Section 1

Porous bodies preparation by a modified gelcasting procedure: a model system based on alpha-alumina
1. An introduction to porous ceramics

In the last years the demand of porous materials able to work in extreme conditions such as at high temperature, or even under extensive wear or in presence of aggressive environments was increased. To withstand such harsh conditions, materials must be characterized by a high melting point, a high corrosion and wear resistance and tailored properties. Ceramic-based porous components can be therefore considered as suitable candidates for extreme applications, even if their relevant amount of pores, in many cases having large sizes, implies an increase of their brittleness [1].

The main applications of porous ceramics are high – temperature thermal insulation, filtration of molten metals, support for catalytic reactions, filtration of hot corrosive gases, refractory linings for furnaces, porous implants as biomaterials [1 – 5], lightweight components [6, 7], solid oxide fuel cell electrodes [7 – 9].

Porous ceramics present low mass, low thermal conductivