that a \(\text{CeO}_2\) amount of 10 mol% was already present in the raw zirconia powder and supposing its complete diffusion inside the zirconia grains during thermal treatments.

In particular, a 10Ce-TZP to cerium nitrate weight ratios of 1:0.02, 1:0.04 and 1: 0.06 were employed to have in the final composites 10.5, 11 and 11.5 CeO\(_2\) mol%, respectively.

The final composites will be hereafter referred as \(\text{ZA}_8\text{Sr}_8\text{-Ce10}, \text{ZA}_8\text{Sr}_8\text{-Ce10.5}, \text{ZA}_8\text{Sr}_8\text{-Ce11}, \text{ZA}_8\text{Sr}_8\text{-Ce11.5},\) in order to specify their ceria molar content, being the former composite the only one in which no extra-cerium was added.

For sake of clarity, the samples designation and their composition are reported in the Appendix (A.1).

The spray-dried \(\text{ZA}_8\text{Sr}_8\text{-Ce10.5}, \text{ZA}_8\text{Sr}_8\text{-Ce11} \) and \(\text{ZA}_8\text{Sr}_8\text{-Ce11.5} \) powders were submitted to XRD analyses (Figure 2.16): monoclinic and tetragonal zirconia phases were the only detected phases. Comparable monoclinic volume fraction (about 75 vol%) were obtained in all the samples.

![XRD patterns](image)

Fig. 2.16: XRD patterns of the as spray-dried (a) \(\text{ZA}_8\text{Sr}_8\text{-Ce10.5}, \) (b) \(\text{ZA}_8\text{Sr}_8\text{-Ce10.5} \) and (c) \(\text{ZA}_8\text{Sr}_8\text{-Ce11.5} \) powders \((M=\text{monoclinic zirconia phase JCPDS no. 74-0815 and T= tetragonal zirconia phase JCPDS no. 82-1398)}\)
In order to characterize the obtained composite powders, the thermal behaviour and the phase evolution as a function of the thermal treatment, were investigated.

The thermal behavior of the spray dried ZA₈Sr₈-Ce₁₀, ZA₈Sr₈-Ce₁₀.₅, ZA₈Sr₈-Ce₁₁ and ZA₈Sr₈-Ce₁₁.₅ powders was followed by TG-DTA analyses, carried out up to 1450 °C (heating and cooling rate of 5°C/min, under static air).

A similar behavior was observed in all composites. As example, Figure 2.17 depicts the TG-DTA curves of ZA₈Sr₈-Ce₁₁.

![TG-DTA curves of the spray-dried ZA₈Sr₈-Ce₁₁ powder](image)

**Fig. 2.17:** TG-DTA curves of the spray-dried ZA₈Sr₈-Ce₁₁ powder

The mass loss, imputable to precursors decomposition, was about 30% of the initial weight and it was almost accomplished around 500 °C. In the high-temperature regime of the DTA curve, a broad peak at about 1200 °C was observed, probably imputable to α-alumina or aluminates crystallization.

A first investigation of the phase evolution was performed by treating the as-dried ZA₈Sr₈-Ce₁₀ and ZA₈Sr₈-Ce₁₁ powders in a furnace at different temperatures (heating and cooling rate of 10 °C/min). Precisely, XRD analyses were carried out on powders calcined at 600, 900, 1050, 1150 and 1450 °C for soaking times in the range 30 min-1 h.

The corresponding XRD patterns of ZA₈Sr₈-Ce₁₀ powders are reported, as example, in Figure 2.18. In addition, the monoclinic volume fraction, as a function of the calcination temperatures, of ZA₈Sr₈-Ce₁₀ and ZA₈Sr₈-Ce₁₁ powders is reported in Table 2.7.
2. Elaboration of composite powders by surface modification route

\[
* = \text{Monoclinic ZrO}_2 \\
+ = \text{Tetragonal ZrO}_2 \\
° = \alpha-\text{Al}_2\text{O}_3 \\
# = \text{SrAl}_{12}\text{O}_{19}
\]

Fig. 2.18: XRD patterns of ZA8Sr8-Ce10 powder as a function of the calcination temperature
(*= JCPDS no. 74-0815, + =JCPDS no. 82-1398, ° = JCPDS no. 46-1212 and #=JCPDS no. 80-1195)

Table 2.7: The monoclinic volume fraction (\(V_m\)) of ZA8Sr8-Ce10 and ZA8Sr8-Ce11, as a function of the calcination temperature

<table>
<thead>
<tr>
<th>(V_m) as spray-dried</th>
<th>ZA8Sr8-Ce10</th>
<th>ZA8Sr8-Ce11</th>
</tr>
</thead>
<tbody>
<tr>
<td>(V_m) 600 °C-1h</td>
<td>0.68</td>
<td>0.69</td>
</tr>
<tr>
<td>(V_m) 900 °C-1h</td>
<td>0.27</td>
<td>0.24</td>
</tr>
<tr>
<td>(V_m) 1050 °C-30min</td>
<td>0.07</td>
<td>0.09</td>
</tr>
<tr>
<td>(V_m) 1150 °C-30min</td>
<td>0.05</td>
<td>0.04</td>
</tr>
<tr>
<td>(V_m) 1450 °C-30min</td>
<td>0.34</td>
<td>0.06</td>
</tr>
</tbody>
</table>

As above discussed, XRD patterns of the as spray-dried powders showed only the presence of monoclinic (equal to about 75 vol%) and tetragonal zirconia phases, without evident differences between ZA8Sr8-Ce10 and ZA8Sr8-Ce11 samples.

By increasing the calcination temperature a progressive decrease of the monoclinic volume fraction was observed, reaching the minimum value (\(V_m= 0.06\) and 0.04, for ZA8Sr8-Ce10 and ZA8Sr8-Ce11,
respectively) at 1150 °C where the crystallization degree was higher. No other peaks, imputable to any second/third phases were observed up to 1150 °C.

At higher temperatures, the phase composition starts to change: a deep increase of \( V_m \) was recorded in the \( \text{ZA}_8\text{Sr}_8\text{Ce}10 \) sample, demonstrating a lower zirconia stabilization degree. On the opposite, \( V_m \) was still low (6%) in the \( \text{ZA}_8\text{Sr}_8\text{Ce}11 \) composite calcined at 1450 °C, containing a starting higher ceria content.

In addition, the XRD patterns of the powders treated at 1450 °C show the presence of signals imputable to \( \alpha\text{-Al}_2\text{O}_3 \) and \( \text{SrAl}_{12}\text{O}_{19} \) phases, validating the adopted elaboration process in yielding the expected final composition. However, due to the different absorption coefficient and the low second/third phase volume content (8 vol%), the intensity of the \( \alpha\text{-Al}_2\text{O}_3 \) and \( \text{SrAl}_{12}\text{O}_{19} \) phases is very low but still detectable. On the ground of these results, the exothermal, broad DTA signal (see Figure 2.17) can be reasonably imputed to the crystallization of alumina and aluminates second phases.

The studies performed by Schimid et al.\(^{26}\) and Douy et al.\(^{27}\), the last one about the crystallization of spray-dried amorphous precursors in the \( \text{SrO-Al}_2\text{O}_3 \) system, can help to understand the involved phenomena in the thermal treatment of the dried zirconia composites powder. To synthesize \( \text{SrAl}_{12}\text{O}_{19} \), Douy and colleagues spray dried an aqueous solution of strontium and aluminum nitrates and then, in order to decompose the nitrate ions, the dried powder was submitted to thermal treatments.

The thermal behavior was followed by TG, DSC and XRD analyses as shown in Figures 2.19-2.20.

They observed that the aluminum nitrate nonahydrate decomposed through a single step at about 220 °C, while the strontium nitrate alone decomposed between 535 and 720 °C with a sharp maximum at 703 °C in the rate of weight loss. When the mixture of the two nitrates was spray-dried, the decomposition of strontium nitrate was shifted to lower temperatures as the aluminum content was increased.

![Fig. 2.19: TGA curves of the spray-dried powders of different compositions in the system \( \text{SrO-Al}_2\text{O}_3 \) (the weight losses are normalized to 100 % at 1000 °C for comparison) \(^{27}\).](image)

The system \( \text{SrAl}_{12}\text{O}_{19} \) is reported as \( \text{SrA}_6 \)
2. Elaboration of composite powders by surface modification route

The DSC curves of the $\text{Al}_2\text{O}_3$ and $\text{SrAl}_{12}\text{O}_{19}$ amorphous precursors (Figure 2.20 left), exhibited each two exothermic peaks: the alumina precursor crystallizes into a highly disordered transition alumina phase ($\eta$- or $\gamma$-$\text{Al}_2\text{O}_3$) at 845 °C and then transforms into the stable $\alpha$ phase at 1142 °C.

In the $\text{SrAl}_{12}\text{O}_{19}$ composition the two peaks are sharper and delayed to higher temperatures, 936 °C and 1183 °C. Therefore, a XRD analysis of the $\text{SrAl}_{12}\text{O}_{19}$ powder treated at 950 °C (just beyond the first peak) was performed (Figure 2.20 right), revealing the presence of a broad and diffuse peak characteristic of transition alumina, probably $\gamma$-$\text{Al}_2\text{O}_3$.

Finally, the powder was treated at 1300 °C: only the $\text{SrAl}_{12}\text{O}_{19}$ phase was detected by XRD analysis. For these results, the first exothermic peak in the DSC curve of $\text{SrAl}_{12}\text{O}_{19}$ can be attributed to the $\gamma$-$\text{Al}_2\text{O}_3$ crystallization while the second one reflects the transformation of the transition alumina into the well-ordered hexa-aluminate.

Douy et al.\(^{27}\) proposed that the $\gamma$-$\text{Al}_2\text{O}_3$ becomes more stabilized by replacing the $\text{Al}^{3+}$ and vacancies in the tetrahedral sites by $\text{Sr}^{2+}$, also if the $\text{Sr}^{2+}$ ionic radius is really high for a tetrahedral coordination.

As a consequence, the presence of strontium ions makes the ordering of the structure more difficult, requiring higher temperatures for its formation and transformation.

![Fig. 2.20: DSC curves of the alumina-rich amorphous precursors (left); XRD patterns of the $\text{SrAl}_{12}\text{O}_{19}$ precursor after heating at 950 °C ($\gamma$-$\text{Al}_2\text{O}_3$ solid solution) and 1300 °C ($\text{SrAl}_{12}\text{O}_{19}$ single phase)\(^{27}\)](image)

The results obtained by Douy and coworkers are perfectly consistent with the results of this work: since the studied system is more complicated (due to the presence of the zirconia matrix and the second phase) only a broad peak with an exothermal signal at about 1200 °C was observed in the DTA curve.

It can be associated to a $\gamma$-$\text{Al}_2\text{O}_3$ crystallization followed by: a) transformation to the stable second $\alpha$-alumina phase and b) transition to the $\text{SrAl}_{12}\text{O}_{19}$ third phase.

Our XRD analyses confirm the crystallization of the second and third phases only at high temperatures, as reported by Douy et al.. However, $\gamma$-$\text{Al}_2\text{O}_3$ phase was not detected at low temperature, probably due to its low amount.
Finally, regarding the microstructural development of SrAl<sub>12</sub>O<sub>19</sub>, Vishita et al. proposed two distinct mechanisms as shown in Figure 2.21.

One possibility is (a) that the SrAl<sub>12</sub>O<sub>19</sub> (reported as SA6) nucleates at the interfaces between alumina and SrO-Al<sub>2</sub>O<sub>3</sub> particles (reported as SA) and the reaction proceeds by solid-state diffusion through the reactant phase. However, if the surfaces of the SA6 and the alumina grains were already wet by a liquid phase, the transformation to SA6 would, by necessity, take place via solution-precipitation reaction. This is illustrated in (b), where the reaction by solid state diffusion results in the formation of equiaxed SA6 grains, the solution-precipitation favors the development of plate-like grains. Anyway, in view of a more precise follow-up of alumina and aluminates crystallization on the zirconia grains, HRTEM analyses will be performed on powders thermally treated at different temperatures. In this way, more information about the nucleation and growth mechanism could be obtained.

### 2.3.2 Elaboration and characterization of ZA<sub>8</sub>Mg<sub>8</sub> powder

In order to obtain the tri-phasic zirconia-based composite having α-Al<sub>2</sub>O<sub>3</sub> as second phase and CeMgAl<sub>11</sub>O<sub>19</sub> as third phase, Al(NO<sub>3</sub>)<sub>3</sub> (≥98% purity), (NH<sub>4</sub>)<sub>2</sub>[Ce(NO<sub>3</sub>)<sub>6</sub>] (≥98.5% purity) and Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (≥99% purity), supplied by Sigma Aldrich, were selected as alumina and aluminates precursors. In particular, a 10Ce-TZP to aluminum nitrate weight ratio of 1:0.449 was employed to obtain in the final composite 8 vol% of Al<sub>2</sub>O<sub>3</sub>. A 10Ce-TZP to aluminum, cerium and strontium nitrates weight ratio of 1:0.349, 1:0.046 and 1:0.022, respectively, were employed to obtain in the final composite 8 vol% of CeMgAl<sub>11</sub>O<sub>19</sub>. Once again, the nitrates were dissolved in distilled water and then drop-wise added to the zirconia suspension.
A final suspension dilution of 10 wt%, respect to the solid content, was reached by adding distilled water. Moreover, in order to keep the pH suspension stable (pH = 3) and to avoid hydroxide precipitation, the pH was periodically checked and few drops of diluted HCl were added. Precisely, as experimentally determined, aluminum hydroxide starts to precipitate at pH of 4.5, whereas at pH of 10.5-11 and 7.5-8 precipitation occurs for magnesium and cerium hydroxides, respectively.

This modified suspension, containing zirconia powder and the solution of aluminum, cerium and magnesium nitrates, was kept under magnetic stirring for 2 h before drying, to assure homogeneity. Finally, it was spray-dried, setting the inlet temperature at 140 °C.

Once again, the as spray-dried powder was characterized by means of TG-DTA and XRD analyses. The phase and agglomerate size evolution, as a function of the thermal treatment, were also investigated as well.

The TG-DTA curves are illustrated in Figure 2.22: the mass loss (about 24% of the initial weight), imputed to precursors decomposition, was almost accomplished around 500 °C. In the high-temperature regime of the DTA curve, two broad peaks at about 860 °C and 1100 °C were observed.

On the ground of Douy’s results, assuming a thermal behaviour similar to the one observed in the ZA₈Sr₈ composite, the former peak can be associated to γ-Al₂O₃ crystallization (at about 860 °C) and the latter to CeMgAl₁₁O₁₉ and α-Al₂O₃ crystallization (at about 1100 °C).

Zhu et al., studying the LnMgAl₁₁O₁₉ systems (with Ln=La, Nd, Gd) reported for the LaMgAl₁₁O₁₉ phase a crystallization temperature in the range 1100-1300 °C, in agreement with our results.

The phase and agglomerate size evolution was investigated by collecting granulometer analyses and XRD patterns on the thermal treated ZA₈Mg₈ powder.
As in the previous composition, the temperatures of 600, 900, 1050, 1150 and 1450 °C for a soaking time in the range 30 min-1 h (heating and cooling rate of 10 °C/min) were applied. The corresponding d values and the monoclinic volume fraction, as a function of the calcination temperatures, are reported in Table 2.8 and 2.9 respectively. In addition, the corresponding XRD patterns are illustrated in Figure 2.23.

Table 2.8: $d_{10}$, $d_{50}$ and $d_{90}$ values of particle size distribution of ZA$_8$Mg$_8$ powder as a function of the thermal treatments

<table>
<thead>
<tr>
<th>Treatment</th>
<th>$d_{10}$ (µm)</th>
<th>$d_{50}$ (µm)</th>
<th>$d_{90}$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>as spray-dried</td>
<td>0.6</td>
<td>3.2</td>
<td>9.2</td>
</tr>
<tr>
<td>600 °C-1h</td>
<td>6.1</td>
<td>25</td>
<td>141</td>
</tr>
<tr>
<td>900 °C-1h</td>
<td>5.3</td>
<td>33</td>
<td>160</td>
</tr>
<tr>
<td>1050 °C-30min</td>
<td>5.2</td>
<td>25</td>
<td>154</td>
</tr>
<tr>
<td>1450 °C-1h</td>
<td>9.3</td>
<td>66</td>
<td>221</td>
</tr>
</tbody>
</table>

A significant powder agglomeration was observed by increasing the temperature: mean agglomerate size, in the range 25-66 µm, significantly higher than those related to the as spray-dried powder, were reached. In particular, a strong powder agglomeration was observed after the thermal treatment at 600 °C and 1450 °C (when mean agglomerate size of 66 µm was reached).

Table 2.9: The monoclinic volume fraction ($V_m$) of ZA$_8$Mg$_8$ powder as a function of the calcination temperature

<table>
<thead>
<tr>
<th>Treatment</th>
<th>ZA$_8$Mg$_8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_m$ as spray-dried</td>
<td>0.70</td>
</tr>
<tr>
<td>$V_m$ 600 °C-1h</td>
<td>0.60</td>
</tr>
<tr>
<td>$V_m$ 900 °C-1h</td>
<td>0.27</td>
</tr>
<tr>
<td>$V_m$ 1050 °C-30min</td>
<td>0.05</td>
</tr>
<tr>
<td>$V_m$ 1150 °C-30min</td>
<td>0.05</td>
</tr>
<tr>
<td>$V_m$ 1450 °C-30min</td>
<td>0.11</td>
</tr>
</tbody>
</table>
2. Elaboration of composite powders by surface modification route

* = Monoclinic ZrO$_2$
+ = Tetragonal ZrO$_2$
° = α-Al$_2$O$_3$

As shown in the above Table, the as spray-dried powder was characterized by the presence of the monoclinic phase in a content equal to 70 vol%. The monoclinic volume fraction ($V_m$) progressively decreases by increasing the calcination temperature up to 1150 °C, where the crystallization degree was higher. Then, when a thermal treatment at 1450 °C was performed, $V_m$ starts to increase, reaching the value of 11 vol%, probably due to an increase of the agglomerate size as shown in Table 2.10.

From XRD results, only the presence of the monoclinic and tetragonal zirconia phase can be detected up to 1150 °C. XRD signals imputable to α-Al$_2$O$_3$ phase can be revealed only at higher temperature (1450 °C) but, once again, their intensity is very low. On the opposite, no XRD pattern imputable to the CeMgAl$_{11}$O$_{19}$ phase could be observed by XRD, even on powders calcined at very high temperature (up to 1700 °C).

Therefore, two hypothesis can be envisaged: (i) the formation of a cerium/magnesium-aluminate (CeMgAl$_{11}$O$_{19}$), which was not detectable by the above XRD analysis due to the low peaks intensity and/or (ii) the diffusion inside the zirconia grains of extra-cerium and magnesium added during the elaboration process.
It should be pointed out that to fulfill the first hypothesis, cerium reduction from Ce$^{4+}$ to Ce$^{3+}$ should occur. In order to verify this issue, XPS analysis will be carried out in a next future, allowing deepening the cerium oxidation state.

Instead, the latter phenomenon involves the enhancement of the zirconia stabilization degree as respect to the starting ceria-stabilized ZrO$_2$ powders, as occurred in the ZA$_8$Sr$_8$ system.

On the ground of a theoretical evaluation, if we suppose the complete diffusion of the extra-ceria inside the zirconia grains, a zirconia stabilization degree of about 11 mol% can be estimated. On the ground of this last estimation, these composites will be hereafter referred as ZA$_8$Mg$_{11}$Ce$_{11}$.

Anyway, in order to obtain more precise information about the aluminate phase composition and the real zirconia stabilization degree, HRTEM and EDX analyses will be performed in the next future.
2.4 Conclusions

In this chapter, an innovative procedure to prepare oxide composite powders, consisting on the surface modification of matrix powders by inorganic precursors of the second-phases, was described.

Two kinds of materials were successfully prepared by this method, the former were alumina-based composites (AZ10), the latter zirconia-based ones (ZA₈Sr₈ and ZA₈Mg₈).

In the ZA₈Sr₈ system, the tailoring of the zirconia stabilization degree was also achieved, proving that the adopted elaboration procedure is a promising method to obtain composite powder with the desired composition. Instead, in the ZA₈Mg₈ system, further analyses, such as HRTEM and XPS analyses, are necessary to deepen the phase composition.

The crucial elaboration steps, such as the raw powders dispersion, pH suspension and powder thermal treatments, were investigated and set-up.

The thermal behaviour, phase and agglomerate size evolution, as a function of the thermal treatments, of the composite powders were explored in order to deeper the knowledge of the involved mechanisms. The full control of the powders features is essential in order to tailor the final microstructures, as will be shown in the next chapter.
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2. Elaboration of composite powders by surface modification route


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25 http://www.dow.com/products


2. Elaboration of composite powders by surface modification route
Chapter 3

Elaboration and characterization of porous Alumina-based materials

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This chapter is dedicated to the development and characterization of alumina-based foams in the framework of the MITOR project. As detailed in the Preface, the aims of the MITOR project were: i) developing new methods for the elaboration of composite cellular ceramics, with tailored microstructural features and phase composition and ii) deepening the role of zirconia and its toughening mechanisms in porous materials.

In the first section, the elaboration of Alumina-Zirconia foams is described: The process is based on a combination of the surface modification method, presented in the previous chapter, together with the gel-casting-fugitive phase technology.

In the second section, the porous bodies are characterized in terms of phase composition, microstructure and mechanical properties and compared to pure alumina porous materials developed following the same procedure.

Major efforts are devoted to the study of the toughening mechanisms proper of zirconia materials, such as transformation and microcracking toughening, and to the relationship between microstructural features and mechanical properties.
3. Elaboration and characterization of porous Alumina-based materials

3.1 Elaboration of dense and porous Alumina-based composites

Here it is described the elaboration of ceramic foams, either pure alumina (hereafter referred as A) or alumina-zirconia (referred as AZ10) foams, by using a combined gel-casting-fugitive phase process, in which agar (A7049 from Sigma-Aldrich) was used as gelling agent, whereas commercial polyethylene spheres (supplied by Clariant Italia SpA) were used as pore-forming. This method allows the tailoring of pores shape, size and volume fraction, as reported in some previous papers.\(^1,2\)

The flow chart of the process is reported in Figure 3.1: first, the ceramic powder was dispersed in distilled water in order to reach a fine and narrow particle size distribution. Secondly, polyethylene spheres (PE) were added to the dispersed suspension in a suitable amount to obtain the final desired porosity. The suspension was kept under magnetic stirring for 1 h in order to reach a good homogenization and then agar was added in a proper amount for the gel casting procedure. Finally, the suspension was cast and the as-obtained samples were dried. Porous alumina-10 vol\% zirconia (AZ10) and pure alumina (A) materials with porosity contents in the range 65-75 vol\% were thus developed. More details about the operative conditions of the most important steps are supplied in the following.

![Flow chart of the modified gel casting process to develop porous A and AZ10 materials](image.png)
3.1.1 Set-up of the process for the porous materials

AZ10 composite powder was successfully prepared by the surface modification method of a commercial α-alumina powder (TM-DAR TAIMICRON, supplied by Taimei Chemicals Co., Japan) as described in section 2.2. After calcination at 600 °C for 1 h, a certain degree of agglomeration was determined by laser-granulometry: a mean agglomerate size of about 1 µm was revealed. Therefore, it was necessary to disperse the powder. Dispersion was carried out by ball-milling, at solid loading of 30 vol%, at the natural pH of the AZ10 suspension, equal to about 4.5, and with a powder-to-spheres weight ratio of 1:10. A good dispersion degree was obtained after 15 h of ball milling, halving the mean agglomerate size, as shown in Figure 3.2.

Fig. 3.2: Volume cumulative distribution, as a function of the agglomerate size, of AZ10<sup>600-1h</sup> powders (black-square curve) and of aqueous suspension AZ10<sup>600-1h</sup> powders (solid load of 30 vol%, powder-to-spheres weight ratio of 1:10) after 15 hours of ball milling (red-circle curve)

When pure alumina foams were prepared, α-alumina powder (TM-DAR TAIMICRON, supplied by Taimei Chemicals Co., Japan) was dispersed as described in section 2.2. The powder suspension having solid loading of 30 vol%, at the natural pH value of about 6.5, was dispersed in distilled water under magnetic stirring for 5 days.

Once dispersed the powder (either A or AZ10 powder), polyethylene spheres (PE) were added to the ceramic suspension in the required amount to obtain the final desired porosity. The commercial PE powder was sieved and among the several fractions obtained, the spheres having diameters in the range 224-355 µm were selected. PE spheres belonging to the sieved fraction were observed by SEM, and the particle size distribution was evaluated by image analyses technique.
3. Elaboration and characterization of porous Alumina-based materials

An acquired SEM micrograph and the particle size distribution of the sieved PE spheres are reported in Figure 3.3.

![SEM image and particle size distribution](image)

**Fig. 3.3:** a) SEM image and b) particle size distribution by image analysis of the selected fraction of PE spheres

It is shown that the sieving was not so effective in assuring a strongly controlled size distribution of the spheres. In fact, some very small spheres (referred as anomalies in the figure 3.3 b) are present due to their electrostatic adhesion to the surface of the bigger ones, probably promoted during sieving.

**3.1.2 Set-up of the gel-casting process**

Among the several no toxic gelling agent, Agar (A7049) supplied by Sigma-Aldrich was selected. It is derived from red algae class of seaweed and it is employed in food industry as a thickener and gelling agent. It is a polygalactoside made of agarose and agaropectine, the latter responsible for gelation. As most gelling agent used in gel-casting, it is water-soluble due to the presence of oxygen atoms and hydroxyl groups in the chains which are able to form hydrogen bonding with water molecules. At temperatures higher than 40 °C agarose exists as a random coil and, when cooled it forms strong gels, due to the adoption of an ordered double-helix state.

Agar solutions present a significant hysteresis effect in respect to its thermally reversible changes from gel to solution phase. The structure of agar is shown in Figure 3.4.

![Structure of agar](image)
In order to establish the solid loading and the agar amount suitable for the gel-casting procedure, the viscosities of ceramic suspensions were measured using a viscometer (Brookfield HBDV-II) before and after the agar addition. Several volume fractions of powder having different agar amount were tested maintaining the ceramic slurry at the operative casting temperature (60 °C). After a pre-shear, the apparent viscosity was measured at shear rates ranging from 6.12 to 245 s⁻¹, maintaining each value constant for 10 s. Figure 3.5 shows the effect of the gelling agent, using the alumina slurry as an example.

![Figure 3.5: Viscosity of dispersed suspensions of alumina, before and after agar addition](image)

Even if a very low viscosity was measured for the ceramic suspension, a significant increase was recorded after the agar addition. As expected, the viscosity of the ceramic slurry, for a given solid loading, increases as the agar amount increases.

On the basis of these results, the solid loadings of alumina and AZ10 slurries were set at about 20 vol% and 16 vol% respectively.

An amount of agar of 0.6 wt%, with respect to the final water content, was selected in order to reach an apparent viscosity lower than 1000 mPa·s at 20 s⁻¹, suitable for the casting process⁶. In fact, it is important to have solid loadings as high as possible in the slurry to minimize shrinkage during drying and to enhance fired density. At the same time, the suspension should remain still fluid and pourable⁷.

Therefore, after dispersion, the ceramic solid content of the alumina and AZ10 suspensions was decreased from 30 to 20 and 16 vol%, respectively, by adding distilled water and the agar solution.

When porous bodies were prepared, polyethylene spheres were added to the dispersed ceramic slurry and an increase of viscosity was recorded. Therefore, a decrease of the agar amount to 0.5 wt%, with respect to the final water content, in the case of highest porosity was required.

Anyway, green gel cast bodies still showed sufficient strength to be demoulded.

According to such data, the suitable amount of agar (i.e. 0.6 wt% as respect to the AZ10 powder, as previously detailed) was dissolved in distilled water at 90 °C, cooled down to 60 °C and then added to the ceramic suspension under continuous stirring.
3. Elaboration and characterization of porous Alumina-based materials

The suspension was then out-gassed under vacuum (about $10^{-2}$ Pa) and cast into PMMA molds. In particular, cylindrical Plexiglas molds having internal diameter of 1.5 cm and height of 5 cm were used. Gelation took place in a few minutes thanks to the change of temperature. Finally, the cast samples were dried at high relative humidity (RH>90%) for two days in order to minimize cracking due to non-uniform and differential drying in various regions. Then, the humidity level was progressively decreased.

For the sake of clarity, the sample designation adopted in the next paragraphs is described in the Table 3.1 and in the Section A.1 (Appendix).

Table 3.1: The adopted sample designation for the several materials

<table>
<thead>
<tr>
<th>Composition</th>
<th>Theoretical porosity</th>
<th>Sample designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$</td>
<td>0</td>
<td>A</td>
</tr>
<tr>
<td></td>
<td>65</td>
<td>A65</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>A70</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>A75</td>
</tr>
<tr>
<td>Al$_2$O$<em>3$-10$</em>{\text{vol%}}$ZrO$_2$</td>
<td>0</td>
<td>AZ</td>
</tr>
<tr>
<td></td>
<td>65</td>
<td>AZ65</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>AZ70</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>AZ75</td>
</tr>
</tbody>
</table>

3.1.3. Thermal pre-treatment and sintering

In order to study the thermal decomposition of PE spheres, they were submitted to TG-DTA analyses up to 600 °C (heating rate 2 °C/min) as shown in Figure 3.6.

![Fig. 3.6: TG (solid line) and DTA (dashed line) profiles of the PE spheres](image-url)
The first endothermic DTA peak at 110 °C is imputable to PE melting, in agreement with the data supplied by the producer. Then, two exothermal signals, at 280 and 380 °C, were revealed due to the degradation process. Firstly, it occurs due to oxygen absorption and oxidative scission processes (see broad peak at 280 °C). Then, this major degradation step is followed by ignition of the material, as shown by the exothermic spike at 380 °C. Later, at higher temperature (about 550 °C) PE underwent to a total decomposition⁹,¹⁰.

Therefore, in order to decompose the organic compounds (PE and agar) without inducing relevant internal stresses and green structure damage and cracking, before sintering the ceramic skeleton, a controlled heat treatment must be performed in low-temperature regimes (<600 °C).

The sintering behavior of A and AZ gel-cast green bodies was investigated by dilatometric analysis, up to 1500 °C for 3 h. In fact, in spite the dilatometric behavior of pressed and slip-cast A and AZ samples was already known by some previous studies¹, the gel-casting process could induce some differences in the thermal behavior.

Generally gel-cast materials exhibit higher temperature corresponding to the maximum densification rate and larger shrinkage compared to the pressed one as shown in Figure 3.7 where dilatometric analyses of pressed and gel-cast alumina bodies are compared.

According to the Authors, this discrepancy is due to an improved particle packing efficiency induced by the casting process¹.

Fig. 3.7: Dilatometric analyses of pressed (dash line) and gel-cast (solid line) alumina bodies¹
3. Elaboration and characterization of porous Alumina-based materials

The dilatometric (left) and derivative (right) curves of A and AZ gel-cast bodies sintered at 1500 °C for 3 h are reported in Figure 3.8.

![Dilatometric and derivative curves of A and AZ gel-cast bodies](image)

**Fig. 3.8:** Dilatometric (left) and derivative (right) curves of AZ (dash red line) and A (solid black line) gel-cast samples

The green and fired density, evaluated by geometrical and Archimedes methods respectively, as well as the main data determined by the dilatometric study of A and AZ bodies are collected in Table 3.2. The theoretical densities (TD) were estimated by applying the rule of mixtures for composite systems, on the basis of the ceramic volume fractions, using density values of 3.99 and 4.19 g/cm³ for A and AZ, respectively.

**Table 3.2:** Green and fired density (TD%) as well as the main data determined by the dilatometric study of A and AZ gel-cast bodies sintered at 1500 °C for 3 h

<table>
<thead>
<tr>
<th>Sample</th>
<th>Green density (TD%)</th>
<th>Fired density (TD%)</th>
<th>T&lt;sub&gt;onset&lt;/sub&gt; (°C)</th>
<th>T&lt;sub&gt;max&lt;/sub&gt; (°C)</th>
<th>Total linear shrinkage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>52</td>
<td>99.0</td>
<td>1126</td>
<td>1360</td>
<td>18</td>
</tr>
<tr>
<td>AZ</td>
<td>42</td>
<td>94.0</td>
<td>1225</td>
<td>1374</td>
<td>29</td>
</tr>
</tbody>
</table>

In our study, a linear shrinkage of about 18% was found in A sample whereas an higher shrinkage of 30% was obtained in the case of AZ samples. AZ materials were characterized by lower green density as compared to A samples: a different interaction between Agar and the composite powder as well as the presence of a not-fully crystallized zirconia phase could influenced the particle packing. After the isothermal step of 3 h at 1500 °C, sintered densities of 99.0 and 94.0 TD% were respectively yielded for A and AZ samples. A maximum temperature of 1360 °C was revealed in A sample, in agreement with literature data (Figure 3.7). A slightly higher maximum temperature, equal to 1374 °C, was instead revealed in AZ sample. On the ground of these results, the sintering conditions of the gel-cast A materials are fixed at 1400 °C for 1 h in order to limit the grain growth.
Instead, in order to further increase the fired density, the sintering temperature was increased to 1550 °C, for 3 h, in the case of the gel-cast AZ samples.

In these conditions, both gel-cast materials reached a density of about 96 TD%. As a consequence, a residual micro-porosity of about 4 vol% can be estimated, due to the thermal degradation of the gelling agent. The same behavior was observed by Bartulli et al. and Meille et al., who found a residual micro-porosity of about 7 and 3 vol% in Y-PSZ and alumina samples, respectively, obtained by gel-casting process with agar as gelling agent.

### 3.2 Characterization of dense and porous Alumina-based materials

#### 3.2.1 Porosity and density evaluation

The total and closed porosity were calculated using the following expressions:

\[
\text{Total porosity (\%)} = \left(1 - \frac{\text{geometrical density}}{\text{Theoretical density}}\right) \times 100
\]

\[
\text{Closed porosity (\%)} = \left(1 - \frac{\text{Archimedes density}}{\text{Theoretical density}}\right) \times 100
\]

Once again, the theoretical densities (TD) were estimated by applying the rule of mixtures for composite systems by using density values of 0.93, 3.99 and 4.19 g/cm³ for PE, A and AZ, respectively.

The mean values of the relative densities, with respect to the theoretical one, before and after sintering, and the total and closed porosity for the porous components are reported in Table 3.3.

#### Table 3.3: Mean values of the relative densities and porosity contents for the several studied materials

<table>
<thead>
<tr>
<th>Samples</th>
<th>Green geometrical density (TD%)</th>
<th>Fired geometrical density (TD%)</th>
<th>Total porosity (%)</th>
<th>Fired Archimedes density (%TD)</th>
<th>Closed porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A65</td>
<td>59 ± 4</td>
<td>38 ± 5</td>
<td>62 ± 6</td>
<td>57 ± 7</td>
<td>43 ± 5</td>
</tr>
<tr>
<td>A70</td>
<td>53 ± 3</td>
<td>29.5 ± 1.4</td>
<td>70 ± 2</td>
<td>63 ± 5</td>
<td>37 ± 5</td>
</tr>
<tr>
<td>A75</td>
<td>47 ± 2</td>
<td>16.9 ± 1.3</td>
<td>83 ± 2</td>
<td>87 ± 4</td>
<td>12 ± 3</td>
</tr>
<tr>
<td>AZ65</td>
<td>54 ± 3</td>
<td>44 ± 2</td>
<td>57 ± 3</td>
<td>62 ± 2</td>
<td>38 ± 2</td>
</tr>
<tr>
<td>AZ70</td>
<td>54 ± 3</td>
<td>40 ± 3</td>
<td>60 ± 2</td>
<td>64 ± 2</td>
<td>36 ± 2</td>
</tr>
<tr>
<td>AZ75</td>
<td>48 ± 3</td>
<td>27 ± 3</td>
<td>73 ± 2</td>
<td>75 ± 3</td>
<td>25 ± 6</td>
</tr>
</tbody>
</table>

Even if the PE amount is strictly controlled, lower porosity volumes than expected were created during the sintering treatment of the AZ materials. A separation between the PE spheres and composite ceramic slurry could be supposed during the casting under vacuum.

Instead, in the case of A materials, the total porosity was better controlled: higher total porosity was only observed in the A75 bodies that reached a final total porosity of about 83 vol%.
3. Elaboration and characterization of porous Alumina-based materials

Since the total porosity values were obtained from the geometrical densities, these discrepancies between experimental and expected porosities can be also explained by the final irregular shape of the samples. In fact, the machining of the fired components is a very difficult step due to their brittleness.

In both compositions, the mean green density decreases by increasing the PE amount, moving from 59-54 TD% to 47-48 TD%, for A and AZ materials, respectively. This is due to a lower amount of gelling agent used at highest porosity.

The same behavior was observed for the fired density: as expected, it decreases by increasing the pore volume percentage.

Finally, the closed porosity decreases by increasing the total porosity, since the number and the size of the interconnection among pores increase by increasing the PE spheres content. Since A and AZ samples exhibit different total porosity, the comparison between the closed porosity of the two compositions is quite complex; AZ materials are characterized by higher closed porosity, being lower the total one.

More information about the pore size and distribution were obtained by SEM analyses as will be discussed in the next paragraph.

### 3.2.2 Microstructural and phase characterization

In order to investigate the phase composition, the sintered A and AZ samples were submitted to XRD analyses. The corresponding XRD patterns of the dense A and AZ samples are reported, as an example, in Figure 3.9.

![XRD patterns of dense A and AZ sintered samples.](image)

Fig. 3.9: XRD patterns of dense A and AZ sintered samples.

Sintering cycles: 1400 °C for 1 h and 1550°C for 3 h in the case of A and AZ samples, respectively. (M= Monoclinic zirconia phase JCPDS no. 74-0815, T= Tetragonal zirconia phase JCPDS no. 82-1398 and α=α-alumina phase JCPDS no. 10-0173)
Both tetragonal and monoclinic zirconia phases were detected in the AZ samples. With regard to the dense AZ material, a low monoclinic volume fraction of 0.14 was calculated using the Toraya equation. As a consequence, relevant tetragonal zirconia volume fraction was successfully retained at room temperature (after sintering), even without the addition of a phase stabilizer. As suggested by Garvie, this is probably due to the presence of very small crystals with smaller surface energy that hinder the tetragonal to monoclinic transformation.

In addition, the constraining effect of the stiffer alumina matrix can improve the stability of the tetragonal zirconia grains at room temperature.

In order to investigate the microstructure, both A and AZ gel-cast bodies were submitted to SEM analyses. Firstly, the microstructure of A and AZ gel-cast samples without pore formers, were observed revealing a fine-grained and homogeneous materials as illustrated in Figure 3.10.

![SEM micrographs](a) A (20µm) (b) AZ (5µm)

**Fig. 3.10:** SEM micrographs at different magnifications of a) A and b) AZ gel-cast samples without pore formers. Sintering cycles: 1400°C for 1 h and 1550°C for 3 h in the case of A and AZ samples, respectively.

The use of a well-dispersed alumina suspension allowed obtaining a homogeneous microstructure, characterized by well-packed and very fine alumina particles (Figure 3.10 a).
3. Elaboration and characterization of porous Alumina-based materials

White zirconia grains, homogeneously distributed inside the alumina matrix (dark particles) can be observed in the AZ microstructure (Figure 3.10b), thus indicating that the adopted processing method was successful in producing homogeneous materials.

However, a residual, intergranular porosity was also observed, as expected on the basis of the final density, probably due to the gelling agent, as above discussed.

An image analysis software was used to establish the grain size: mean value of 1.4±0.7 µm was obtained for alumina grains in A samples. Whereas, mean grain size of 0.9±0.4 µm and 0.5±0.2 µm were respectively found for alumina and zirconia particles in composite materials.

In spite of the significantly higher sintering temperature of AZ materials (1550 °C) as compared to A ones (1400 °C), a finer microstructure was obtained thus demonstrating the effective pinning exerted by the zirconia particles on the alumina grain boundaries.

For the sake of clarity, the particle size distributions by number of the two compositions are reported in Figure 3.11, further demonstrating the decrease of the alumina grain size in the AZ materials compared to the A ones.

![Particle size distribution by number of A (bottom) and AZ (top) without pore formers.](image)

**Fig. 3.11:** Particle size distribution by number of A (bottom) and AZ (top) without pore formers.

White empty bars: alumina; patterned bars: zirconia

Secondly, the microstructure of the green gel-cast materials with the pore formers was investigated: the corresponding SEM images for the A sample, as an example, are reported in Figure 3.12.

A well-packed green ceramic microstructure characterized by a quite homogeneous distribution of the PE spheres inside the ceramic matrix can be observed.

![SEM images of the green porous A materials](image)

**Fig. 3.12:** SEM images of the green porous A materials
Finally, the polished surfaces of the fired A65, A70, A75, AZ65, AZ70, and AZ75 specimens were submitted to SEM analyses.

The acquired micrographs for the several samples are reported in Figure 3.13.

![SEM images of: (a) A65, (b) A70, (c) A75, (d) AZ65, (e) AZ70, and (f) AZ75 samples; Higher magnification images of: (g) A, and (h) AZ struts](image)

The SEM observations of the porous materials revealed a uniform distribution of the macro-pores (Fig. 3.13a–f) and the presence of a diffuse micro-porosity with dimensions of about 1 μm (Fig. 3.13 g–h), as already observed in the previous gel-cast samples without the pore formers.

A partly damage of the porous structure can be observed, especially at high porosity, due to the polishing step.

The SEM image analysis performed measuring about 400 pores for each composition, allowed the evaluation of the pore size distribution.

However, it is well known that the size distribution obtained measuring the diameters of the pores in the 2D sections is related, but not equivalent, to the actual size distribution of pores in the 3D space."
In fact, when a random plane intersects a distribution of objects, particles or pores, spherical or not, in a volume, it cuts the objects at different height, not necessarily through their centres. Consequently, the frequency of measured diameters for a particular class in the distribution is given by the contribution of some pores having that size, and to other pores characterized by a larger diameter that the cut-plane intersects far from the centre.

The particle size distribution of PE spheres and the apparent pore size distributions of A and AZ materials, as obtained by SEM image analysis, are reported in Figure 3.14.

![Graph showing particle size distribution](image)

**Fig. 3.14:** Particle size distribution of PE spheres and the apparent pore size distributions of A and AZ materials as obtained by SEM image analysis.

Different pore size distributions were revealed for the two compositions: A samples show larger pore diameters, with a mean value of about 190 µm, whereas lower values are determined for the AZ specimens, in which a mean diameter of 130 µm was observed.

The lower mean pore size in AZ body is justified by its higher linear shrinkage during sintering.

In fact, starting from an average PE particle size of 230 µm and considering linear shrinkages of about 18% and 30% for A and AZ, respectively, average pore diameters of about 190 µm for the former sample and of 160 µm for the latter one can be estimated, in agreement with the experimental values.

The particle size distributions of alumina and zirconia particles were also evaluated by image analyses on SEM micrographs of the AZ struts. Mean grain size of 0.7±0.2 µm and 0.3±0.1 µm were found for alumina and zirconia particles, respectively.

The comparison with the particle size distributions of the dense AZ components revealed lower grain size of both zirconia and alumina particles in porous components. This is clearly illustrated in Figure 3.15 where, the particle size distributions of AZ samples, with and without pore formers, are compared.
A possible explanation for such difference lies in the thermal treatment that the samples withstood. In fact, in order to prevent the structure collapsing during the decomposition of the PE spheres, several isotherms have been introduced in the thermal cycle, in particular in the temperature range 400-600 °C. As reported by Naglieri et al.¹⁶ and discussed in section 2.2, this temperature range promotes the homogeneous crystallization of very small zirconia crystallites on the alumina particles surface. Therefore, an effective pinning during the subsequent higher temperature treatment can be exerted by the zirconia grains, thus retaining the alumina grain growth during sintering.

This can explain that both alumina and zirconia grains were finer in cellular AZ as compared to the dense materials.

The SEM images revealed an increase in the interconnections among the pores, and consequently a decrease of the volume fraction of the solid phase, as the amount of the fugitive phase increases. Therefore, an estimation of the wall thickness and its dependence from the relative porosity was performed using the following equation¹⁷:

\[
e = \phi \left( \left( \frac{P_{\text{max}}}{P} \right)^{1/3} - 1 \right)
\]

where \(e\) is the wall thickness, \(\phi\) the mean pore diameter (evaluated by image analysis), \(P_{\text{max}}\) the maximum porosity and \(P\) the total porosity reported in Table 3.3. The maximum porosity was calculated with the maximal packing of pores without interpenetration and equal to 0.8, as estimated by Meille et al.¹¹.

The wall thickness as a function of the total porosity of A and AZ materials is reported in Figure 3.16.
3. Elaboration and characterization of porous Alumina-based materials

![Graph showing wall thickness as a function of total porosity for A and AZ materials.](image)

**Fig. 3.16:** The wall size as a function of the total porosity of A and AZ materials

As expected, when the pore volume increases, the mean distance between two neighboring pores and, consequently, the wall dimensions decrease.

Figure 3.16 also highlights the influence of the pore diameter on the wall thickness: for a given porosity, cellular materials characterized by lower pore diameters present smaller wall thickness with respect to cellular materials characterized by bigger pore diameters.

Since AZ materials are characterized by lower pore diameters (see Figure 3.13), their wall thickness is always smaller compared to the A materials, as clearly shown in the above Figure.

In summary, AZ materials exhibited finer grain size, smaller pores and smaller struts among them, compared to the A ones.

### 3.2.3 Mechanical characterization

The mechanical properties were investigated by uniaxial compressive tests (Instron 4201).

The measurements were made in displacement control mode and the load was applied at a crosshead rate of 1 mm/min. Cylindrical samples, with a diameter of 10 mm and an height of 20 mm, previously machined in order to obtain flat and parallel surfaces, were used.

At least 10 specimens for each composition were tested.

The influence of the composition as well as of the porosity degree on the mechanical properties were investigated.

The means of the obtained compressive strength values as a function of the total porosity of the A and AZ materials are reported in Table 3.4.
Characterization of dense and porous Alumina-based composites

Table 3.4: Mean values of the total porosity and the compressive strength of A and AZ materials

<table>
<thead>
<tr>
<th>Samples</th>
<th>Total Porosity (%)</th>
<th>MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>A65</td>
<td>62 ± 6</td>
<td>12 ± 8</td>
</tr>
<tr>
<td>A70</td>
<td>70 ± 2</td>
<td>4 ± 2</td>
</tr>
<tr>
<td>A75</td>
<td>83 ± 2</td>
<td>1.0 ± 0.5</td>
</tr>
<tr>
<td>AZ65</td>
<td>57 ± 3</td>
<td>28 ± 11</td>
</tr>
<tr>
<td>AZ70</td>
<td>60 ± 2</td>
<td>25 ± 6</td>
</tr>
<tr>
<td>AZ75</td>
<td>73 ± 2</td>
<td>5 ± 1</td>
</tr>
</tbody>
</table>

Logically, the strength strongly decreases by increasing the total porosity, dropping from 12 to 1 MPa in the A65 and A75 and from 28 to 5 MPa in the AZ65 and AZ75 materials, respectively. At the same time, the standard deviation of the strength decreases as the porosity increases, since the strength becomes more and more related to the development of a damage zone rather than the propagation of micro-cracks.

Compressive strength values too close to the maximum measurable strength of the employed machine were recorded on dense gel-cast A and AZ materials, leading to unreliable results. On the basis of a previous work\(^4\), a compressive strength value of about 900 MPa could be expected for alumina dense components.

The results of this study are in agreement with those obtained by Prabhakaran et al.\(^1\), who reported for alumina materials a decrease of the compressive strength from 5.9 to 2.0 MPa when the porosity increases from 67 to 76.7 vol%.

On the other hand, higher compressive strength values, equal to about 7 MPa, were obtained by He et al.\(^1\) for alumina bodies having about 87 vol% of porosity.

Wu et al.\(^2\) and coworkers reported compressive strength values in the range of 3.8-27 MPa for alumina bodies characterized by porosity in the range 82-64 vol%, respectively.

These discrepancies can be ascribed to the different pore size distributions, being the former materials characterized by two distinctive pore ranges of around 40 and 120 µm and the latter ones by smaller pore size of about 2 µm.

In our study, an increase of the compressive strength in AZ materials with respect to the A ones was revealed but, since the total porosity deeply influences the mechanical response, only A and AZ materials having the same porosity level can be compared.

The A and AZ bodies having about 60 vol% of porosity exhibited a compressive strength of 12 and 25 MPa, while in the case of about 70 vol% of porosity, compressive strength of 4 and 5 MPa were recorded for A and AZ, respectively.

In order to investigate the different behavior of A and AZ materials, the compressive stress-strain curves of both, at porosities of 60 and 70 vol%, are shown in Figure 3.17 a and b, respectively.
3. Elaboration and characterization of porous Alumina-based materials

Typical stress-strain curves of foams were observed: a linear elastic region was recorded at low stresses, then the ceramic struts progressively broke and the damage accumulated layer by layer\textsuperscript{21}. The materials undergo to a progressive collapse, with the formation and propagation of small cracks in the cell walls\textsuperscript{11}. When the crack length is larger than the distance between two pores, the solid wall breaks propagating the fracture to the neighbor wall.

Once again, it was confirmed the decrease of the stress by increasing the porosity, both in A and AZ materials: for a given pore size, the wall thickness decreases by increasing the porosity (see Figure 3.16), thus more easily linking two neighbor pores.

The different compressive behavior of A and AZ components are mainly evident at lower porosity levels, as illustrated in Figure 3.17. In fact, for samples having 60 vol\% of porosity, the area under the stress-strain curves is higher for AZ with respect to A composition. Since this area is proportional to the work of fracture, it can be expected that the porous composite ceramics present not only higher compressive strengths, but are also less brittle.

This behavior is also observed in the stress-strain curves of the 70 vol\% porous materials (Fig. 3.17b), even if the decrease in wall thickness makes it less evident.

Although an effective reinforcement of the second phase was assumed by Yu et al.\textsuperscript{22} and Vogt et al.\textsuperscript{23} to explain the improvement of the mechanical properties of the composite materials with respect to the pure alumina ones, a deeper analysis has to be performed. Particularly, the influence of the pore size on the mechanical properties has to be investigated.

Among the several literature studies described in section 1.3\textsuperscript{19,24-26}, Meille and coworkers\textsuperscript{11} reported an increase of the fracture strength of about 68\% in porous alumina having smaller pores, with respect to alumina materials having the same porosity level but bigger pores. Moreover, they highlighted that the dependence of the fracture strength on the pore size becomes more and more important as the porosity increases.

On the ground of these results, in our study, the improvement of the mechanical properties in AZ materials can also be ascribed to the presence of smaller pores.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.17.png}
\caption{Compressive curve of A and AZ samples with a porosity of: (a) 60 vol\%, and (b) 70 vol\%}
\end{figure}
The mechanical behavior of cellular solids can be described, as stated in section 1.3, following the Gibson and Ashby model\textsuperscript{21} in which the brittle crashing strength, $\sigma_{cr}^*$, is correlated to the relative density, $\rho^*/\rho_s$, by the following equation:

$$\sigma_{cr}^* = \sigma_{fs} \cdot C_6 \left( \frac{\rho^*}{\rho_s} \right)^{3/2}$$

where $\sigma_{fs}$ is the modulus of rupture of the solid cell wall material and $C_6$ is a constant equal to about 0.2.

In order to verify if the samples tested in this study follow this model, the log-log of the compressive strength as a function of the relative density was plotted and reported in Figure 3.18.

The power dependence of strength (n) on the relative density, can be found as the angular coefficient of the fitted curve.

![Fig. 3.18: Compressive strength as a function of the relative density of A (square) and AZ (circle) materials, plotted on log scales](image)

Once again, for the two investigated compositions, the compressive strength increases as the relative density increases.

As shown in the above Figure, very close n values, equal to 4.4 and 4.5 for A and AZ samples, respectively, were found, demonstrating almost the same power dependence of strength on the relative density.

However, these values are different from the exponent of the Gibson and Ashby model (equal to 1.5) for open cellular ceramics with a constant cell size.

This difference can be attributed to \textit{i}) the different nature of the porosity, which in these materials is not exclusively open, as in the case of Gibson and Ashby model, and to \textit{ii}) the cell features (size distribution, non-periodic and disordered distribution, volume fraction of solids in the cell faces), as well as to \textit{iii}) the presence of closed voids or defects in the struts, as reported in the literature\textsuperscript{27-29}. 
Consequently, the different microstructural features, such as pore size distribution, wall thickness and grain size, have to be taken also into account in order to explain the improvement of the mechanical properties in the porous AZ materials. In fact, as above discussed, composites materials are characterized by finer grains and smaller pores with respect to the A ones, which positively affect their mechanical behavior.

3.2.3.1 Toughening mechanisms

As discussed in the first chapter, in ZTA materials alumina provides high strength while zirconia exerts a toughening effect due to its controlled transformation into the monoclinic phase and interaction of the crack front with microcracks induced by the same transformation\textsuperscript{14}. In order to study the effect of the second phase, both mechanisms were studied.

Since the transformation toughening is recognized to be the most important toughening mechanism, first of all, the transformability of the tetragonal zirconia phase was investigated. XRD analyses were performed on both as-sintered and fractured surfaces of AZ samples, with and without pore formers: the corresponding monoclinic volume fractions are illustrated in Figure 3.19. The transformability, calculated as the difference between the monoclinic volume fraction of the sintered and fractured surfaces, is also reported in Figure 3.19.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig3.19.png}
\caption{Monoclinic volume fraction of sintered (black-square) and fractured (red-circle) surfaces and transformability (blue-triangle) of the several AZ samples}
\end{figure}

A relatively low content of the monoclinic zirconia phase, in the range between 0.14 and 0.07 vol\% as the porosity changed from 0 to 75 vol\%, was found on the surface of all sintered materials. With regard to the fractured surfaces, AZ without pore former showed a relatively low transformability (27\%), but still in agreement with literature values for unstabilized zirconia\textsuperscript{30,31}.
On the contrary, in the porous materials the transformability was much lower, being less than 10%, probably due to the smaller tetragonal zirconia grains in AZ cellular samples as compared with the dense reference materials (see Fig. 3.15). In fact, a critical zirconia size in the range 0.38-0.46 μm, below which the t-m transformation is hindered, was found by Garvie\textsuperscript{13} reported for Al\textsubscript{2}O\textsubscript{3}-ZrO\textsubscript{2} materials.

The critical diameters for t-m transformation can be deduced combining the cumulative distribution curves of zirconia grains size (Fig. 3.15) and the related amounts of the monoclinic zirconia (vol\%) on the as-sintered and fractured surfaces (Fig. 3.19)\textsuperscript{32}. The results related to dense and porous AZ materials are shown in Figure 3.20, highlighting the influence of the porosity on the critical diameters for transformation.

![Fig. 3.20: Cumulative volume distribution of zirconia grains size and related critical diameters for t-m transformation of porous (black-square line) and dense (red-circle line) AZ materials. The red and black arrows refer to the zirconia monoclinic volume fraction on the as-sintered and fractured surfaces and related grains size](image)

Critical diameters for t-m transformation in the range 0.45-0.6 and 0.25-0.3 μm were found for dense and porous AZ materials, respectively. Therefore, the lowest transformability of porous materials can be explained by comparing these values with the mean zirconia grains size: the transformation was hindered since the observed tetragonal zirconia grains size is outside this range.

In addition, in composite materials the transformability of the tetragonal zirconia grains is influenced by the matrix constraint and the residual stresses due to the thermal mismatch. On one side, a higher transformability in porous than in dense bodies can be assumed due to the less effect of the constraining matrix as the porosity increases.
On the other side, a progressive decrease of residual tensile stresses on the zirconia grains can be assumed by increasing porosity, thus affecting in a negative way their tendency to transform.

In fact, zirconia grains shrink more than alumina ones due to their higher coefficient of thermal expansion (about 8 and $11 \times 10^{-6} \, ^\circ C^{-1}$ for alumina and tetragonal zirconia, respectively).

By applying the formalism of Gregori et al., residual stresses in alumina in dense AZ material ($\langle \sigma \rangle_A$) can be calculated according to this equation:

$$\langle \sigma \rangle_A = K^* \cdot \left( E_{ETM} + X_m \varepsilon^T \right)$$

where $\varepsilon^T$ is the transformation strain, equal to 0.016, $X_m$ is the volume fraction of the tetragonal transformed to monoclinic zirconia, $K^*$ is the effective elastic modulus of the composite and $E_{ETM}$ is the elastic thermal mismatch strain.

The elastic thermal mismatch is given by

$$E_{ETM} = \left( \alpha_Z - \alpha_A \right) \cdot \left( T_0 - T_{st} \right)$$

in which $\alpha$ is the CTE (A and Z refer to alumina and zirconia, respectively), $T_0$ is the room temperature and $T_{st}$ is the temperature below which elastic stresses are frozen-in, here assuming as the sintering temperature.

Instead, $K^*$, following the approach developed by Kreher and Pompe, can be expressed as:

$$K^* = \frac{3nK_AK_zf_z}{K_zf_A + nK_Af_A + nKzf_z + Kzf_z}$$

where $K$ is the bulk modulus (the subscripts have the usual meaning) equal to 250 and 150 GPa for alumina and zirconia respectively, $f$ is the constituent volume fraction and $n$ is given by:

$$n = \frac{2(1 - \nu_A)}{1 + \nu_A}$$

where $\nu_A$ is the Poisson modulus of alumina equal to 0.27.

By applying this formalism and considering a $X_m$ starting value of 0.14, a compressive hydrostatic stress of about 170 MPa in the matrix and a tensile stress of about 1538 MPa for the dispersion can be obtained for the dense AZ materials.

Tensile residual stresses have a considerable positive effect on the tetragonal zirconia transformability, since it decreases the critical transformation stress. Consequently, the crack tip transformation will occur at a much lower stress level. This can explain the relatively good transformability of the tetragonal zirconia grains in AZ sample without the pore former.

However, according to Gregori et al., the compressive stress in alumina decreases as the monoclinic zirconia fraction increases, reaching the reverse situation, with the matrix under tensile stress, above 25-29% of transformation.
Characterization of dense and porous Alumina-based composites

However, when porous bodies are considered, by applying the same Gregory formalism, a decrease of the tensile stress on the zirconia grains in the range 35-60 %, depending on the porosity, can be estimated, thus affecting in a negative way their tendency to transform.

In particular, the bulk modulus of the porous material, $K^*$, was calculated by applying the Gibson Ashby model \(^{21}\) in which it is expressed as:

$$K^* = E_s \frac{1}{9} \left( \frac{\rho^*}{\rho_s} \right)$$

where $E_s$ is the Young modulus of the dense material, assumed to be 383 GPa\(^{\text{35}}\) and $\rho^*/\rho_s$ is the relative density.

Since some important approximations were done, the result represents an estimated value that highlights the decrease of the tensile stress on the zirconia grains as the porosity increases.

Finally, the microcracking toughening mechanism was investigated. Since it is possible only when the size of the zirconia grains exceeds a critical size ($D_s$), the following expression\(^{36}\) was applied in order to calculate the critical size of our composite:

$$D_s = \frac{10 \cdot \gamma_m}{(\Delta \varepsilon)^2 \cdot E}$$

where $\gamma_m$ is the fracture energy for microcracking and $E$ is the elastic modulus of the composite, estimated by Kern\(^{29}\) to about 1 J/m\(^2\) and 400 GPa, respectively. $\Delta \varepsilon = \Delta \alpha \cdot \Delta T$ is the product of CTE and temperature differences.

A critical zirconia size of about 1.2 \(\mu m\) was hence determined, which is higher than the values experimentally determined in both porous and dense AZ materials (equal to 0.5 and 0.3 \(\mu m\), respectively, as shown in Fig. 3.15), thus reducing the microcracking toughening mechanisms in our composites.

Since too low transformability and too smaller zirconia grains were found in AZ samples, both the well-known zirconia toughening mechanisms (transformation and microcracking toughening) can be reasonably ruled out in the examined composite cellular materials.

Therefore, the improvement in the mechanical properties of AZ samples with respect to A materials can be ascribed to the finer microstructure (finer grains and smaller pores).
3. Elaboration and characterization of porous Alumina-based materials

3.3 Conclusions

In this chapter, the modified gel-casting process for the development of dense and porous A and AZ materials was described. Cellular ceramics with tailored microstructural features and phase composition were successfully prepared by coupling the surface modification method with the gel-casting technology.

The porosity features, such as the amount of porosity, the pore shape and size distribution was quite easily controlled by adding a fixed amount of polyethylene spheres sieved in a restricted dimensional range.

A and AZ samples with porosity amounts ranging from about 60% to about 80 vol% were thus produced and characterized in terms of their microstructure and mechanical properties.

The mechanical behavior in compression can be described as cellular-like: the fracture occurs by tensile cracking of the solid walls.

For all the examined compositions, the strength decreases with decreasing the relative density.

From a compositional point of view, porous AZ composites showed higher compressive strength as compared to pure alumina ones.

The well-known zirconia toughening mechanisms (transformation and microcracking toughening) were investigated, revealing a very poor influence on the mechanical properties.

In fact, the presence of smaller tetragonal grains as well as their lower tensile residual stresses after sintering probably reduce their transformability to monoclinic phase under the applied stress.

Finer grains and smaller pores of AZ materials, with respect to A ones, can be reasonably responsible of the improved mechanical properties.

Further studies will be necessary to better tailor the zirconia grain size and amount in order to verify if the well-known reinforcing mechanisms of zirconia in alumina matrix could be exploited also in porous materials.
3. Elaboration and characterization of porous Alumina-based materials

References


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3. Elaboration and characterization of porous Alumina-based materials


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3. Elaboration and characterization of porous Alumina-based materials
Chapter 4

Elaboration and characterization of dense Ce-TZP based materials

In this chapter the elaboration and characterization of dense Ce-TZP-based composites, in the framework of the Longlife project, is described.

Firstly, the composites were developed by slip casting technique, then characterized in terms of dispersibility, microstructure and phase composition. The influence of some parameters, like the calcination and sintering cycles, on these properties were also discussed.

With the aim of developing zirconia-based materials exhibiting high strength and toughness without suffer of low temperature degradation in the lifetime of an implant, major efforts were devoted to their mechanical (by means of Vickers hardness, fracture strength and toughness tests) and physical (optical properties, transformability, aging behavior) characterization.

The necessity to deepen the relationship between the final properties and the composition/microstructure is also highlighted.
4.1. Processing and sintering of Ce-TZP-based composites

Ce-TZP based composite powders, precisely ZA₆Sr₈ and ZA₆Mg₈ powders, were prepared according to the method described in Section 2.3.

Here, the process used to develop green bodies and sintered composite materials is described.

Whatever the ceramic shaping method applied, the powder dispersion step is fundamental for achieving high microstructural homogeneity in the green and sintered states.

Depending on the moisture content, ceramic shaping methods can be divided into dry pressing (moisture<15%), plastic forming (15-25% moisture) and slip casting (moisture > 25%).

Even if the dry pressing is the most economic process for large production runs, the slip-casting technique was used in this work since it allows obtaining optimal particle packing and homogeneous green microstructures from nanopowders. Moreover, the safety of this process is high due the confinement of nanoparticles in a liquid phase.

Suitable suspensions for slip casting should exhibit a compromise between high solid loading, low viscosity and homogenous dispersion of all the constituents. Therefore, a deep investigation on the composite powder dispersion was performed and described in the following.

With the aim of promoting the by-product burn out and the crystallization of the second/third phases, the ZA₆Sr₈ and ZA₆Mg₈ powders were submitted to specific thermal treatments. The influence of such thermal treatments on the powder dispersibility and final microstructure was investigated.

Three calcination treatments, taking into account the second/third phases crystallization temperatures, were selected and performed at (1) 900 °C for 1 h, (2) 1050 °C for 30 min and (3) 1150 °C for 30 min.

In fact, on the ground of the thermal analyses results previously discussed (sections 2.3.1-2.3.2) and in agreement with literature data [1], the second/third phases crystallization should occur at about 1200 °C. Therefore, the thermal treatments at 900 and 1150 °C represent temperatures quite far and close, respectively, of this point and 1050 °C, an intermediate temperature. Thermal treatments at higher temperatures were ruled out since a strong agglomeration of powders can occurs (see Table 2.8-2.10) having a negative consequence on the dispersibility of powders.

In addition, at these three selected temperatures, a relatively low fraction of zirconia monoclinic phase was determined by XRD analyses on ZA₆Sr₈ and ZA₆Mg₈ composites, as shown in the Tables 2.7-2.11 (Chapter 2), respectively.

In agreement with the sample designation described in the Appendix (section A.1), the thermal treatment will be hereafter specified as the superscript of the sample name: as example, ZA₆Sr₈-Ce111150-30m refers to the 11 mol%Ce-TZP-8 vol% Al₂O₃-8 vol% SrAl₁₂O₁₉ sample thermally treated at 1150 °C for a soaking time of 30 min.

All the thermal treated powders were dispersed in distilled water by ball milling, at solid loading of 8 vol% (corresponding to 33 wt%), with a powder-to-spheres weight ratio of 1:10.
In order to yield stable suspensions with a minimum degree of particle agglomeration, various anionic dispersants were tested; the best results were obtained by the addition of Duramax D-3005, supplied by Rohm and Haas Company, Philadelphia, PA (USA) (technical data reported in Chapter 2, Table 2.5).

The optimum Duramax D-3005 content was found to be 3 wt% with respect to the powder amount. A suspension pH value of about 8 was reached after the addition of the dispersant.

The particle size distribution was checked by laser granulometry during more than one day in order to evaluate the dispersion degree obtained by ball milling.

As an example, particle size distributions for the ZA₈Sr₈Ce₁₁₁₅₀₃₀m powder measured at different milling time are reported in Figure 4.1.

In addition, the corresponding d₁₀, d₅₀ and d₉₀ values are reported in Table 4.1.

As supported by these results, the best d values were obtained after 29 h of ball milling, reaching agglomerate size comparable with the size of the zirconia primary particles.

![Fig. 4.1: Volume cumulative distribution as a function of the agglomerate size of ZA₈Sr₈Ce₁₁₁₅₀₃₀min powder (black-square curve) and aqueous suspension after 20 (red-circle curve), 24 (blue-triangle curve) and 29 (green-star curve) hours of ball milling, with 3wt% of Duramax D-3005](image-url)
4. Elaboration and characterization of dense Ce-TZP based materials

Table 4.1: \(d_{10}, d_{50}, d_{90}\) values of the cumulative particle size distributions of \(\text{ZA}_8\text{Sr}_8\text{Ce}^{1150-30\text{min}}\) powder and aqueous suspensions after 20, 24 and 29 h of ball milling, with 3wt% of Duramax D-3005

<table>
<thead>
<tr>
<th></th>
<th>(d_{10}) ((\mu)m)</th>
<th>(d_{50}) ((\mu)m)</th>
<th>(d_{90}) ((\mu)m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{ZA}_8\text{Sr}_8\text{Ce}^{1150-30\text{min}})</td>
<td>11</td>
<td>42</td>
<td>255</td>
</tr>
<tr>
<td>20h-ball milled (in the presence of Duramax D-3005)</td>
<td>0.4</td>
<td>0.6</td>
<td>1.2</td>
</tr>
<tr>
<td>24h-ball milled (in the presence of Duramax D-3005)</td>
<td>0.33</td>
<td>0.6</td>
<td>1.1</td>
</tr>
<tr>
<td>29h-ball milled (in the presence of Duramax D-3005)</td>
<td>n.d*</td>
<td>0.5</td>
<td>0.9</td>
</tr>
</tbody>
</table>

n.d, non-detected by the instrument, as described in the Appendix

A similar dispersion behavior was observed for \(\text{ZA}_8\text{Sr}_8\text{Ce}^{900-1\text{h}}\) and \(\text{ZA}_8\text{Sr}_8\text{Ce}^{1050-30\text{min}}\) powders as well as for the thermally treated \(\text{ZA}_8\text{Sr}_8\text{Ce}^{10}, \text{ZA}_8\text{Sr}_8\text{Ce}^{10.5}\) and \(\text{ZA}_8\text{Sr}_8\text{Ce}^{11.5}\) powders, thus demonstrating no influence of the calcination temperature (in the studied range 900-1150 °C) and of the ceria amount on the powder dispersibility.

As regards of \(\text{ZA}_8\text{Mg}_8\text{Ce}^{1150-30\text{min}}\) powder, it reached a similar de-agglomeration degree after 29 h of ball-milling, characterized by a monomodal size distribution with \(d_{50}\) and \(d_{90}\) of 0.46 and 0.79 \(\mu\)m, respectively.

Figure 4.2 and Table 4.2 show the particle size distributions and the \(d_{10}, d_{50}\) and \(d_{90}\) values of \(\text{ZA}_8\text{Mg}_8\text{Ce}^{1150-30\text{min}}\) powder as a function of the milling time.

Fig. 4.2: Volume cumulative distribution, as a function of the agglomerate size of \(\text{ZA}_8\text{Mg}_8\text{Ce}^{1150-30\text{min}}\) powder (black-square curve) and aqueous suspension after 24 (red-circle curve), 29 (blue-triangle curve) and 48 (green-star curve) hours of ball milling, with 3wt% of Duramax D-3005
Table 4.2: $d_{10}$, $d_{50}$, $d_{90}$ values of the cumulative particle size distributions of ZA$_8$Mg$_8$-Ce$_{11}$ $^{1150-30min}$ powder and aqueous suspension after 24, 29 and 48 hours of ball milling, with 3 wt% of Duramax D-3005

<table>
<thead>
<tr>
<th></th>
<th>$d_{10}$ (µm)</th>
<th>$d_{50}$ (µm)</th>
<th>$d_{90}$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZA$_8$Mg$<em>8$-Ce$</em>{11}$ $^{1150-30min}$</td>
<td>6.1</td>
<td>28</td>
<td>211</td>
</tr>
<tr>
<td>24h-ball milled</td>
<td>0.34</td>
<td>0.6</td>
<td>1.1</td>
</tr>
<tr>
<td>(in the presence of Duramax D-3005)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>29h-ball milled</td>
<td>n.d.*</td>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td>(in the presence of Duramax D-3005)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

n.d., non-detected by the instrument, as described in the Appendix

In order to reach an high solid loading suitable for the slip casting process, once stated the best dispersion conditions at 8 vol% (33 wt%), in terms of powder/sphere weight ratio (1:10) as well as dispersant concentration (3 wt%), the solid loading was enhanced to about 26 vol% (65 wt%) by progressive addition of small amount of powder (2 wt% at each addition).

The suspensions were de-aired, by keeping them under vacuum for few minutes, and then the slips were slip-casted into pure alumina porous molds and kept into humidity-controlled chamber for about 1 week, during which the moisture level was progressively reduced.

After complete drying, a mean green density of about 3.10 g/cm³, corresponding to about 53 TD% was obtained. The theoretical density was calculated on the ground of the rule of mixtures for composite systems (taking values of 6.19, 3.99, 4.02 and 4.16 g/cm³ for tetragonal ZrO₂, α-Al₂O₃, SrAl₁₂O₁₉ and CeMgAl₁₃O₁₉, respectively).

Such shaping technique allowed the preparation of either pellets (sintered dimensions about Ø=12 mm in diameter and h=2 mm in height) and bars (sintered dimensions 45 x 4 x 3 mm) suitable for the mechanical characterization.

In order to define the best sintering cycle (heating and cooling rate, maximum temperature and holding time), some samples were submitted to dilatometric analyses, performed in an absolute dilatometer which measures the expansion of the sample relative to the sample holder (as described in the Appendix).

In order to investigate the effect of the second/third phases on the sintering behavior, both pure 10Ce-TZP and ZA$_8$Sr$_8$-Ce$_{11}$ bodies were analyzed.

Also the bi-phasic Ce-TZP based composites having 16 vol% of Al₂O₃ (referred as ZA$_{16}$) and 16 vol% of SrAl₁₂O₁₉ (referred as ZSr₁₆) were submitted to dilatometric analyses. Both of last composites were processed following the same surface modification route from a commercial Ce-TZP powder as previously described.

The corresponding dilatometric (left) and derivative (right) curves performed at 1500 °C for 1 h (heating and cooling rate of 5 °C/min) are displayed in Figure 4.3 for 10Ce-TZP (black line), ZA$_{16}$ (purple line), ZSr$_{16}$ (blue line) and ZA$_8$Sr$_8$ (green line).
The green densities as well as the main data determined from the dilatometric study are collected in Table 4.3.

![Graph showing dilatometric and derivative curves](image)

**Figure 4.3:** Dilatometric (left) and derivative (right) curves of 10Ce-TZP (black line), ZA16 (purple line), ZSr16 (blue line) and ZA8Sr8 (green line) sintered at 1500°C for 1 h.

**Table 4.3:** Green density and main data from the dilatometric analysis of 10Ce-TZP, ZA16, ZSr16 and ZA8Sr8-Ce11 sintered at 1500°C for 1 h

<table>
<thead>
<tr>
<th>Sample</th>
<th>Green density g·cm⁻³ / TD%</th>
<th>T_onset (°C)</th>
<th>T_transformation (°C)</th>
<th>T_max (°C)</th>
<th>Total linear shrinkage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10Ce-TZP</td>
<td>3.45 / 61.7</td>
<td>1026</td>
<td>-</td>
<td>1175</td>
<td>17.9</td>
</tr>
<tr>
<td>ZA16</td>
<td>2.83 / 53.1</td>
<td>1160</td>
<td>1222</td>
<td>1390</td>
<td>21.7</td>
</tr>
<tr>
<td>ZSr16</td>
<td>2.87 / 53.7</td>
<td>1160</td>
<td>1225</td>
<td>1305</td>
<td>20.5</td>
</tr>
<tr>
<td>ZA8Sr8-Ce11</td>
<td>2.82 / 52.8</td>
<td>1195</td>
<td>1232</td>
<td>1370</td>
<td>23.2</td>
</tr>
</tbody>
</table>

After sintering at 1500°C for 1 h, all the materials reached full densification (>99.9 %TD). The 10Ce-TZP sample, whose green density was higher as compared to the other composite bodies, underwent to a total linear shrinkage of about 18%, whereas linear shrinkages in the range 20.5-23.2% were recorded on the three composite systems. In addition, it can be observed that the presence of second-phase constituents (Al and Sr) induced a significant increase of the onset sintering temperature (T_onset, data in Table 4.3): it was about 1030°C for pure ceria-stabilized zirconia, 1160°C for the two bi-phasic materials and even higher (about 1200°C) for the tri-phasic body.

The derivative curves show the existence of some inflection points during the heating up to 1500°C. In the case of 10Ce-TZP sample, almost a single inflection point at about 1175°C was detected, attributed to the temperature at which the maximum sintering rate occurs (referred as T_max in Table 4.3).
Furthermore, a very limited linear shrinkage (of about 1 %) can be observed in the 1300-1500 °C range, probably due to a significant grain growth.

For what concerns ZA16, two inflection points, located at about 1222 °C and 1390 °C can be noticed. The first one (hereafter referred as T_{transformation}) can be reasonably assigned to the α-alumina crystallization from transition phases, which commonly occurs in that temperature range. The latter can be again related to the maximum sintering rate (T_{max}) of this bi-phasic material.

The derivative curve of ZSr16 evidences inflection points at temperatures quite similar to those of ZA16, precisely located at 1225 and 1305 °C. Once again, the first signal can be attributed to aluminate crystallization and the latter on to T_{max}.

Finally, for ZA8Sr8-Ce11 the two inflection points are located at about 1232 °C and 1370 °C.

On the ground of the results obtained on the bi-phasic systems, the first one can be ascribed both to α-alumina and aluminate crystallization while the latter can be related to T_{max}.

It is interesting to note that the T_{transformation} was almost the same for the three composite materials. The comparison with the pure ceria-stabilized zirconia data highlights the role of the second/third phases in delaying the densification of zirconia, as already stated in the literature.

However, the delay due to the aluminate phase seems to be lower compared to that of alumina.

In the following dilatometric analysis, the effect of the heating rate on the composite densification behavior will be clarified. Samples of ZA8Sr8-Ce11 were sintered up to 1500 °C for 1 h at the heating rates of 2, 5 and 10°C/min.

Figure 4.4 shows the dilatometric curves recorded under these different conditions, showing that the faster heating rate (10°C/min) induced an overall displacement (of about 40-50 °C) of the onset sintering temperature as well as higher T_{max} values. In contrast, almost superimposed dilatometric curves were obtained by heating at 2 °C/min and 5 °C/min.

![Dilatometric curves of ZA8Sr8-Ce11 bars up to 1500 °C for 1 h, at heating rates of 2 °C/min (blue curve), 5 °C/min (red curve) and 10 °C/min (black curve)](image_url)
In accordance with the dilatometric results, the following thermal cycle was set for sintering composites: (a) heating rate of 2 °C/min up to 600 °C for 2 h (in order to perform the thermal decompose of the organic dispersant slowly), (b) heating rate of 5 °C/min up to the final sintering temperature (in the range 1400-1450°C for 1 to 4h) and (c) cooling rate of 5°C/min until the room temperature.

In the studied final sintering range, this cycle allowed producing fully dense composites, characterized by a homogeneous and tailored microstructure, as described in the following section.

### 4.2 Phase and microstructural characterization of the sintered bodies

In order to investigate the microstructural features and the phase composition, the tri-phasic zirconia based composites (ZA8Sr8-Ce10, ZA8Sr8-Ce10.5, ZA8Sr8-Ce11, ZA8Sr8-Ce11.5 and ZA8Mg8-Ce11) were characterized by means of SEM and XRD analyses. Moreover, for estimating the monoclinic volume fraction and the fired or final density, the Toraya equation and the Archimedes method were respectively applied.

HRTEM analysis coupled with EDX was also performed on the sintered ZA8Sr8-Ce11 sample, in order to investigate in a deeper way the phase composition and the zirconia stabilization degree.

#### 4.2.1 ZA8Sr8 sintered composites

In the case of ZA8Sr8 composites, the effect of i) ceria amount, ii) powder thermal pre-treatment (900°C/1h, 1050°C/30 min and 1150°C/30 min) and iii) the sintering cycle (in the range 1400-1450 °C for 1-4 h) on the microstructural development was investigated.

In agreement with the sample designation described in the Appendix (A.1), the sample name will be followed by the letters sc to indicate the slip casting process and by the sintering cycle.

For sake of clarity, (ZA8Sr8-Ce11)1150-30minsc/1450-1h is referred to the tri-phasic ZA8Sr8-Ce11 powder thermally treated at 1150 °C for 30 min, then dispersed, slip-cast and finally sintered at 1450 °C for a soaking time of 1 h.

In Figure 4.5, the SEM images of several ZA8Sr8 composites, thermal pre-treated at 1150 °C for 30 min and sintered at 1450 °C for 1 h, are reported.
Phase and microstructural characterization of the sintered bodies

Fig. 4.5: SEM images of: a) ZA₈Sr₈-Ce10, b) ZA₈Sr₈-Ce10.5, c) ZA₈Sr₈-Ce11 and d) ZA₈Sr₈-Ce11.5 materials sintered at 1450 °C/1h (Higher magnification micrographs on the right)
4. Elaboration and characterization of dense Ce-TZP based materials

From the lower magnification images (on the left), and whatever the composition of the system, a quite homogeneous and fully dense microstructures, composed by grains having both different phase contrast and morphology, can be appreciated.

In order to associate different morphological features with a specific composition or phase, EDX analysis was carried out. According to this analysis, the bright and bigger grains were associated to the ceria-stabilized zirconia phase. Strontium was statistically detected in all the dark elongated grains, but completely absent in the dark round-shaped ones. So, strontium aluminates were associated to the first morphology (elongated or needle-like grains), whereas $\alpha$-alumina phase was associated to the latter one (round-shaped grains).

From the higher magnification micrographs (on the right) a well distributed and relative fine alumina grains, predominantly located in inter-granular positions, were observed. Also, a good distribution of the needle-like grains in all composite materials can be stated.

In order to obtain the main microstructural parameters, the image analysis technique$^5$ was applied on several sintered microstructures.

The mean zirconia, alumina and aluminates grain size, as well as the fired density and the monoclinic volume fraction for the several investigated composites are reported in Table 4.4.

Microstructural features seem to be independent of the ceria content, being the grain distribution and size very similar in all four composites.

In addition, is worth noting that the same microstructural features were observed in samples prepared using different sintering and calcination temperatures, thus underlying the minor role of such parameters on the microstructure development.
Table 4.4: Fired density, monoclinic volume fraction ($V_m$), mean zirconia, alumina and aluminates grains size of the several studied samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fired density (TD%)</th>
<th>$V_m$ (%)</th>
<th>ZrO$_2$ mean size (µm)</th>
<th>Al$_2$O$_3$ mean size (µm)</th>
<th>Aluminate mean length (µm); aspect ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>($ZA_8Sr_8$–Ce11)$^{900,\text{sc}/1450,-,1\text{h}}$</td>
<td>99.0</td>
<td>2</td>
<td>0.7 ± 0.3</td>
<td>0.37 ± 0.09</td>
<td>0.8 ± 0.2 a.r. 6 ± 2</td>
</tr>
<tr>
<td>($ZA_8Sr_8$–Ce11)$^{1050,-,30\text{min sc}/1450,-,1\text{h}}$</td>
<td>99.9</td>
<td>1</td>
<td>0.6 ± 0.3</td>
<td>0.3 ± 0.1</td>
<td>0.6 ± 0.2 a.r. 4 ± 2</td>
</tr>
<tr>
<td>($ZA_8Sr_8$–Ce11)$^{1150,-,30\text{min sc}/1450,-,1\text{h}}$</td>
<td>&gt;99.9</td>
<td>1</td>
<td>0.5 ± 0.3</td>
<td>0.3 ± 0.1</td>
<td>0.6 ± 0.2 a.r. 6 ± 2</td>
</tr>
<tr>
<td>($ZA_8Sr_8$–Ce11)$^{1150,-,30\text{min sc}/1400,-,1\text{h}}$</td>
<td>&gt;99.9</td>
<td>1</td>
<td>0.5 ± 0.2</td>
<td>0.3 ± 0.1</td>
<td>0.5 ± 0.2 a.r. 5 ± 2</td>
</tr>
<tr>
<td>($ZA_8Sr_8$–Ce11)$^{1150,-,30\text{min sc}/1400,-,2\text{h}}$</td>
<td>&gt;99.9</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>($ZA_8Sr_8$–Ce10)$^{1150,-,30\text{min sc}/1400,-,2\text{h}}$</td>
<td>99.6</td>
<td>15</td>
<td>0.5 ± 0.2</td>
<td>0.26 ± 0.06</td>
<td>0.6 ± 0.2 a.r. 5 ± 2</td>
</tr>
<tr>
<td>($ZA_8Sr_8$–Ce10)$^{1150,-,30\text{min sc}/1450,-,1\text{h}}$</td>
<td>99.8</td>
<td>5</td>
<td>0.6 ± 0.2</td>
<td>0.26 ± 0.08</td>
<td>0.7 ± 0.2 a.r. 6 ± 2</td>
</tr>
<tr>
<td>($ZA_8Sr_8$–Ce10)$^{1150,-,30\text{min sc}/1450,-,2\text{h}}$</td>
<td>&gt;99.9</td>
<td>5</td>
<td>0.7 ± 0.2</td>
<td>0.39 ± 0.09</td>
<td>0.7 ± 0.2 a.r. 6 ± 2</td>
</tr>
<tr>
<td>($ZA_8Sr_8$–Ce10.5)$^{1150,-,30\text{min sc}/1450,-,1\text{h}}$</td>
<td>&gt;99.9</td>
<td>5</td>
<td>0.6 ± 0.2</td>
<td>0.3 ± 0.1</td>
<td>0.6 ± 0.2 a.r. 5 ± 2</td>
</tr>
<tr>
<td>($ZA_8Sr_8$–Ce11.5)$^{1150,-,30\text{min sc}/1450,-,1\text{h}}$</td>
<td>99.7</td>
<td>1</td>
<td>0.7 ± 0.3</td>
<td>0.3 ± 0.1</td>
<td>0.9 ± 0.2 a.r. 5 ± 2</td>
</tr>
</tbody>
</table>

- values not available or analysis not yet performed

All the materials reached full densification with a low monoclinic volume fraction in the range 1-15%. Higher $V_m$ values were observed in the $ZA_8Sr_8$–Ce10 material where the ceria content for a stabilizing zirconia was the lower.

In all composite materials, zirconia and alumina mean grains sizes were in the range 0.5-0.7 and 0.26-0.39 µm, respectively, demonstrating a very fine microstructure as already reported in literature $^6$-$^9$. Regarding the aluminates phases, the mean length was in the range of 0.5-0.9 µm, and the aspect ratio (length/width) was 4-6, in a good agreement with previous results $^10$. 

Cette thèse est accessible à l’adresse : http://theses.insa-lyon.fr/publication/2014ISAL0035/these.pdf
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Even if the small differences in grain size among the various composites are within the calculated standard deviations (as detailed in Table 4.4), some considerations can be done.

In fact, the ZA₈Sr₈-Ce11 composite shows an increase of the main microstructural parameters by decreasing the calcination temperature: the zirconia mean grain size moves from 0.5, 0.6 to 0.7 µm by decreasing the calcination temperature from 1150, 1050 to 900 °C, respectively.

In addition, as expected, a grain growth was also observed by increasing the sintering temperature and the dwell time. In particular, in the ZA₈Sr₈-Ce10 case, the zirconia and the alumina mean grain size increases from 0.5 to 0.7 µm and from 0.26 to 0.39 µm, respectively, by increasing the sintering temperature from 1400 to 1450 °C.

All sintered materials were submitted to XRD analyses: once again, neither the calcination pre-treatment nor the sintering cycle affected in a significant way their phase composition. Therefore, as an example, the XRD patterns of the four compositions sintered at 1450 °C for 1 h are shown in Figure 4.6.

The XRD analyses revealed the presence of peaks related to tetragonal and monoclinic zirconia phases. Due to the difference in the absorption coefficients and the low second/third phase volume content (8 vol%), the intensity of peaks corresponded to α-Al₂O₃ and SrAl₁₂O₁₉ phases is very low but still detectable with respect to the zirconia peaks.

Among the several compositions here studied, the only difference is the decrease of the monoclinic volume fraction as the ceria amount increases (thus by increasing the zirconia stabilization degree).
The mean value of the $V_m$ drops from 5 to 1 vol% moving from $ZA_8Sr_8$-$Ce10$ to $ZA_8Sr_8$-$Ce11.5$ composition (as shown in the Table 4.4).

Nevertheless, in order to obtain further information on the material compositional features, HRTEM and EDX nanoprobe analyses, were carried out in a selected composition ($ZA_8Sr_8$-$Ce11$).

The HAADF images are reported in Figure 4.7, highlighting again the different phase compositions on this material: brighter regular-shaped, dark elongated and dark rounded grains can be easily recognized.

![Fig. 4.7: HAADF images of the sintered $ZA_8Sr_8$-$Ce11$ sample](image)

A preliminary EDX analysis on a global zone revealed an atomic composition of about 28.0, 61.0, 8.0, 3 and 0.4 at% of Zr, O, Al, Ce and Sr respectively. Taking into consideration the theoretical composition of 84 vol% ZrO$_2$-8 vol% Al$_2$O$_3$-8 vol% SrAl$_{12}$O$_{19}$, an almost perfect agreement was obtained.

A more precise analysis allowed to confirm that the strontium was detected only in the dark elongated grains, being completely absent in the dark round-shaped particles. Moreover, cerium was detected only in the brighter grains, being completely absent in the dark phases.

EDX point analyses were performed on several elongated grains and on zirconia grains in order to estimate the aluminate phase composition and the ceria amount into the zirconia.

A mean atomic Sr:Al ratio equal to 1:15 with an error of about 20% corroborated an aluminate phase composition matching well with the stoichiometric SrAl$_{12}$O$_{19}$ phase.

Regarding the zirconia stabilization degree, a mean ceria amount of 10.4 mol%, with respect to the zirconia, was revealed: taking into account the standard deviation, a good agreement with the ceria theoretical value of 11.0 mol% (estimated on the basis of the ceria precursors added during the elaboration step) was obtained.

However, more precise information could be yield by carrying out the EDX point analysis on the raw material (i.e., the as-received 10Ce-TZP powder), thus determining the ceria content in the unmodified starting powder.
4. Elaboration and characterization of dense Ce-TZP based materials

Therefore, thanks to the work of characterization here done, it is possible to state that in ZA₈Sr₈-type materials:

- the brighter grains seem to be made of tetragonal zirconia stabilized with ceria;
- the extra-cerium content added during the synthesis is incorporated into the zirconia phase;
- the dark round-shaped particles are made of pure α-Al₂O₃;
- the dark grains with elongated morphology can be attributed to the strontium aluminate phase (most probably SrAl₁₂O₁₉).

Despite of the work of Misevicius et al., who reported the possibility to obtain Ce-doped strontium aluminates by adding cerium nitrate during the sol-gel synthesis, in our study any cerium trace was detected in the aluminate phase. In particular, he reported that a successful cerium doping, in the concentration range of 0.25–1.00 Ce mol%, was achieved during the sol–gel synthesis of SrAl₂O₄.

In addition, a cerium doping in the range of 0.25–3.00 mol% was also achieved in the Sr₃Al₂O₆ or Sr₂Al₆O₁₀ phases.

Even if the cerium concentration range investigated by Misevicius et al. is with the range of our study, the discrepancy could be due to the use of Ce³⁺ rather than Ce⁴⁺ nitrate (as in our case), during the synthesis process.

To conclude, HRTEM analyses allowed demonstrating that the adopted elaboration process is a very promising manner to develop tri-phasic composites with tailored microstructure, phase composition and a good control over the zirconia stabilization degree.

4.2.2 ZA₈Mg₈ sintered composites

Similar to the ZA₈Sr₈ composites, the ZA₈Mg₈-Ce11 slip cast bodies were submitted to the following sintering cycle: (a) heating rate of 2 °C/min up to 600 °C for 2 h, (b) heating rate of 5 °C/min up to 1450 °C and (c) cooling rate of 5 °C/min until the room temperature.

The as-sintered ZA₈Mg₈ body was characterized by a very high monoclinic zirconia phase (above 80 vol%) and quite large zirconia grains (of 0.9 ± 0.2 µm) as revealed by XRD and SEM analyses.

Consequently, other two different sintering cycles were adopted: the sintering temperature was set at 1350 °C for 2 h and at 1400 °C for 1 h.

Once again, any effect of the calcination temperature on the phase composition and microstructural features was observed.

Figure 4.8 shows some SEM images taken on ZA₈Mg₈-Ce11 composites thermally pre-treated at 1150 °C for 30 min and sintered at 1400 °C for 1 h (a) and at 1350°C for 2 h (b).
Phase and microstructural characterization of the sintered bodies

Fig. 4.8: SEM images of ZA₈Mg₈Ce₁₁ materials sintered at 1400 °C for 1 h (a) and at 1350°C for 2 h (b)
The microstructure is composed by grains having both different phase contrast and morphology. The EDX analysis confirmed that the brighter, regular-shaped grains can be associated to the stabilized zirconia phase. Magnesium was systematically detected into the elongated grains, but completely absent into the dark, rounded grains, allowing associating the first morphology to a magnesium-based aluminate.

However, a deepening on the compositional and microstructural features of the different observed grains can be only obtained by HRTEM analysis equipped by an EDX nanoprobe, as done in the case of ZA$_8$Sr$_8$ composites.

In particular, this analysis will be useful to confirm the formation of a cerium/magnesium-aluminate (whose formula can be CeMgAl$_2$O$_{19}$). It should be pointed out that to fulfill this hypothesis, cerium reduction from Ce$^{4+}$ to Ce$^{3+}$ should occur. In order to verify this issue, XPS analysis will be also carried out in a next future, allowing deepening the cerium oxidation state.

As discussed in the Section 2.3, a second hypothesis envisages the complete diffusion of extra-cerium and/or magnesium added during the elaboration process inside the zirconia lattice. In this case, an enhancement of the zirconia stabilization degree as respect to the starting ceria-stabilized ZrO$_2$ powders could be achieved, as occurred in the ZA$_8$Sr$_8$ system.

In contrast with the behavior observed in ZA$_8$Sr$_8$-based materials, the microstructure of ZA$_8$Mg$_8$-Ce$_{11}$ developed after the two different sintering cycles appeared completely different.

Very long (> 4 µm) and complex magnesium aluminates grains were observed at the higher sintering temperature (1400 °C) while very few and shorter grains with elongated morphologies can be observed at the lower one (1350 °C).

Nevertheless, both of these elongated phases appear very different from the magnesium aluminates grains observed by Magnani et al.$^{12}$ in alumina/zirconia composites (see Figure 1.26 section 1.1).

By analogy with the results obtained on ZA$_8$Sr$_8$-Ce$_{11}$ composite, dark round-shaped grains could be attributed to α-Al$_2$O$_3$.

Hence, a quite homogeneous distribution of the alumina secondary phase, predominantly located at inter-granular positions into the zirconia matrix, was observed in both samples.

Additionally, in some areas of these microstructures larger zirconia grains of some microns in size were observed, mainly around the elongated grains.

In order to summarize the main microstructural features observed in these materials, image analysis results are shown in Table 4.5, where the mean zirconia, alumina and aluminate grain sizes are reported. The fired density and the monoclinic volume fraction were also added to this Table.
Table 4.5: Fired density, monoclinic volume fraction \((V_m)\), mean zirconia, alumina and aluminates grains size of the several studied samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fired density (TD%)</th>
<th>(V_m) (%)</th>
<th>(\text{ZrO}_2) mean size ((\mu)m)</th>
<th>(\text{Al}_2\text{O}_3) mean size ((\mu)m)</th>
<th>Aluminate mean length ((\mu)m); aspect ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{ZA}_8\text{Mg}_8-\text{Ce11})^{1150-30\text{min sc/1400-1h}})</td>
<td>&gt;99.9</td>
<td>1</td>
<td>(0.8 \pm 0.3)</td>
<td>(0.3 \pm 0.1)</td>
<td>(4 \pm 2) a.r. (9 \pm 3)</td>
</tr>
<tr>
<td>((\text{ZA}_8\text{Mg}_8-\text{Ce11})^{1150-30\text{min sc/1350-2h}})</td>
<td>&gt;99.9</td>
<td>1</td>
<td>(0.4 \pm 0.2)</td>
<td>(0.25 \pm 0.06)</td>
<td>(2 \pm 1) a.r. (6 \pm 3)</td>
</tr>
</tbody>
</table>

The Archimedes measurements and XRD analyses revealed near fully dense materials with a very low monoclinic volume fraction (about 1 vol%).

Zirconia and aluminate grain sizes significantly increased by increasing the sintering temperature while alumina grain size remained almost unchanged.

Finally, in Figure 4.9 the XRD patterns of the two \(\text{ZA}_8\text{Mg}_8-\text{Ce11}\) sintered materials are depicted. From these patterns it is clear that the same phases were crystallized in both materials, thus demonstrating that their very different microstructural features cannot be related to a difference on the phase development.

Fig. 4.9: XRD patterns of \(\text{ZA}_8\text{Mg}_8-\text{Ce11}\) samples sintered at: a) 1350 °C/2h and b) 1400 °C/1h
\(*=\text{JCPDS no. 74-0815}, + =\text{JCPDS no. 82-1398} \text{ and } ^* =\text{JCPDS no. 46-1212}\)
4. Elaboration and characterization of dense Ce-TZP based materials

The tetragonal zirconia is the predominant phase, beside traces of monoclinic zirconia and α-alumina phases. Any peaks corresponding to the CeMgAl11O19 phase were revealed, probably due to the overlapping with the characteristic peaks of the monoclinic zirconia phase, its low volume amount (8 vol%) and absorption coefficient. As already mentioned, further analyses, in particular HRTEM with EDX nanoprobe and XPS analyses, will be performed on the ZA8Mg8 system, in order to obtain more precise information about the phase compositions.

4.3 Mechanical characterization

In this section, the mechanical properties of five different tri-phasic zirconia composites (ZA8Sr8-Ce10, ZA8Sr8-Ce10.5, ZA8Sr8-Ce11, ZA8Sr8-Ce11.5 and ZA8Mg8-Ce11) are characterized by means of Vickers hardness, biaxial flexural and four point bending tests. The optical properties and the stability versus ageing are discussed as well. A short description of the employed characterization techniques and of the samples preparation procedure is presented at the beginning of each paragraph.

When possible, the results are compared with those obtained on bi-phasic 10Ce-TZP composites containing 16 vol% of Al2O3 processed by the same route. Since no extra-cerium was added during the elaboration process, a zirconia stabilization degree of 10 mol% is present in the bi-phasic materials, referred hereafter as ZA16-Ce10.

ZA16-Ce10 materials sintered at 1450 °C for 1 h are characterized by high fired density (99.9 TD%), low monoclinic volume content (1%) and a zirconia and alumina mean grain sizes of 0.5±0.2 µm and 0.3±0.1 µm, respectively.

Since the processing of pure 10Ce-TZP ceramics (un-cracked and with a low monoclinic volume fraction) is quite difficult, 3Y-TZP ceramics (Tosoh TZ-3YSB-E [12]) were also used as reference. They were obtained by Cold Isostatic Pressing (CIP) and sintering at 1450 °C for 2 h: high density (>99.9 TD%), pure tetragonal zirconia phase, and a zirconia mean grain size of 0.4±0.1 µm were thus found.
4.3.1 Vickers Hardness

A preliminary mechanical characterization of zirconia based tri-phasic composites was performed by means of Vickers hardness: a diamond pyramid with 90° base angles and 136° face angle was used. The hardness was calculated from the mean length of the two imprint diagonals (d), and the applied load (P) by following the equation given in ASTM E384:

\[ Hv = \frac{1.8544 \cdot P_{(Kgf)}}{d^2_{(mm^2)}} \]

The hardness values were calculated by applying three different loads, 5-10-30 Kgf, for 10 s and as the average value of five indentations for each tested load.

A TESTWELL FV700 equipment allowing the application of a maximum load of 30 Kgf was used.

The unit of hardness given by the test is known as the Vickers Pyramid Number (Hv). The hardness number can be converted into units of Pascals, but should not be confused with a pressure.

For sample preparation, specimens were encapsulated into an acrylic resin and polished up to 1 µm. As reported in the literature, there is no significant influence of the used resin for test loads up to 30 Kgf\textsuperscript{14}. The other face of the resin was also polished in order to obtain two plane and parallel surfaces.

After the Vickers indentation test, the imprints were characterized by optical microscopy (Zeiss Axio phot). If cracks were generated at the tip of the indentation imprint, the crack length was measured. If the crack length c, was higher than the diagonal length a (c>>a) the fracture toughness was estimated by applying three different empirical equations\textsuperscript{15,16,17}.

In order to have a correct hardness measurement, the diagonal lengths should not deviate more than 5% each other, the distance between indents should be at least three times the diagonal length and the specimen thickness should be at least 1.5 times the diagonal length of the indentation.

Since Vickers hardness testing is easy to implement and relatively fast, it was used as a preliminary test in order to select the optimal calcination and sintering temperatures.

Three different pre-treatment or calcination cycles (in the range 900-1150 °C (with soaking times of 30 min-1 h) and five different sintering cycles (in the range 1350-1450 °C (with soaking times of 1-2 h) were investigated on ZA\textsubscript{8}Sr\textsubscript{8}-Ce11 and ZA\textsubscript{8}Mg\textsubscript{8}-Ce11 materials.
4. Elaboration and characterization of dense Ce-TZP based materials

- **Influence of the pre-treatment cycle**

In order to evaluate the influence of the pre-treatment or calcination cycle, the (ZA₈Sr₈-Ce₁₁)⁹₀₀⁻¹₉, (ZA₈Sr₈-Ce₁₁)¹₀₅₀⁻³₀ᵐ and (ZA₈Sr₈-Ce₁₁)¹₁₅₀⁻³₀ᵐ samples were analyzed. All specimens were sintered up to 600 °C for 2 h (heating rate of 2 °C/min) and then up to 1450 °C for 1 h (heating rate of 5 °C/min). In Figure 4.10, their corresponding hardness values for the applied loads (5-10-30 Kgf) are reported.

High Vickers hardness, in the range of 9.3 -10.4 GPa, were found in tested samples. These values are in agreement with the literature data in which Vickers hardness around 9-12 GPa were reported for Ce-TZP materials.

Lower hardness values were obtained in (ZA₈Sr₈-Ce₁₁)⁹₀₀⁻¹₉ sample since it was characterized by a lower final density and slightly larger zirconia grains with respect to (ZA₈Sr₈-Ce₁₁)¹₀₅₀⁻³₀ᵐ and (ZA₈Sr₈-Ce₁₁)¹₁₅₀⁻³₀ᵐ materials (as shown in Table 4.4).

In addition, in the first sample, some defects were present on its surface, thus causing a higher standard deviation.

The best results, at the three applied loads, were obtained on (ZA₈Sr₈-Ce₁₁)¹₁₅₀⁻³₀ᵐ sample which is characterized by the higher fired density and smaller zirconia grains as compared to the other two composites.

On the ground of these results, it was decided to perform the pre-treatment or calcination cycle at 1150 °C for 30 min.

From a general point of view, it has been recognized that the hardness usually exhibits a significant load-dependence. In some cases, the measured hardness decreases with increasing the applied load but, in other cases the opposite behavior can be observed. The first phenomenon is often
referred as the indentation size effect (ISE) and the latter one as the reversed indentation size effect (RISE).

In our study both phenomena were observed: the hardness increased by increasing the load (RISE effect) up to 10 Kgf, then it decreased.

Although, for most brittle ceramics the hardness decreases with increasing the indentation load\(^2\), a reversed indentation size effect was reported by Gong \textit{et al.}\(^2\) and Kern \textit{et al.}\(^2\) in zirconia-alumina composites. The comparison between these data and our results, seems to indicate that the hardness indentation size effect depends not only on the tested material but also on the characteristics of the test procedure.

The experimental data should be analyzed to yield a so-called load-independent hardness for which several approaches\(^2,2\) were proposed but a deeper investigation is out of the aim of this study.

- **Influence of the sintering cycle**

In order to study the influence of the sintering cycle, the \((ZA_{0.8}Sr_{0.2}Ce_{1.1})_{1150-30m}\) bodies were sintered in the temperature range 1400-1450 °C for a different soaking times (1-2 h) and then submitted to Vickers hardness tests.

Their corresponding hardness, as a function of the applied load, are reported in Figure 4.11.

![Figure 4.11: Vickers hardness number (Hv) as a function of the applied load of \((ZA_{0.8}Sr_{0.2}Ce_{1.1})_{1150-30m}\) bodies sintered in the temperature range 1400-1450 °C for a different soaking times (1-2 h)](image)

With the only exception of the sample sintered at 1450 °C, the hardness decreased by increasing the applied load, thus showing an indentation size effect.

Once again, high Vickers hardness, in the range of 10.1 -10.5 GPa, were found in tested samples in agreement with the literature data\(^8,18,19\). It is observed that when the load of 5 Kgf was applied, the sample sintered at 1400 °C for 1 h showed the highest hardness, while the best result was observed...
4. Elaboration and characterization of dense Ce-TZP based materials

for the material sintered at 1450 °C tested at 30 Kg. Hence, taking into account the results obtained at higher applied loads (10 and 30 Kg), the sintering cycle performed at 1450 °C for 1 h was selected as the best one for ZA₈Sr₈-Ce₁₁ material.

It should be remembered that in this system, the microstructural features remained almost the same after sintering (ZA₈Sr₈-Ce₁₁)₁¹⁵⁰-³⁰m bodies at 1450 and 1400 °C for 1 h (see Table 4.4).

The same study was conducted on (ZA₈Mg₈-Ce₁₁)₁¹⁵⁰-³⁰m. The Vickers hardness, as a function of the applied load and of the several sintering cycles, are reported in Figure 4.12.

![Figure 4.12: Vickers hardness number (Hv), as a function of the applied load, of (ZA₈Mg₈-Ce₁₁)₁¹⁵⁰-³⁰m sintered in the temperature range 1350-1400 °C for different soaking times](image)

As it can be observed from the above Figure, a slight reversed indentation size effect and an important role of the sintering cycle were observed on Mg-containing composition.

This result was expected since, as previously discussed, the sintering cycle has a strong influence on the microstructure of this composite. In fact, higher Vickers hardness of about 10.7 GPa was measured when the sintering cycle of 1350 °C for 2 h was applied, being the microstructure finer (see Table 4.5). Moreover, good hardness values in the range 10.2-10.4 GPa were obtained in (ZA₈Mg₈-Ce₁₁)₁¹⁵⁰-³⁰m sintered at 1400 °C for 1 h.

Thus, in order to study the influence of the microstructure differences onto the strength and toughness, both sintering cycles were applied on the Mg-containing bodies.
- **Influence of the composition**

In this section, the Vickers hardness of several Ce-TZP composites (ZA₈Sr₈-Ce10, ZA₈Sr₈-Ce10.5, ZA₈Sr₈-Ce11, ZA₈Sr₈-Ce11.5, ZA₈Mg₈-Ce11) is presented and compared to the bi-phasic ZA₁₆-Ce10 material.

First of all, for sake of clarity, the hardness values of the composites containing strontium, as a function of the ceria amount, are reported in Figure 4.13. On the ground of the results above reported, the calcination and sintering temperatures of 1150 °C and 1450 °C were applied for 30 min and 1 h, respectively.

Finally, Vickers hardness values of all studied composites are compared in Figure 4.14.

In the case of ZA₈Mg₈-Ce11 the hardness values corresponding to the two sintering cycles (1350 and 1400 °C) are reported.

![Fig. 4.13: Vickers hardness number (Hv), as a function of the applied load and the ceria amount, in the ZA₈Sr₈ system](image)
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The above Figures show a quite strong influence of the composition on the Vickers hardness. The minimum value of about 9.6 GPa was found in the ZA₈Sr₈-Ce10.5 sample while the maximum one, about 10.7 GPa, belongs to the sample ZA₈Mg₈-Ce11 sintered at 1350 °C, characterized by the finest microstructure.

Vickers hardness values measured in all the samples are in agreement with previous reported works done on the same type of materials. Moreover, as clearly shown in Figure 4.13, in the Sr-containing system the Vickers hardness generally increases by increasing the ceria amount whatever the applied load, with the exception of ZA₈Sr₈-Ce10.5 sample. 10 Kg, hardness values of about 10.2, 10.4 and 10.6 GPa were found moving from ZA₈Sr₈-Ce10, ZA₈Sr₈-Ce11 and ZA₈Sr₈-Ce11.5, respectively.

Since comparable microstructural features were observed in all these samples, the influence of the zirconia stabilization degree on the hardness can be considered. As already reported by Nawa et al., a slight increase of the hardness of Ce-TZP composites due to an increase of the ceria amount was observed.

The comparison between the tri- and bi-phasic materials reveals a lower hardness value on the ZA₁₆-Ce10 sample with respect to ZA₈Mg₈-Ce11 sintered at 1350 °C and ZA₈Sr₈-Ce11.5 materials (Figure 4.14), in disagreement with the mixture rule.

In fact, even if the bi-phasic material is characterized by a lower ceria amount, a higher hardness value on the ZA₁₆-Ce10 sample was expected being the volume fraction of the α-alumina harder phase higher. Since neither the density nor the microstructure can explain this discrepancy, further analyses are needed.

Fig. 4.14: Vickers hardness number (HV), as a function of the applied load, for the several studied samples: ZA₈Sr₈ and ZA₁₆-Ce10 sintered at 1450 °C for 1 h and ZA₈Mg₈-Ce11 sintered at 1350 and 1400 °C.
4.3.1.1 Transformability assessed by the indentation method

In order to investigate and compare the capability of zirconia to undergo a stress-induced tetragonal to monoclinic phase transformation in composites, the size of the transformed area around each indentation was measured by means of optical microscopy. The area was calculated as the average of five indentations for each applied load.

Figure 4.15 displays the transformed area after indentation, as a function of the applied load, for the several studied samples. For sake of clarity, only the data of the ZA₈Sr₆-based samples pre-treated at 1150 °C/30 min and sintered at 1450 °C/1h are shown.

In the case of Mg-containing samples as the microstructure is strongly dependent on the sintering cycle, results of both 1350 and 1400°C-sintered materials are reported. Also, the transformed area of the bi-phasic ZA₁₆-Ce10 reference material is shown.

![Transformed area chart](image)

**Fig. 4.15:** The transformed area after indentation, as a function of the applied load, for the several studied samples.

As expected, for all the samples, the transformed area increases by increasing the applied load. Moreover, as it can be observed from the above Figure, the transformability is strongly dependent on the composition, mainly on the zirconia stabilization degree: maximum and minimum transformed areas were found in the ZA₈Sr₆-Ce10 and ZA₈Sr₆-Ce11.5 samples, respectively.

Considering the Sr-containing system, a clear trend was observed: moving from the sample with the lowest ceria content (ZA₈Sr₆-Ce10) to the one with the highest amount (ZA₈Sr₆-Ce11.5), the transformed area, and so the transformability, decreases further demonstrating an increase in the zirconia stabilization degree, as already revealed by HRTEM analysis.
4. Elaboration and characterization of dense Ce-TZP based materials

Taking into account $Z_{\text{A}8}\text{Mg}_{8}\text{-Ce11}$ samples sintered at different temperatures, any significant differences was revealed, further demonstrating the influence of the composition rather than of the sintering temperature and corresponding microstructure on the transformability.

Comparing $Z_{\text{A}8}\text{Sr}_{8}\text{-Ce11}$ and $Z_{\text{A}8}\text{Mg}_{8}\text{-Ce11}$ specimens, lower transformed areas were found in Mg-containing samples. This behavior seems to support the hypothesis that not only extra-cerium but also magnesium could diffuse inside the zirconia lattice, providing further zirconia stabilization and decreasing its transformability.

However, comparing $Z_{\text{A}8}\text{Sr}_{8}\text{-Ce10}$ and $Z_{\text{A}16}\text{-Ce10}$ materials in which there is no extra-ceria addition, a higher stabilization was found in the $Z_{\text{A}16}\text{-Ce10}$ sample. Therefore, not only the ceria stabilization degree, but also the amount and properties of the second and third phases should play an important role on the transformability. For example, it is well known that an increase of the more stiffness alumina phase content can hinder the $t\rightarrow m$ transformation.

In addition, residual stresses generated in zirconia due to the thermal expansion mismatch can strongly affect the $t\rightarrow m$ transformation.

In our study, thermal expansion coefficients (CTE) of the second phases are lower than that of zirconia, thus zirconia is expected to be under tension. Moreover, the CTE of the aluminate phase ($\approx 10^{-6}\text{°C}^{-1}$) is lower than that of the alumina phase ($\approx 8 \cdot 10^{-6}\text{°C}^{-1}$), giving rise to a higher zirconia tensile stresses in the $Z_{\text{A}8}\text{Sr}_{8}$ material with respect to $Z_{\text{A}16}\text{-Ce10}$. Consequently, in the tri-phasic composite the $t\rightarrow m$ transformation should be more favored compared to the reference, thus explaining the lower transformability of $Z_{\text{A}16}\text{-Ce10}$ with respect to $Z_{\text{A}8}\text{Sr}_{8}\text{-Ce10}$ material.

In order to characterize more in detail the magnitude or type of stresses developed in zirconia-based materials, fine Raman analysis could be implemented.

Figure 4.16 collects the images at the same magnification of some indentations for each composition when a load of 30 Kgf was applied, as acquired by the optical microscope using the Nomarski contrast.
The brighter zone around the indentation is associated to the zone in which the tetragonal to monoclinic transformation took place, providing an increase of the volume. 

The above images confirm the results about the transformed area and the samples stability shown in the Figure 4.15. 

A clearly bigger transformed area was revealed in the ZA₈Sr₈-Ce10, ZA₈Sr₈-Ce10.5 and ZA₁₆-Ce10 samples (Figure 4.16 a-b-e), further demonstrating a higher transformability and so a lower zirconia stability degree of these compositions with respect to the others. 

Taking into consideration the Sr-containing composites (Figure 4.16 a-d), a clear decrease of the transformed area around the indentations can be observed moving from a ceria amount of 10.0 to 11.5 mol% thus corroborating an increase of the material stability. 

Moreover, a different morphology of the transformed zone can be noticed.
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Smaller round-shaped transformed areas were observed in samples containing more than 11 mol% of ceria (ZA8Sr8-Ce11, ZA8Sr8-Ce11.5 and ZA8Mg8-Ce11) while large number of deformation branches radially propagated were observed for ceria contents below 10.5 mol% (ZA8Sr8-Ce10, ZA8Sr8-Ce10.5 and ZA16-Ce10).

This last morphology puts in evidence the autocatalytic nature of the tetragonal to monoclinic phase transformation of zirconia. As reported by Reyes et al.\textsuperscript{23}, autocatalysis initiates by a multiple-nucleation event which, once realized, can stimulate further transformation to propagate rapidly over an extended region.

- **Fracture toughness by indentation method**

In all the examined samples, no cracks from the indentation tip were observed when loads of 5 and 10 Kg were applied and only few very short cracks were generated in some samples tested at 30 Kg. Nevertheless, the cracks length was not enough to allow the toughness estimation by indentation techniques\textsuperscript{24}.

As example, Figure 4.17 shows several indentations performed on ZA8Sr8-Ce10 and ZA8Mg8-Ce11, and collected by optical (on the left) and scanning electron (on the right) microscopy. This behaviour qualitatively demonstrates that ceria-stabilized zirconia based composites exhibit a high crack propagation resistance.

Fig. 4.17: Vickers indentations performed on a) ZA8Sr8-Ce10 and b) ZA8Mg8-Ce11 collected by optical (on the left), and scanning electron microscopy (on the right)
4.3.2 Fracture strength by biaxial flexural test

The biaxial flexural strength was evaluated according to the international standard ISO 6872:2008 that specifies the requirements and the corresponding test methods for dental ceramic materials for fixed all-ceramic and metal-ceramic restorations and prostheses.

Samples used for the evaluation of the biaxial flexural test were pellets having the following dimensions: diameter of 12–15 mm and thickness about 2 mm.

Before the test, the sintered specimens were machined on both faces, in order to ensure that opposite faces were flat and parallel and did not differ more than 0.05 mm in parallelism.

As required by the ISO standard, the samples were then ground and finally polished with 16 μm diamond grit, in order to reach the final thickness of 1.2 ± 0.2 mm.

About 10 specimens were prepared for each composition (ZA₈Sr₈-Ce10, ZA₈Sr₈-Ce10.5, ZA₈Sr₈-Ce11, ZA₈Sr₈-Ce10.5, ZA₈Mg₈-Ce11); moreover also 3Y-TZP samples were considered as reference.

As reported before, for both the Sr-containing and Mg-containing samples, calcination treatment was set at 1150 °C for 30 minutes. Sintering cycle was fixed to 1450 °C for a soaking time of 1 hour in the former case; for the latter samples, both the cycles (1350 °C for 2 hours and 1400 °C for 1 hour) were considered in order to evaluate the influence of the different microstructures on the mechanical properties.

The monoclinic volume fraction was evaluated on the tensile surface (the one object of the mechanical test) by X-Ray diffraction.

The samples were placed in the appropriate sample holder and loaded in the centre of the specimen with a 1.4 mm diameter steel rod in a universal testing machine (Instron 8500). The cross-head speed was set at 1mm/min until failure.

Calculation of the biaxial flexural strength was performed with the following equation:

$$\sigma = \frac{-0.2387 \cdot F \cdot (X - Y)}{d^2}$$

where $\sigma$ is the maximum centre tensile stress (MPa), $F$ the load at fracture (N), $X$ and $Y$ are expressed by:

$$X = (1 + \nu) \cdot \ln \left( \frac{r_1}{r_3} \right)^2 + \left( \frac{1 - \nu}{2} \right) \left( \frac{r_2}{r_2} \right)^2$$

$$Y = (1 + \nu) \cdot \left[ 1 + \ln \left( \frac{r_1}{r_3} \right)^2 \right] + (1 - \nu) \left( \frac{r_2}{r_2} \right)^2$$

In which, $\nu$ is the Poisson’s ratio (assumed 0.3), $r_1$ the radius of the support circle (mm), $r_2$ the radius of the loaded area (mm), $r_3$ the radius of the specimen (mm) and $d$ the specimens thickness at the fracture origin (mm).

The average fracture strength value and the monoclinic volume fraction on the tensile surface are reported in Table 4.6 for the several studied compositions. The maximum strength value recorded for each composition is reported in the same Table.
4. Elaboration and characterization of dense Ce-TZP based materials

Table 4.6: The monoclinic volume fraction on the tensile surface ($V_m$) and the average and maximum biaxial flexural strength ($\sigma$) for the several studied compositions.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$V_m$ (%)</th>
<th>$\sigma$ (MPa)</th>
<th>$\sigma$ (Mpa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(ZA$_8$Sr$<em>8$-Ce10)$</em>{1150-30min}^{sc}$/1450-1h</td>
<td>15</td>
<td>719 ± 22</td>
<td>755</td>
</tr>
<tr>
<td>(ZA$_8$Sr$<em>8$-Ce10.5)$</em>{1150-30min}^{sc}$/1450-1h</td>
<td>10</td>
<td>885 ± 128</td>
<td>1058</td>
</tr>
<tr>
<td>(ZA$_8$Sr$<em>8$-Ce11)$</em>{1150-30min}^{sc}$/1450-1h</td>
<td>3</td>
<td>778 ± 47</td>
<td>872</td>
</tr>
<tr>
<td>(ZA$_8$Sr$<em>8$-Ce11.5)$</em>{1150-30min}^{sc}$/1450-1h</td>
<td>6</td>
<td>672 ± 70</td>
<td>813</td>
</tr>
<tr>
<td>(ZA$_8$Mg$<em>8$-Ce11)$</em>{1150-30min}^{sc}$/1400-1h</td>
<td>7</td>
<td>866 ± 40</td>
<td>950</td>
</tr>
<tr>
<td>(ZA$_8$Mg$<em>8$-Ce11)$</em>{1150-30min}^{sc}$/1350-2h</td>
<td>4</td>
<td>718 ± 132</td>
<td>793</td>
</tr>
<tr>
<td>3Y-TZP/1450-2h</td>
<td>0</td>
<td>1427 ± 443</td>
<td>1776</td>
</tr>
</tbody>
</table>

A monoclinic phase in the range of 4-15 vol%, slightly higher than the monoclinic fraction observed in the as-sintered samples (Table 4.4-4.5), was revealed, probably due to the ground step. Since the monoclinic phase reduces the tensile stress in the matrix, an improvement of the mechanical properties, due to the surface finishing, have to be considered. This phenomenon could be especially important on the ZA$_8$Sr$_8$-Ce10 and ZA$_8$Sr$_8$-Ce10.5 material, where the revealed monoclinic phase amount is higher.

For sake of clarity, the average and the maximum fracture strength values of all studied composites are shown in Figure 4.18. In Figure 4.19 the fracture strength values of ZA$_8$Sr$_8$ and ZA$_8$Mg$_8$ systems are reported separately.
Fig. 4.18: Maximum and average fracture strength values for the several studied composites and 3Y-TZP as reference.

Fig. 4.19: Maximum and average fracture strength values: ZA₈Sr₈ (on the left) and ZA₈Mg₈ (on the right) systems.

The fracture strength is strongly dependent on the composition: mean values in the range of about 672-885 MPa were obtained. High and very promising mean strength values, in agreement with the ISO 6872 standard requirements for prostheses involving molar restorations, were found for (ZA₈Sr₈-Ce10.5)₁₁⁵₀-₁₅₀min-sc/1450-1h and (ZA₈Mg₈-Ce11)₁₁⁵₀-₁₅₀min-sc/1400-1h materials. Maximum strength values of 1058 and 950 MPa were revealed for these two composites, respectively.

As expected and reported in literature²⁶, 3Y-TZP showed the highest fracture strength mean value equal to 1427 MPa. Nevertheless, a very high standard deviation was observed in 3Y-TZP sample, revealing a material very sensitive to processing flaws.
Regarding Ce-TZP materials, results obtained were in agreement with those reported in the literature. Comparable maximum strength values (in the range 900-1000 MPa) were found by Apel et al.\textsuperscript{19}, Nawa et al.\textsuperscript{8} and Benzaid et al.\textsuperscript{27}. Lower strength values (in the range 600-800 MPa) were instead reported by Cutler et al.\textsuperscript{18} and Kern et al.\textsuperscript{22}.

However, the comparison between different literature data could be very difficult since the final results strongly depend on the applied test\textsuperscript{28} and on the sample preparation.

Furthermore, some reproducibility issues were noted, which are related to the ‘laboratory scale’ features of the samples. For example, in same samples were present quite large defects which strongly compromised the strength; this is the reason of a high standard deviations in the ZA\textsubscript{8}Sr\textsubscript{8}−Ce10.5 and ZA\textsubscript{8}Mg\textsubscript{8}−Ce11−1350 materials as well as of a very higher maximum values compared to the mean ones.

Anyway, these reproducibility issues might be overcome by a still more careful follow up of all steps of the processing.

Regarding the ZA\textsubscript{8}Sr\textsubscript{8} system, (Figure 4.19 left) a clear trend was observed: the flexural strength increases by increasing the ceria amount moving from 10 to 10.5 Ce mol% (maximum value of 885 MPa) then for higher ceria content decreases (until 672 MPa).

Similar trends were observed by Nawa et al.\textsuperscript{8} and Tsukuma et al.\textsuperscript{29} who evaluated the bending strength on Ce-TZP materials containing different ceria amount and gran size (Figure 4.20).

![Fig. 4.20: Bend strength of Ce-TZP materials as a function of the ceria amount and gran size: Tsukuma\textsuperscript{29} (left) and Nawa\textsuperscript{8} (right)(black symbols: Ce-TZP/30 vol% Al\textsubscript{2}O\textsubscript{3} composites)](http://theses.insa-lyon.fr/publication/2014ISAL0035/these.pdf)

Since the Sr-containing composites showed almost the same microstructural features, the improvement of the strength by increasing the ceria up to 10.5 mol% could be related to the increase of the critical stress that induces the tetragonal-to-monoclinic transformation.

Over 10.5 mol% of ceria the material become too stable, the phase transformation is limited and the strength is ruled by the size defect.
Hence, in this type of material, characterized by the grain size shown in Table 4.4, the best strength belongs to the composition having 10.5 mol% of ceria. These results confirm the enhanced zirconia stability moving from 10 mol% (Ce10) to 11.5 mol% (Ce11.5) of ceria, as already observed through indentation tests.

Concerning the Mg-containing materials, a strong influence of the sintering temperature and consequently of the microstructure can be underlined. Strength values obtained for the (ZA8Mg8-Ce11)1150-30minsc/1400-1h and (ZA8Mg8-Ce11)1150-30minsc/1350-2h samples were 866 and 718 MPa, respectively. Since the latter one showed the finest microstructure and highest hardness than the former, best strength values were expected. On the contrary, the former showed higher strength values, so an important role of the elongated phases must be considered in addition to the zirconia stability.

For a deeper analysis of the mechanical behavior of the different Ce-TZP composites, also a detailed failure analysis, performing a load-unload test, was conducted.

4.3.2.1 Failure analysis by the load-unload test

As highlighted in literature\textsuperscript{30}, the fracture strength of Ce-TZP materials is strongly limited by the stress at which the tetragonal to monoclinic transformation first proceeds.

In order to study this phenomenon, a load-unload test was performed on several samples. Optical microscope examinations (with Nomarski contrast) were conducted on some samples at different stage of loading until failure.

In order to observe the transformation zone, one pellet of each composition was polished up to 1 µm. X-Ray diffraction analyses were performed on these polished tensile surfaces and not detectable monoclinic content was revealed compared to the previous ones (polished up to 16 µm). The load-unload tests were conducted with the same equipment above described for the biaxial flexural test but the cross-head speed was set at 100 MPa/s to avoid slow crack propagation.

Starting for a load of 500 MPa, the load was increased of 100 MPa each time until failure, and optical images were acquired for each load. The acquired images, as a function of the applied load, for the several studied compositions, are reported in Figures 4.21-4.26.
4. Elaboration and characterization of dense Ce-TZP based materials

Fig. 4.21: Optical images of the tensile surface, as a function of the applied load, of $(ZA_bSr_3-Ce10)^{1150-30min}_{30min}$ sc/1450-1h

500 MPa

600 MPa

680 MPa
Fig. 4.22: Optical images of the tensile surface, as a function of the applied load, of (ZA₆Sr₇-Ce10.5)¹¹⁵⁰⁻³⁰min⁰₀⁶⁰sc/1450-1h
4. Elaboration and characterization of dense Ce-TZP based materials

![Optical images of the tensile surface, as a function of the applied load, of (ZA$_8$Sr$_8$Ce$_{11}$)$_{1150-30min}$sc/1450-1h](image)

Fig. 4.23: Optical images of the tensile surface, as a function of the applied load, of (ZA$_8$Sr$_8$Ce$_{11}$)$_{1150-30min}$sc/1450-1h
Mechanical characterization

Fig. 4.24: Optical images of the tensile surface, as a function of the applied load, of \((ZA_8Sr_{11.5})_{1150-30\min sc/1450-1h}\)

Fig. 4.25: Optical images of the tensile surface, as a function of the applied load, of \((ZA_8Mg_{11})_{1150-30\min sc/1350-2h}\). (The transformation bands are indicated by the arrows)
4. Elaboration and characterization of dense Ce-TZP based materials

Fig. 4.26: Optical images of the tensile surface, as a function of the applied load, of (ZA₈Mg₈-Ce₁₁)₁₁₅⁰⁻³⁰₁₅⁰/Sc/1400-1h. (The transformation bands are indicated by the arrows)

As we can see from the above Figures, two completely different failure behaviors were observed for the ZA₈Sr₈ and ZA₈Mg₈ systems.

In the ZA₈Mg₈-Ce₁₁ composites the tetragonal to monoclinic transformation took place only around the fracture surface. None, or very weak transformation zones were revealed before failure.

On the other hand, in the Sr-containing composites, an important plastic deformation, associated to the tetragonal to monoclinic transformation was easily revealed before failure.
The transformed zone extended as the stress increased, reaching out in the ZA₈Sr₈-Ce10 and ZA₈Sr₈-Ce10.5 samples some mm in size, easily recognized by naked eye.

The different stabilization degree of zirconia was revealed by the extension of the transformed area. In the ZA₈Sr₈-Ce10 sample a very big transformation zone was already observed applying a load of 500 MPa (Figure 4.21). Also in the ZA₈Sr₈-Ce10.5 specimen, the transformation started at load below 500 MPa but the zone was smaller (Figure 4.22), thus revealing a higher critical transformation stress (σₜ₋ₘ) and so a higher stabilization degree.

As already observed during the indentation test, the morphology of these transformation bands could be associated to an auto-catalytic behavior. Therefore, the strength of these two composites is transformation driven and, since a clear transformation zone is already present at this stage of loading (Fig. 4.21-4.22), the critical transformation stress (σₜ₋ₘ) is below 500 MPa.

For samples containing 11 and 11.5 mol% of ceria, any transformed zone was observed by applying a load of 500 MPa and the critical transformation stress (σₜ₋ₘ) was about 600 MPa.

Finally, it is possible to underline that at the failure stage, moving from 10 to 11.5 Ce mol%, the transformed zone decreases, since the zirconia stabilization increases thus decreasing the transformability.

The obtained fracture strength values for each composition are reported and compared to the previous ones obtained by the biaxial flexural test in the Table 4.7.

<table>
<thead>
<tr>
<th>Samples</th>
<th>σ (MPa) (load-unload test)</th>
<th>σ (MPa) (mean ± s.d.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZA₈Sr₈-Ce10 [1150-30min sc/1450-1h]</td>
<td>680</td>
<td>719 ± 22</td>
</tr>
<tr>
<td>ZA₈Sr₈-Ce10.5 [1150-30min sc/1450-1h]</td>
<td>1100</td>
<td>885 ± 128</td>
</tr>
<tr>
<td>ZA₈Sr₈-Ce11 [1150-30min sc/1450-1h]</td>
<td>772</td>
<td>778 ± 47</td>
</tr>
<tr>
<td>ZA₈Sr₁₁.₅ [1150-30min sc/1450-1h]</td>
<td>756</td>
<td>672 ± 70</td>
</tr>
<tr>
<td>ZA₈Mg₈-Ce11 [1150-30min sc/1400-1h]</td>
<td>972</td>
<td>866 ± 40</td>
</tr>
<tr>
<td>ZA₈Mg₈-Ce11 [1150-30min sc/1350-2h]</td>
<td>752</td>
<td>718 ± 132</td>
</tr>
</tbody>
</table>

Strength values observed during the load-unload tests are quite in agreement with those achieved by applying the biaxial flexural test. As already underline, the main difference between these two tests is related to the different zirconia tensile stresses developed in the matrix, being different the
monoclinic phase revealed by XRD. Since the strength values are comparable, it seems that the mean strength is not affected by the matrix tensile stress and it can be considered as an “intrinsic” value.

Considering the Sr-containing composites, the same trend was observed as before: the strength increases by increasing the ceria amount up to 10.5 Ce mol% then it decreases.

As already discussed, the lower strength in the case of ZA8Sr8-Ce10 material was due to the lower stress at which the tetragonal to monoclinic transformation first occurred. For higher ceria content, (above 10.5 mol%), the strength decreases since the materials become too stable and the transformation is hindered.

Also the influence of the sintering temperature (and then of the microstructure), was confirmed by the load-unload tests carried out on the Mg-containing composites. Strength values of 752 and 972 MPa were obtained when the sintering temperatures of 1350 °C and 1400 °C were respectively applied.

4.3.3 Fracture toughness by four point bending test

The fracture toughness was evaluated according to the international standard ISO 6872:2008 by the single edge V-notch beam (SEVBN) method.

During the four-point bending test, a crack propagates from the notch tip of the specimen until failure. As reported in the standard, the fracture toughness is very important for dental ceramics, since it is «inherent» to the material and allows meaningful comparison among ceramic materials used for structural purposes.

Bars having a rectangular cross section were prepared. After sintering they were machined on all the faces in order to ensure that opposing faces were flat and parallel (they should not differ more than 0.05 mm in parallelism).

The samples were ground up to 16 μm in order to reach the final dimension of (4.0 ± 0.2) and (3.0 ± 0.2) mm. The specimen length was at least 2 mm longer than the support span used for testing, as required by the standard.

In order to create the notch of approximately 0.5 mm in depth over all specimens, the face one (3 mm wide) was cut with a diamond blade having thickness of 0.3 mm. Then, the V-notch was obtained by using a razor blade with diamond polishing paste having a grain size of 3 μm. The final V-notch depth, in the range of 0.8-1.2 mm, was measured by the optical microscope with the higher magnification, since it influences the final fracture toughness 31.

Finally, the samples were thermally treated at 1200 °C for 30 min in order to avoid residual stresses. After this thermal annealing step, the specimens were fully dense and the monoclinic phase was not detectable in any samples, thus the residual stresses were avoid.

For the study, at least 3 bars for each compositions (ZA8Sr8-Ce10, ZA8Sr8-Ce10.5, ZA8Sr8-Ce11, ZA8Sr8-Ce11.5, ZA8Mg8-Ce11 and 3Y-TZP, as reference) were prepared.
Once again, on the ground of the Vickers hardness results, the pre-treatment and sintering temperatures for the Sr-containing materials were set at 1150 °C and 1450 °C for 30 min and 1 h, respectively.

In Mg-containing materials the calcination cycle was maintained unchanged and both the sintering cycles (1350-1400 °C for a soaking time of 2-1 h, respectively) were investigated again, since related microstructures were very different each other.

The samples were placed centrally on the bearers of the universal test machine (Instron 8500) so that the load was applied to a 4 mm wide face along a line perpendicular to the long axis of the specimen. The cross-head speed was set at 0.5 mm/min until failure. The test was considered valid only if the fracture started at the bottom of the V-notch and continued over its entire length.

Calculation of the fracture toughness was performed with the following equation:

\[
K_{IC} = \frac{P}{b\sqrt{w}} \cdot \frac{S_1 - S_2}{w} \cdot \frac{3\sqrt{\alpha}}{2(1-\alpha)^{3/2}} \cdot Y
\]

where \(P\) is the fracture load (N), \(b\) and \(w\) are the specimen thickness and width, respectively, \(S_1\) and \(S_2\) are the support spans, \(\alpha\) is the relative V-notch depth and \(Y\) is the stress intensity shape factor

\[
Y = 1.9887 - 1.326 \cdot \alpha - \frac{(3.49 - 0.68\alpha + 1.35\alpha^2) \cdot \alpha(1-\alpha)}{(1+\alpha)^2}
\]

The average fracture toughness value and the related standard deviation are reported in Table 4.8. The monoclinic volume fraction is also reported in the same Table.
4. Elaboration and characterization of dense Ce-TZP based materials

Table 4.8: The monoclinic volume fraction after the thermal annealing \((V_m)\) and the mean fracture toughness value \((K_{ic})\) for the several studied compositions

<table>
<thead>
<tr>
<th>Samples</th>
<th>(V_m) (after annealing)</th>
<th>(K_{ic}) (MPa√m) (mean ± s.d.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>((ZA_8Sr_8-Ce10)_{1150-30min}^{sc/1450-1h})</td>
<td>0</td>
<td>8.2 ± 0.1*</td>
</tr>
<tr>
<td>((ZA_8Sr_8-Ce10.5)_{1150-30min}^{sc/1450-1h})</td>
<td>0</td>
<td>10.2 ± 0.2*</td>
</tr>
<tr>
<td>((ZA_8Sr_8-Ce11)_{1150-30min}^{sc/1450-1h})</td>
<td>0</td>
<td>9.3 ± 0.8</td>
</tr>
<tr>
<td>((ZA_8Sr_8-Ce11.5)_{1150-30min}^{sc/1450-1h})</td>
<td>0</td>
<td>8.6 ± 0.2</td>
</tr>
<tr>
<td>((ZA_8Mg_8-Ce11)_{1150-30min}^{sc/1400-1h})</td>
<td>0</td>
<td>8 ± 1</td>
</tr>
<tr>
<td>((ZA_8Mg_8-Ce11)_{1150-30min}^{sc/1350-2h})</td>
<td>0</td>
<td>7.1 ± 0.2</td>
</tr>
<tr>
<td>3Y-TZP/1450-2h</td>
<td>0</td>
<td>6.6 ± 0.6</td>
</tr>
</tbody>
</table>

*some bars did not break during the test

The fracture toughness values were for all the compositions higher than the one observed for 3Y-TZP. In fact, they were in the range 7.1-10.2 compared to 6.6 MPa√m obtained for the reference. In particular, a very high toughness value (>10 MPa√m) was observed in the \((ZA_8Sr_8-Ce10.5)\) composite. This behavior is ascribed to its high transformability, as revealed during the indentation and the biaxial flexural tests where a great transformation zone was easily observed by the optical microscope.

In addition, some \((ZA_8Sr_8-Ce10)\) and \((ZA_8Sr_8-Ce10.5)\) bars did not reach the fracture during the 4-point bending test, further corroborating the high toughness values.

Considering the R-curve behavior, which reports the fracture toughness as a function of the crack length, this means that in these two samples, the toughness did not reach the plateau associated to failure. This phenomenon was already reported by El Attoui et al.\textsuperscript{32} who studied the R-curve in a 10Ce-TZP material (Figure 4.27).
Fig. 4.27: R-curves on SENB Ce-TZP samples

El Attoui et al. underlined that, as result of the high shielding effect due to transformation, the crack arrests, traducing this instability in a sudden load drops during the test. He connected these instabilities to a crack branching. Hence, it is possible to state that for these type of materials, the recorded toughness value was underestimated and probably more related to the threshold toughness value $K_{I0}$.

In order to solve this problem a careful consideration on the adequate method to analyze this toughness materials should be carried out.

Once again, the comparison between different literature data is very difficult since the final results strongly depend on the applied test. Fracture toughness in the range of 8.8-11.8 MPa$\sqrt{\text{m}}$ was reported by Benzaid et al.\textsuperscript{27} for 10Ce-TZP/Alumina composites while values higher than 15 MPa$\sqrt{\text{m}}$ were reported by Apel et al.\textsuperscript{19} for 10Ce-TZP/MgAl$_2$O$_4$. Anyway, in both cases a double torsion method was applied.

For sake of clarity, the fracture toughness of the several composites are reported in Figures 4.28. In Figure 4.29, the fracture toughness of the Strontium and Magnesium-containing composites are reported separately.
4. Elaboration and characterization of dense Ce-TZP based materials

Fig. 4.28: The fracture toughness by SEVBN method for the several studied compositions. The red arrows underline an underestimated toughness values for the two composites

Fig. 4.29: Fracture toughness by SEVBN method: ZA₈Sr₈ composites (on the left) and ZA₈Mg₈-Ce₁₁ composites (on the right). The red arrows underline an underestimated toughness values for the two composites

Concerning the Sr-containing composites, an expected trend is shown in the above Figures (4.29-4.30, left): the toughness decreases by increasing the ceria amount and so the zirconia stability. Moving from a ceria amount of 10.5 mol% to 11.5 mol%, the toughness decreases from 10.2 to 8.6 MPaVm.

A value higher than 10.5 MPaVm was expected for the 10 Ce mol% composite. As discussed before, this is probably causes by the use of a not fully appropriate method for the evaluation of very high toughness values which causes an underestimation of this property.

Since microstructures of the Sr-containing composites are very close each other (Table 4.4) the fracture toughness trend can be only related to the different stabilization degree.
As already observed in previous tests, by increasing the ceria amount, the zirconia stability increases and the transformability, as well as the toughness, decreases.

Also in this case, the values obtained are in agreement with the ones reported in literature by Tsukuma et al.\textsuperscript{29} and Nawa et al.\textsuperscript{8} as shown in Figure 4.30.

Fig. 4.30: Fracture toughness of Ce-TZP as a function of the ceria content and the grain size: Tsukuma et al. (indentation method)\textsuperscript{29} on the left and Nawa et al.\textsuperscript{8} on the right (black symbols: Ce-TZP/30 vol% Al\textsubscript{2}O\textsubscript{3} composites)

Toughness values by double torsion method, equal to 14- 11- 8 MPa\textsubscript{vm} were also reported by Curtois\textsuperscript{33} in his PhD thesis for the Ce-TZP/16vol%MgAl\textsubscript{2}O\textsubscript{4} system containing a ceria content of 10, 10.5, 11 mol\%, respectively, further demonstrating the decrease of toughness by increasing the ceria amount, for a given grain size.

For what concerns the ZA\textsubscript{8}Mg\textsubscript{8}-Ce11 composites (Figure 4.28-4.29 right), a higher fracture toughness value (8 MPa\textsubscript{vm}) was observed for the material sintered at 1400 °C compared to the one sintered at 1350 °C (7 MPa\textsubscript{vm}).

Since the same stabilization degree is expected in both Mg-containing samples, (the procedure for the preparation was the same), the difference observed on $K_{IC}$ could be ascribed to microstructural features and above all, to the morphology of the elongated phase. Moreover, also the zirconia grain size could have an important role.

Regarding the influence of the elongated phase on the toughness, a toughening effect by crack bridging, $\Delta K_{IC}$\textsuperscript{B} have been proposed. According to Becher et al.\textsuperscript{34}, it can be expressed as:

$$\Delta K_{IC}^B = \sqrt{f_p \cdot T \cdot D \cdot E}$$

Where $f_p$ is the volumetric content of the aluminate phase, $T$ is the frictional bridging stress (30 MPa), $D$ the debonding length (equal to the half-length of the elongated phase) and $E$ is the elastic modulus of the bridging grains. It is clear that as the length of the elongated phase increases, the toughness increases as well.
4. Elaboration and characterization of dense Ce-TZP based materials

4.3.4 Relationship strength-toughness

In zirconia-based ceramics the relationship strength-toughness is very important since an increase of strength is not always correlated with an increase of toughness. As highlighted by Swain et al.\textsuperscript{30}, the limitation of strength could be due to: a) the flow size at low toughness or the critical stress to induce the tetragonal to monoclinic transformation at higher toughness values and b) the inherent R-curve behavior of these materials.

As a consequence, two classes of materials could be considered: a) very high strength and lower toughness materials sensitive to processing flaws and b) high toughness and lower strength ceramics, flaw and damage tolerant.

The stress-toughness curve for the Strontium- and Magnesium-containing composites are reported in Figure 4.31 a-b, respectively.

![The stress-toughness curve of: a) Sr-containing composites as a function of the ceria amount and b) Mg-containing composites as a function of the sintering temperature. The red arrow underlines an underestimated toughness values.](image)

The typical curve for Ce-TZP materials (described in Section 1.1), was obtained for ZA\textsubscript{8}Sr\textsubscript{8} composites. Considering an underestimated toughness value for ZA\textsubscript{8}Sr\textsubscript{8}-Ce10, the maximum of the stress-toughness curve was reached in the composite having a ceria amount of 10.5 mol%.

When the ceria amount is increased up to 11 and 11.5 mol%, both toughness and strength decrease since the materials become too stable and the transformation toughening is limited.

On the other hand, the decrease of the ceria content until 10 mol% produces an increase of toughness but a relevant decrease of the strength: the transformability is very high but the strength is limited by the low critical transformation stress.

Hence, the ZA\textsubscript{8}Sr\textsubscript{8}-Ce10.5 composite represents up to now the best compromise with a toughness and strength equal to about 10.2 MPa\textsuperscript{m} and 900 MPa, respectively.
A simple calculation based on the Griffith equation, reveals for this type of composite, extraordinary values of about 100 µm as critical defect size. The use of this “flaw tolerant” material could increase the reliability of products and will reduce the influence of the processing steps on strength. This excellent combination of properties could be explained by the role of both the second and third phases: on one hand $\alpha$-Al$_2$O$_3$ aids to maintain a small zirconia grain size increasing the critical zirconia stress during the tetragonal to monoclinic transformation. On the other hand an important role of the aluminate have to be considered, even if further analyses are needed in order to study the real toughening contribution of the elongated phase.

In the case of Mg-containing composites, the ZA$_8$Mg$_8$-Ce11 composite sintered at 1400 °C shows the highest fracture toughness and strength (about 8 MPa$\sqrt{m}$ and 866 MPa, respectively).

As discussed previously, the toughness improvement with respect to the one sintered at 1350 °C, can be due to a bigger zirconia grain size and longer aluminate phase.

The comparison between ZA$_8$Sr$_8$-Ce10.5 and ZA$_8$Mg$_8$-Ce11 sintered at 1400 °C reveals similar strength values of about 900 MPa but different toughness values. In the former one a higher $K_{IC}$ value (>10.2 MPa$\sqrt{m}$) was obtained with respect to the latter one (8 MPa$\sqrt{m}$) in agreement with the different mechanical behavior observed during the load-unload test. On one hand, a very big transformation zone was observed during the test in the ZA$_8$Sr$_8$-Ce10.5 sample, thus revealing a higher transformation toughening. On the other hand, the transformation zone was smaller and located only around the fracture surface.

Consequently, ZA$_8$Sr$_8$-Ce10.5 material is more flaw and damage tolerant with respect to the ZA$_8$Mg$_8$-Ce11 composite sintered at 1400 °C. This difference could allow using them in different medical applications, on the basis of the required properties.

Although, the comparison between literature data is complicated since different methods and samples preparation were performed, a summary of the most important results is reported in Figure 4.32 and compared with the most important samples of this study.
4. Elaboration and characterization of dense Ce-TZP based materials

Fig. 4.32: Fracture toughness, $K_{IC}$, and strength, $\sigma_f$, for several materials. In blue the results of this study.

Literature data: $K_{IC}$ was measured by double torsion, except * measured by double cantilever beam;
$\sigma_f$ was measured by biaxial flexural except * measured by four-point bending.

As shown in the above Figure, ZA$_8$Sr$_8$-Ce10.5 and ZA$_8$Mg$_8$-Ce11 (sintered at 1400 °C) materials are an excellent alternative to current oxide ceramics used for structural applications.

Comparable strength value was reported by Apel et al.$^{19}$ for 10Ce-TZP/16$_{vo1}$MgAl$_2$O$_4$. However, the lower toughness by us obtained, with respect to this last work, could be due to the applied test (4-point bending versus double torsion). The tri-phasic composites proposed by Cutler et al.$^{18}$ showed lower strength and toughness with respect to the composites of this study.

Higher strength values belong to 10Ce-TZP/30$_{vol}$Al$_2$O$_3$ and 3Y-TZP materials but they are associated to a lower toughness.
4.4 Physical characterization

4.4.1 Transformability

In order to study the tetragonal to monoclinic transformation, X-Ray diffraction analyses were performed on the fractured surfaces, after the 4-point bending test. The comparison between the amount of the monoclinic phase before and after failure for the several compositions and the 3Y-TZP as reference, are reported in Figure 4.33. X-Ray diffraction patterns related to polished and fractured surfaces of a Ce-TZP sample, are also reported in the same Figure, as example.

![XRD patterns](image)

Fig. 4.33: The monoclinic volume fraction on the polished and fractured surfaces for the several compositions (bottom). XRD analysis of polished and fractured surfaces for one studied sample (top)

By the observation of XRD patterns, it is clear that the monoclinic phase, absent on the polished surface, appeared on the fractured one.

In all Ce-TZP samples, very high transformability was revealed compared to the 3Y-TZP. Therefore, a monoclinic volume fraction in the range of 55-70 vol% was detected in Ce-TZP composites while only 3 vol% was found in Y-TZP. This difference in the monoclinic phase content on fractured surfaces, and thus on the zirconia transformability, was a further confirmation of the different mechanical behaviors we have observed.

As shown in Figure 4.33, the monoclinic volume fraction on fractured surface decreased by increasing the zirconia matrix stabilization and thus the ceria amount. In fact, concerning the Sr-containing materials, the monoclinic phase lowered from 70 to about 60 vol% moving from 10 to 11.5 mol% of ceria amount.
Considering the Mg-containing samples, a slight decrease of the monoclinic phase was observed moving from the specimen sintered at 1400 °C to the ones sintered at 1350 °C: also in this case, and assuming that both samples have the same cerium amount, a role of the microstructure and of the elongated phase have to be considered and, as already here proposed, a deeper investigation of the real stabilization degree of zirconia is being carried out by HRTEM.

Comparing the two systems of material, the Strontium-containing one reveals a higher transformability, in agreement with the toughness values previously discussed. The higher the toughness, the bigger the zone in which the tetragonal-monoclinic transformation occurs.

### 4.4.2 Ageing behavior

As described in Section 1.1, 3Y-TZP has the major drawback of LTD, which is an important limiting factor for its development as biomaterial. Some preliminary ageing tests were performed on the several Ce-TZP materials (ZA8Sr8-Ce10, ZA8Sr8-Ce10.5, ZA8Sr8-Ce11, ZA8Sr8-Ce11.5, ZA8Mg8-Ce11) here prepared in order to evaluate their LTD resistance. As in the case of the mechanical characterization, 3Y-TZP sample was used as reference. Since the tetragonal-monoclinic transformation is thermally activated and accelerated by the presence of water, the test was performed in autoclave (Fisher Bioblock Scientific) at 134 °C under 2 bar pressure. After controlled period of time, XRD analysis was carried out in order to evaluate the content of the monoclinic phase during the aging test. The corresponding results are reported in Figure 4.34.

It is well known that the low temperature degradation is strongly affected by several factors, such as grain size, density, residual stress and surface finish. Since polished surfaces show an enhancement aging resistance, in order to analyze the worst condition, the aging test was performed on the assintered materials.
As expected, a high degradation was observed in the 3Y-TZP material: 20 h of ageing were enough to reach a monoclinic fraction of 20 vol% and after 50 h the monoclinic phase increases up to 70 vol%.

For Ce-TZP materials, the behavior was very different and, also in this case, a strong influence of the zirconia stabilization degree was evident.

ZA₈Sr₈-Ce10 was the most transformable material and the monoclinic volume fraction moved from 15 to 40 vol% after 20 hours, then it remained almost unvaried.

For materials with higher cerium amount (10.5 and 11 mol%), an increased stability and a negligible degradation, also after 50 hours of treatment, were observed.

Finally, ZA₈Sr₈-Ce11.5 and ZA₈Mg₈-Ce11 materials showed any degradation during the entire ageing test duration, confirming their higher stabilization degree.

On the basis of the extrapolation proposed by Chevalier et al. 37, since 50 hours of test correspond to about 180 years in vivo, composites containing more than 10.5 mol% of ceria are in agreement with the time-scale of medical or engineering applications.
4. Elaboration and characterization of dense Ce-TZP based materials

4.4.3 Optical properties

In the dental field of a prosthetic rehabilitation the material should combine wear resistance, toughness, strength and excellent aesthetic properties. Due to the complex optical characteristics of tooth, achieving similar optical property with an artificial restoration is very difficult. Hence, a preliminary optical characterization was performed on ZA₈Sr₆-Ce11 and ZA₈Mg₆-Ce11 specimens using a spectrophotometer (Byk CHEMIE Gardner TCSII) that collects the L*, a* and b* parameters following the CIELab system. In this system, L* value is the degree of lightness of an object, a* value is the degree of redness/greenness, and b* value is the degree of yellowness/blueness as shown in Figure 4.35.

![Three-dimensional model of the CIELab system](image)

As reference, the same analysis was performed on pure 10Ce-TZP and on other two Ce-TZP composites (not involved in this study) having 16 vol% of MgAl₂O₄ as second phase and a different ceria amount (10.5 and 11 Ce mol%). 3Y-TZP was also used as reference materials. The specimens, having a thickness of about 2 mm, were polished using SiC discs up to P1200. The optical parameters for the several compositions are collected in Table 4.9.
Table 4.9: L*, a* and b* parameters for several materials

<table>
<thead>
<tr>
<th>Samples</th>
<th>L</th>
<th>a</th>
<th>b</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZAsSr8-Ce11</td>
<td>95,0</td>
<td>-3,09</td>
<td>9,56</td>
</tr>
<tr>
<td>ZAsMg8-Ce11</td>
<td>91,5</td>
<td>-0,49</td>
<td>4,61</td>
</tr>
<tr>
<td>10Ce-TZP</td>
<td>81,1</td>
<td>-3,40</td>
<td>11,30</td>
</tr>
<tr>
<td>10.5Ce-TZP/16vol%MgAl2O4</td>
<td>93,8</td>
<td>-2,60</td>
<td>6,97</td>
</tr>
<tr>
<td>11Ce-TZP/16vol%MgAl2O4</td>
<td>93,8</td>
<td>-2,51</td>
<td>9,06</td>
</tr>
<tr>
<td>3Y-TZP</td>
<td>95,4</td>
<td>-0,3</td>
<td>2,1</td>
</tr>
</tbody>
</table>

As shown in the above Table, Ce-TZP based materials, reveals an increase of the lightness (L* parameter) and a decrease of greenness and yellowness (negative a* and positive b* values, respectively) compare to pure Ce-TZP.

Moreover, the amount of the ceria as well as the type and content of the second/third phase seem to affect the optical properties.

The comparison between 10.5Ce and 11Ce-TZP/16vol%MgAl2O4 shows a decrease of the b* value (and so of the yellow component) by decreasing the ceria amount while the other parameters remain almost unchanged.

Taking into account ZAsSr8-Ce11 ZAsMg6-Ce11, for which the same ceria amount could be supposed, it seems that the presence of the Mg-aluminate phase allows the decrease of the green and yellow component.

Finally, the comparison between Y and Ce-TZP reveals, as expected, the best optical properties of Y-TZP materials in terms of the decrease of the green and yellow components. Furthermore, also if it is not here analysed, another important aspect of Y-TZP material is its translucency, absent in the Ce-TZP composites. Since the importance of the aesthetic performance for dental applications and the few data available in the literature, many efforts should be now directed to this aspect.
4.5 Conclusions

In the first section, a preliminary investigation of the properties of the three-phase zirconia based composites (ZA₈Sr₈ and ZA₈Mg₈) was described. The surface modification technique of a commercial Ce-TZP powder was successful in the developing composites having highly homogeneous and complex microstructures characterized by a very good distribution of the secondary phases (round-shaped alumina and elongated aluminate grains) inside a fine zirconia matrix.

A good control of the zirconia stabilization degree by the addition of extra-ceria during the elaboration process was achieved. In this way, four different ceria amount in the range 10-11.5 mol% were investigated on the ZA₈Sr₈ composite.

Fully dense materials with a low monoclinic volume fraction were obtained by slip casting.

The influence of the pre-treatment temperature and sintering cycles on the dispersibility, phase composition and microstructure was investigated. Any influence of the pre-treatment temperature on the dispersibility and microstructure were revealed in the examined temperature range. However, a strong influence of the composition and sintering temperature on the microstructure, mainly on the features of the elongated phase, was observed. Strontium aluminate grains having length of about 0.7 µm with respect to the Magnesium ones having length of about 2-4 µm, depending on the sintering cycle, were observed.

In the second part, the characterization of the several ZA₈Sr₈ (ZA₈Sr₈-Ce10, ZA₈Sr₈-Ce10.5, ZA₈Sr₈-Ce11, ZA₈Sr₈Ce11.5) and ZA₈Mg₈Ce11 composites, in terms of mechanical and optical properties, as well as the ageing behaviour and the transformability, was reported and discussed.

First of all, the Vickers hardness test was applied in order to select the optimal pre-treatment and sintering cycles. Then, biaxial flexural and four-point bending tests were performed in order to obtain fracture strength and toughness values according to the international standard ISO 6872:2008.

The comparison between the strength of ZA₈Sr₈ and ZA₈Mg₈Ce11 materials revealed two completely different behaviors. In the first one the strength is transformation driven and the t→m transformation phase took place well before failure. Big transformation bands, related to an autocatalytic phenomenon, was observed as the ceria amount decreases from 11 to 10 mol%.

In the latter case, the tetragonal-monoclinic transformation took place only around the fracture surface where weak transformation bands can be observed.

Two very promising composites with high fracture strength, of about 900 MPa, were found: ZA₈Sr₈Ce10.5 and ZA₈Mg₈Ce11 (sintered at 1400 °C). Both of them well satisfy the ISO 6872-2008 requirements for molar restoration.

The toughness measurements corroborated the crack resistance capability of these materials but highlighted the limits of the applied method for measuring very high toughness values as in Ce-TZP composites with lower ceria contents (ZA₈Sr₈Ce10 and ZA₈Sr₈Ce10.5). In these two cases, bars did not break during the test, so the Kï¿½ value was underestimated.
In the case of Sr-containing composites, a strong influence of the ceria amount was revealed on the mechanical properties. The strength was observed to increase as the ceria amount increases up to 10.5 mol% then it decreases since the material become more stable. For the same reason, the toughness was observed to decrease by increasing the ceria amount. The same trend was revealed for the critical transformation stress.

Considering the strength-toughness curve, the maximum was observed in the ZA₈Sr₈-Ce₁₀.₅ material for which a strength and toughness values equal to about 900 MPa and 10.2 MPa√m were measured, respectively.

The presence of the second/third phase allows an important grain size reduction which increases the critical zirconia stress during the tetragonal to monoclinic transformation improving the mechanical properties, still preserving a high transformability.

In addition, the high toughness value confirm the properties of a “flaw tolerant” and crack resistance material. Extraordinary values of about 100 µm as critical defect size can be obtained by applying the Griffith equation.

The transformability was investigated by comparing the size of the transformed area around the Vickers indentations and by XRD on the fractured surfaces. Both the techniques revealed high transformability for all the studied composites.

A transformability decrease as the ceria amount increases, was observed in the ZA₈Sr₈ materials, further proving the influence of the zirconia stabilization degree on the tetragonal to monoclinic transformation.

The ageing tests showed stable materials in the presence of water in the time-scale of medical applications. The only exception was the ZA₈Sr₈-Ce₁₀ composite, being characterized by a lower critical transformation stress. However this is only a preliminary result and a deeper investigation is necessary.

The influence of the composition (as the amount and nature of the second/third phase and the ceria content) on the optical properties was preliminary investigated. The absence of translucency remains at the moment the most drawback for some dental restoration.
4. Elaboration and characterization of dense Ce-TZP based materials

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4. Elaboration and characterization of dense Ce-TZP based materials


4. Elaboration and characterization of dense Ce-TZP based materials
Conclusions

The experimental activities carried out during this PhD work referred to two different projects: the first, named MITOR project was carried out under the supervision of Professor Jean-Marc Tulliani of Politecnico di Torino and was devoted to the elaboration and mechanical characterization of macro-porous Alumina-Zirconia (ZTA) composites. The latter is a European Project named Longlife, coordinated by Professor Jérôme Chevalier of INSA of Lyon and devoted to the preparation and characterization of ZrO$_2$-based composites for dental and spine implants.

The common aspect of these two projects was the set-up of new processes for the development of composite structures having tailored compositional and microstructural features, toward the achievement of increased physical and mechanical properties.

For these reasons, the surface modification approach of commercial powders with inorganic precursors of the secondary phases was exploited as alternative elaboration method, being it able to assure a high degree of control of the size and distribution of the second-phase grains on the surface of the parent material.

More in detail, by following this innovative method, the selected commercial powder ($\alpha$-Al$_2$O$_3$ or Ceria-stabilized ZrO$_2$) was dispersed in distilled water in order to reach a fine and narrow particle size distribution. Then, the inorganic precursors of the secondary phases (preferred as chlorides or nitrates) were dissolved in water and drop-wise added to the ceramic slurry. After homogenisation under magnetic stirring, the doped suspension was spray-dried inducing the precipitation of the precursors onto the commercial particles surface by liquid evaporation. After drying, the obtained product was submitted to a proper thermal treatment to promote the second phases crystallization, yielding the desired final composition. It was shown that each step in the elaboration process must be carefully set-up for achieving a full control of the powders features.

Particularly, in the framework of the MITOR project, Al$_2$O$_3$/10 vol%ZrO$_2$ (referred as AZ10) cellular materials were successfully prepared by combining the surface modification method with the gel-casting technology and a sacrificial phase.

The porosity features, such as the amount of porosity, the pore shape and size distribution was quite easily controlled by adding a fixed amount of polyethylene spheres sieved in a restricted dimensional range.

Alumina and AZ10 samples with porosity amounts ranging from about 60% to 80 vol% were produced and characterized in terms of their microstructure and mechanical properties.

Different pore size distributions were revealed for the two compositions: alumina samples showed larger pore diameters with respect to AZ10 specimens, justified by the higher linear shrinkage during sintering of the alumina-zirconia bodies.

The comparison between the particle size distributions of the dense and porous AZ10 components revealed lower grain size of both zirconia and alumina particles in the porous specimens.

The mechanical behavior in compression was described as cellular-like: the fracture occurred by tensile cracking of the solid walls.
Conclusions

The strength decreased with decreasing the relative density and, from a compositional point of view, the porous AZ10 composites showed higher compressive strength as compared to the pure alumina ones.

The well-known zirconia toughening mechanisms (transformation and microcracking toughening) were investigated, revealing any influence on the mechanical properties. A relatively low content of the monoclinic zirconia phase, in the range between 0.14 and 0.07 vol% as the porosity changed from 0 to 75 vol%, was found on the surface of the AZ10 sintered materials. Nevertheless, with regard to the fractured surfaces, the transformability was very low and it decreased as the porosity increased. Such behavior is probably due to the smaller tetragonal zirconia grains in AZ10 cellular samples as compared with the dense reference materials. In fact, the presence of smaller tetragonal grains as well as their lower tensile residual stresses after sintering, can reduce their transformability to monoclinic phase under the applied stress.

The improved mechanical properties of the AZ10 materials with respect to the pure alumina bodies can be reasonably due to their finer microstructure, being characterized by smaller grains and pores.

Further studies will be necessary to better tailor the zirconia amount and grain size, in order to verify if the well-known reinforcing mechanisms of the zirconia in the alumina matrix could be exploited also in porous materials. For instance, the alumina-zirconia composites having 15 vol% of ZrO₂ could be investigated in order to clarify the role of the zirconia amount on the mechanical properties. Further analyses, such as X-Ray tomography and four bending test, could be performed in order to deepen the microstructure and the fracture toughness of cellular materials.

Major efforts will be devoted in the understanding the effect of the porosity level on the zirconia transformability.

The Longlife project dealt with the development of new compositions of Ce-TZP based materials exhibiting no low temperature degradation in the lifetime of an implant, still keeping high strength and toughness, thus overcoming the stability problems related to the Y-TZP materials.

On the ground of the previous literature on this topic, zirconia-based three-phase composites were developed in which both round-shaped and elongated secondary phase particles were added (the former for retaining the zirconia grain growth during sintering, the latter for further increasing the fracture toughness of the ceramics).

For this purpose, α-Al₂O₃ as round-shaped phase and two different elongated-shaped aluminates, CeMgAl₁₁O₁₉ and SrAl₁₂O₁₉, were selected, thus giving rise to two different Ce-ZrO₂ systems: Ce-ZrO₂/8 vol%Al₂O₃/8 vol%SrAl₁₂O₁₉ (referred as ZA₈Sr₈) and Ce-ZrO₂/8 vol%Al₂O₃/8 vol%MgAl₁₂O₁₉ (referred as ZA₈Mg₈).

The surface modification route of a commercial Ce-TZP powder was successful in the developing composites having highly homogeneous and complex microstructures characterized by a very good distribution of the secondary phases inside a fine zirconia matrix.

In addition, the developed process was also suitable for tailoring the ceria amount inside the zirconia lattice, thus allowing an effective control of the mechanical and physical properties. In this way, four different ceria amount in the range 10-11.5 mol% were investigated on the ZA₈Sr₈ composites.
Conclusions

Fully dense materials with low monoclinic volume fraction were obtained by slip casting and pressureless sintering in the 1350-1450 °C range.

The influence of the pre-treatment temperature and sintering cycles on the dispersibility, phase composition and microstructure was investigated. Any influence of the pre-treatment temperature on the dispersibility and microstructure were revealed in the examined temperature range.

However, a strong influence of the composition and sintering temperature on the microstructure, mainly on the features of the elongated phase, was observed. Strontium aluminlate grains having length of about 0.7 µm with respect to the Magnesium ones having length of about 2-4 µm, depending on the sintering cycle, were observed.

The mechanical and optical properties as well as the transformability and aging behavior of the several ZA8Sr8 and ZA8Mg8-Ce11 composites, were investigated and discussed.

First of all, Vickers hardness tests were carried out in order to select optimal pre-treatment and sintering cycles. Then, biaxial flexural and four-point bending tests were performed in order to obtain fracture strength and toughness values according to the international standard ISO 6872:2008.

A direct comparison between the properties of ZA8Sr8 and ZA8Mg8 samples can be hardly made, since these two kinds of composites differ not only in the composition but also in the microstructural features. However, two completely different mechanical behaviors were revealed by the failure analysis of specimens submitted to load-unload tests until failure. In the ZA8Sr8 system the strength is transformation driven and the t→m transformation phase took place well before failure.

Big transformation bands, related to an autocatalytic phenomenon, was observed as the ceria amount decreases.

Instead, in the ZA8Mg8 system the tetragonal-monoclinic transformation took place only around the fracture surface where weak transformation bands can be observed.

Two very promising composites with high fracture strength, of about 900 MPa, were found: ZA8Sr8-Ce10.5 (sintered at 1450 °C) and ZA8Mg8-Ce11 (sintered at 1400 °C).

Both of them well satisfy the ISO 6872-2008 requirements for molar restoration.

The toughness measurements revealed the properties of crack resistance materials (Kic in the range 7-10.2 MPaVm depending on the composition) but highlighted the limits of the applied method for high toughness materials as Ce-TZP composites.

In the case of Sr-containing composites, a strong influence of the ceria amount on the mechanical properties was revealed. The strength was observed to increase as the ceria amount increases up to 10.5 mol% then it decreases since the material become more stable. For the same reason, the toughness was observed to decrease by increasing the ceria amount.

The maximum of the strength-toughness curve was recognized in the ZA8Sr8-Ce10.5 material for which a strength and toughness values equal to about 900 MPa and 10.2 MPaVm were recorded, respectively.
Conclusions

Both these values can be reasonably improved since: i) a strength value equal to 1100 MPa was revealed during the load-unload test, demonstrating a reproducibility problem due to the laboratory scale production and ii) the four-point bending test was found to be not suitable for this type of composition.

These excellent mechanical properties have been ascribed to the presence of second/third phases that allows an important grain size reduction which increases the critical zirconia stress during the tetragonal to monoclinic transformation, still preserving a high transformability.

The high toughness value confirms the properties of a flow tolerant and crack resistance material. Extraordinary values of about 100 μm as critical defect size can be obtained by applying the Griffith equation.

The transformability was investigated by comparing the size of the transformed area around the Vickers indentations and by XRD on the fractured surfaces. Both the techniques revealed high transformability for all the studied composites.

A transformability decrease as the ceria amount increases was observed in the ZA₈Sr₈ materials, further proving the influence of the zirconia stabilization degree on the mechanical properties.

The preliminary ageing tests showed stable materials in the presence of water in the time-scale of medical applications. The only exception is the ZA₈Sr₈-Ce10 composite, being characterized by a lower critical transformation stress.

In the framework of the Longlife project, many efforts will be devoted to further investigate the ZA₈Mg₈ system, especially the crystallization phenomena of the aluminate phase on the surface of the zirconia particles by TEM/HRTEM analyses on thermal treated powders as well as on sintered bodies. In this way, further information about the aluminate composition and the role of the calcination and sintering temperatures on its morphology could be obtained.

At the same time the real zirconia stabilization degree can be probed.

Once deepen these aspects, the role of the ceria amount on the mechanical behavior could be investigated, for instance by developing new ZA₈Mg₈ composites having a ceria amount in the 10.5-11.5 mol% range.

With regards to the ZA₈Sr₈ system, the role of the ceria amount on the mechanical behavior was clearly shown and, thanks to the adopted elaboration route, further compositions having a ceria amount slightly higher and lower than 10.5 mol% could be investigated.

They may led to an even better balance between strength and toughness that could be adapted depending on the final application.

Finally, further work will be necessary to deepen the role of the elongated grains on the mechanical properties: new ZA₈Sr₈ and ZA₈Mg₈ specimens suitable for the double torsion method will be prepared in order to obtain fracture toughness values and crack growth rate versus stress intensity curves.
Following this thesis project, the importance of the powder engineering approach in tailoring the powder features and, as a consequence, the properties of the final materials was clearly highlighted. It was shown that the deep knowledge of all the involved mechanisms (such as raw powders dispersion, pH suspension, drying, powder thermal treatments) is crucial for achieving a full control of the powders features and final microstructures.

The adopted elaboration route can be further optimized in order to avoid processing flaws and reproducibility issues related to the laboratory scale production.

A preliminary feasibility study on the technological transfer at industrial level of the protocol here described could be performed.

The achievement of both alumina- and zirconia-based composites with tailoring composition and complex microstructures by the surface modification route envisages the possibility to extend this elaboration method also for the production of other ceramic composites.

In addition, it can be easily combined with forming methods (such as gel-casting and slip casting techniques) to develop both dense and cellular ceramics, thus demonstrating the versatility of this elaboration route.

Finally, this thesis emphasizes the necessity to carefully investigate the relationship between the final properties and the composition/microstructure. The design of the final materials having precise composition and architecture is fundamental in order to reach the desired properties.
Appendix

A.1 Sample Designation

The following designation code has been used to identify the samples as a function of their composition, thermal treatments and related soaking times and sintering cycles.

Composition

- A refers to $\alpha$-$\text{Al}_2\text{O}_3$ components;
- AZ10 refers to $\alpha$-$\text{Al}_2\text{O}_3$-10 vol% (un-stabilized)ZrO$_2$ synthesized through the surface modification of $\alpha$-$\text{Al}_2\text{O}_3$ powder with zirconium chloride;

In order to clarify the porosity level, A and AZ designations are followed by the total porosity degree (vol%) (see Table 3.1, chapter 3). For sake of clarity,
- A65 refers to $\alpha$-$\text{Al}_2\text{O}_3$ body having 65 vol% of total porosity
- A75 refers to $\alpha$-$\text{Al}_2\text{O}_3$ body having 75 vol% of total porosity
- AZ75 refers to $\alpha$-$\text{Al}_2\text{O}_3$-10 vol% ZrO$_2$ composite having 75 vol% of total porosity

- 10Ce-TZP refers to ZrO$_2$-10 mol% CeO$_2$ powder supplied by Daiichi;
- ZA$_{16}$ refers to ZrO$_2$-16 vol%Al$_2$O$_3$ composites synthesized through the surface modification of 10Ce-TZP powder with aluminum nitrate;
- ZSr$_{16}$ refers to ZrO$_2$-16 vol%SrAl$_{12}$O$_{19}$ composites synthesized through the surface modification of 10Ce-TZP powder with aluminum and strontium nitrates;
- ZA$_{8}$Sr$_{8}$ refers to ZrO$_2$-8 vol% Al$_2$O$_3$-8 vol% SrAl$_{12}$O$_{19}$ composites, synthesized through the surface modification of 10Ce-TZP powder with aluminum and strontium nitrates;
- ZA$_{8}$Mg$_{8}$ refers to ZrO$_2$-8 vol% Al$_2$O$_3$-8 vol% CeMgAl$_{11}$O$_{19}$ composites, synthesized through the surface modification of 10Ce-TZP powder with aluminum, strontium and cerium nitrates.

In order to clarify the zirconia stabilization degree, the ZA$_{8}$Sr$_{8}$ or ZA$_{8}$Mg$_{8}$ designation is followed by the ceria amount (mol%) inside the zirconia grains.

For instance, ZA$_{8}$Sr$_{8}$-Ce10.5 refers to ZrO$_2$-8 vol% Al$_2$O$_3$-8 vol% SrAl$_{12}$O$_{19}$ in which the zirconia is stabilized with 10.5 mol% of ceria.

Thermal treatments

All bi- and tri-phase composite powders were thermally pre-treated at 600 °C for a soaking time of 1 h (heating and cooling rate of 10 °C/min) after the drying step to promote the burn out of by-products.
As consequence, this thermal pre-treatment is not shown in the sample designation.

- (Sample)\textsuperscript{T,\textsubscript{t}} refers to sample powder thermally treated at the temperature T (°C) for a soaking time of t (h or min).

For sake of clarity, 10Ce-TZP \textsuperscript{900-1h} refers to the as-received 10Ce-TZP powder thermally treated at 900 °C for a soaking time of 1 h.

(ZA\textsubscript{8}Sr\textsubscript{8}-Ce\textsubscript{10})\textsuperscript{1150-30min} refers to ZA\textsubscript{8}Sr\textsubscript{8}-Ce\textsubscript{10} powders thermally treated at 1150 °C for a soaking time of 30 min.

**Forming process and sintering cycle**

Gel- and slip casting forming methods were applied during this work to produce porous and dense bodies, respectively. The former (A and AZ10 bodies) are related to the MITOR project while the latter (Ce-TZP based composites) are related to the Longlife project.

In this last case, slip cast specimens are identified by the sc letters followed by the sintering cycle (temperature (°C) and soaking time (h)).

For sake of clarity, (ZA\textsubscript{8}Sr\textsubscript{8}-Ce\textsubscript{11})\textsuperscript{1150-30min\textsubscript{sc}/1450-1h} refers to the tri-phasic ZA\textsubscript{8}Sr\textsubscript{8}-Ce\textsubscript{11} powder thermally treated at 1150 °C for 30 min, then dispersed, slip cast and finally sintered at 1450 °C for a soaking time of 1 h.
A.2 Abbreviations

The abbreviations used all over the text are reported in the following.

- a.r. refers to the aspect ratio, length to thickness ratio
- ASTM refers to American Society for Testing Materials
- BET refers to Brunauer Emmett Teller theory
- BM refers to Ball Milling technique
- CTE refers to Coefficient of Thermal Expansion
- \(d_{10}, d_{50}\) and \(d_{90}\) refer to the values of the diameters corresponding to 10%, 50% and 90% of the cumulative particle size distribution, respectively
- FESEM refers to Field Emission Scanning Electron Microscopy
- ICDD refers to International Centre for Diffraction Data
- ICP-AES refers to Inductively Coupled Plasma – Atomic Spectroscopy
- ISO refers to International Standard Organization
- LTD refers to Low Temperature Degradation
- MS refers to Magnetic Stirring
- m-ZrO\(_2\) refers to the monoclinic zirconia phase
- PE refers to polyethylene
- PMMA refers to Polymethylmethacrylate
- PSZ refers to Partially Stabilized Zirconia
- SEM refers to Scanning Electron Microscopy
- S.S.A. refers to the Specific Surface Area
- SEVNB refers to Single Edge V-Notch Beam
- \(\sigma_{c-m}\) refers to the critical transformation stress
- (HR)TEM refers to (High Resolution) Transmission Electron Microscopy
- TG-DTA refers to Thermogravimetric and Differential Thermal Analyses
- TD refers to Theoretical Density
- t-ZrO\(_2\) refers to the tetragonal zirconia phase
- t-m refers to the tetragonal monoclinic phase transformation
- TZP refers to Tetragonal Zirconia Polycrystals
- \(V_m\) refers to the volume fraction of the monoclinic zirconia phase
- XRD refers to X-Ray Diffraction
- XPS refers to X-Ray Photoelectron Spectroscopy
- ZTA refers to Zirconia-Toughened-Alumina
A.3 Experimental techniques

A.3.1 Thermal analyses: TG-DTA

The thermal analyses evaluate the behaviour of the sample under controlled temperature cycles. They were carried out by using a simultaneous TG-DTA apparatus (Netzsch STA 409C). In the Differential Thermal Analysis (DTA), the difference in temperature between the sample and the reference (α-Al₂O₃) is monitored: the same amount of heat energy is added to the sample and the reference. The Thermogravimetric Analysis (TGA) follows the mass loss of the sample during heating thanks to a microbalance, in order to study phenomena associated to a mass change. Thermal analyses were carried out on powdered samples (about 150 mg) up to 1400 °C, heating and cooling rate of 10 °C/min under static air.

A.3.2 X-Ray diffraction

The X-ray diffraction (XRD) technique allows to detect the crystalline phase composition of the sample. It is employed to determine the crystalline structure (through crystal parameters) and to measure the mean crystallite size of the sample. X-ray diffraction analyses were carried out by using a diffractometer (Philips PW3830) using Cu Kα radiation (λ=1.5405 Å). XRD patterns were recorded in the 5-70 2θ range with step size of 0.05° and a time per step of 5 s.

The instrument is equipped with a goniometer having a Bragg-Brentano geometry related to the Bragg equation:

\[ n\lambda = 2d \cdot \sin \theta \]

where θ is the incident angle, d is the inter-planar distance, λ is the wavelength of the X-rays beam and n is a number.

On the basis of the inter-atomic distances it is possible to evaluate the geometry and the dimensions of the elementary cell. The whole diffraction pattern allows the identification of the crystalline phases through the comparison with the ICDD (International Centre for Diffraction Data) files.

The JCPDF files used during this work to investigate the phase composition have been:
- JCPDF no. 74-0815 to identify the monoclinic zirconia phase,
- JCPDF no. 82-1398 to identify the tetragonal zirconia phase stabilized with ceria,
- JCPDF no. 07-0007 to identify the ammonium chloride phase,
- JCPDF no. 80-0965 to identify the tetragonal un-stabilized zirconia phase,
- JCPDF no. 10-0173 or 46-1212 to identify the α-alumina phase,
- JCPDF no. 80-1195 to identify the Strontium aluminate phase (SrAl₁₂O₁₉),
- JCPDF no. 26-0872 to identify the Magnesium aluminate phase (CeMgAl₁₁O₁₉)
XRD analyses also allow to investigate the average crystallite size by applying the Scherrer’s equation:

\[ D = \frac{k \cdot \lambda}{\beta \cdot \cos \theta} \]

where \( D \) is the crystallite size, \( \lambda \) is the wavelength of the Cu K\( \alpha \) line, \( k \) is the Scherrer constant equal to 0.9 and \( \beta \) is the full width at half maximum of the main phase peak, assuming a Gaussian profile.

During this work the Scherrer equation was applied on powders thermally treated at different temperatures in order to investigate the crystallization evolution.

In addition, on the ground of literature \([H.\ Toraya,\ M.\ Yoshimura,\ S.\ Somiya,\ Calibration\ curve\ for\ quantitative\ analysis\ of\ the\ monoclinic\ tetragonal\ ZrO_2\ system\ by\ X-ray\ diffraction.\ Journal\ of\ the\ American\ Ceramic\ Society,\ 67,\ 119-121\ (1982)\] \XRD\ pattern allows the evaluation of the monoclinic zirconia fraction.

The weight fraction of monoclinic zirconia is evaluated by the following equation:

\[ X_m = \frac{I_m(111) + I_m(111)}{I_m(111) + I_m(101) + I_m(111)} \]

where \( I_x \) \((hkl)\) designates the intensity of the peak corresponding to the plane \( hkl \) for the phase \( x \) \((m\ for\ monoclinic\ and\ t\ for\ tetragonal)\).

The volume fraction is therefore obtained by the following equation:

\[ V_m = \frac{1.311 \cdot X_m}{1 + 0.311 \cdot X_m} \]

A.3.3 Laser granulometry

Granulometric analyses of aqueous suspensions were performed by using a laser granulometer (Fritsch model Analysette 22 Compact), ables to detect granule diameters in the range 0.31 -300.74 \( \mu \)m.

A laser beam strikes the particle suspended in a inert medium producing diffracted rays which intensity and diffraction angle depend on the size of the impacted particles.

The Fraunhofer theory was used to calculate the particle size distribution, thus obtaining the volume cumulative distribution as a function of the agglomerate size and the diameters corresponding to 10%, 50% and 90% of the distribution, namely \( d_{10} \), \( d_{50} \) and \( d_{90} \) respectively.

A.3.4 Dilatometry

The dilatometric analysis allows to investigate the sintering behaviour of a ceramic green body under a controlled thermal cycle, with the aim to set up an optimal sintering cycle reaching a high density, even controlling the final microstructural features. An absolute dilatometer (Netzsch 402E) was used.

The dilatometric study was usually performed on uniaxially pressed bars by applying the following
thermal cycle: heating up to 1500 °C (heating and cooling rate of 2, 5 or of 10 °C/min) and soaking time of 1 or 3 h at the maximum temperature (these experimental parameters have been specified for each test in the text).

A.3.5 SEM/FESEM observations

The microstructure of powders and sintered materials was observed by FESEM (Hitachi S4000) and SEM (Zeiss SUPRA VP55 or SUPRA VP40).
In order to increase the sample conductivity, a graphite coating was sputtered on polished and thermally etched samples surface. Thermal etching was carried out at 50 °C below the sintering temperature, for a very short time (6 min), allowing to reveal grain boundary by SEM observations.

A.3.6 TEM/HRTEM observations

High Resolution Transmission Electron Microscopy (HRTEM) was performed on selected sintered zirconia-based composites in order to investigate the phase composition and the zirconia stabilization degree. A JOEL 2010 F and a 200 CX Microscopes were used.

A.3.7 Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES)

ICP-AES is an analytical technique used for the detection of trace metals. The sample is introduced in the plasma torch (in form of an aerosol) where metals are atomized. In the plasma, metal atoms are excited thus to emit the absorbed wavelength. By analyzing the recorded spectrum, it is possible to calculate the metal concentration.
Two different instruments were used to perform the analyses: an ICP-AES spectrometer Optima 2100 (supplied by Perkin Elmer) for the determination of the hafnium content in the as-received powder and an Optima 7000 DV instruments (supplied by Perkin Elmer) for the determination of the cerium content in the acidified water after powder dispersion.

A.3.8 Spray drying

The drying step was performed in a Mini Spray Dried (Buchi B-209) equipped with a conventional two-fluid nozzle where an air jet disperses the liquid into fine droplets.
The suspension is continuously stirred during drying in order to assure homogeneity. These droplets meet a stream of hot air and they are quickly dried.
The dried powder is separated from the moist air by centrifugal action in a cyclone: the moist air is directed trough the exhaust pipes while the dried powder is directed to the bottom of the cyclone where it is collected in a vessel.
In our case, the inlet temperature was set at 140 °C while the measured temperature at the outlet of the dry chamber was about 70-80 °C.
A.3.9 Archimedes method

The Archimedes method was employed to determine the density of fired bodies. It is based on weighting the sample in air and in water and calculating its density by considering the force that water exerts on the immersed body, according to the following equation:

\[ \rho = \frac{W_{air}}{W_{air} - W_{aq}} \]

where \( \rho \) is the density, \( W_{air} \) the weight in air and \( W_{aq} \) the weight in water.

In the case of porous bodies, the Archimedes density is also used to calculate the closed porosity according to the following equation:

\[ \text{Closed porosity (\%)} = \left( 1 - \frac{\text{Archimedes density}}{\text{Theoretical density}} \right) \times 100 \]

The as-obtained densities were then related to the theoretical density (TD) of the composite by applying the rule of mixture (ROM) to all the constituent phases. In detail, it has been used:

- for the monoclinic zirconia phase, a theoretical density of 5.82 g/cm\(^3\) (JCPDF no. 74-0815);
- for the tetragonal zirconia phase stabilized with ceria, a theoretical density of 6.23 g/cm\(^3\) (JCPDF no. 82-1398);
- for the tetragonal un-stabilized zirconia phase, a theoretical density of 6.12 g/cm\(^3\) (JCPDF no. 80-0965);
- for alpha-alumina, a theoretical density of 3.99 g/cm\(^3\) (JCPDF no. 10-0173 and 46-1212);
- for the magnesium/cerium aluminate, a theoretical density of 4.24 g/cm\(^3\) (JCPDF no. 26-0872);
- for the strontium aluminate, a theoretical density of 4.024 g/cm\(^3\) (JCPDF no. 80-1195)
L’objectif de cette thèse est le développement de composites dans le système alumine-zircone par une approche d’ingénierie des poudres permettant de façonner les caractéristiques microstructurales et compositionnelles, et, par conséquent, les propriétés des matériaux finaux. Les poudres composites ont été élaborées à travers la modification de la surface des poudres commerciales par un précurseur inorganique de phases secondaires. Cette approche innovante assure un degré élevé du contrôle de la taille et de la distribution des grains de seconde phase sur la surface du matériau parent.

Les poudres composites à base d’alumine contenant 10 vol% de zircone non-stabilisée et des poudres composites à base de zircone triphasique contenant 8 vol% d’alumine et 8 vol% de phase aluminate, ont été développées. Leur propriétés physiques, chimiques et mécaniques a été caractérisée.

Dans le cas premier, les matériaux porus ont été développés à travers le technique gel-casting avec sphères de PE. Les mécanismes de ténacité de la zircone ont été étudiés, révélant aucun influence sur les propriété mécaniques. Les composites porux présentent des valeurs de résistance à la rupture plus élevées, en comparant à des alumines pures, mais cet amélioration peut être raisonnablement dû à leur microstructure plus fine, celle-ci étant caractérisée par des grains et des pores plus petits.

Dans le deuxième cas, a partir de la Ce-TZP, connue pour sa ténacité et sa stabilité importantes, un travail d’optimisation de la microstructure a été réalisé afin d’obtenir une résistance à la rupture maximale. Les matériaux présentés dans cette étude ont été développés afin de répondre au triple objectif de ténacité, résistance et stabilité.

Deux composites très prometteurs, avec des résistances à la rupture élevées (environ 900 MPa) et ténacités élevées (environ 10Mpa√m), ont été réalisés. De plus, les composites étudiés ont montré de hautes capacités de transformation et pas de faible température de dégradation en atmosphère humide, dans les temps des applications médicales. Il a été démontré que les propriétés mécanique sont vivement affectées par le degré de stabilisation de la zircone.

L’étude de la relation entre les propriétés finales et l’architecture de la composition/microstructure, au but d’obtenir les propriétés désirées, se révèle nécessaire.

MOTS-CLÉS : céramique, alumina, composite, zircone, Ce-TZP, microstructure, propriétés mécaniques

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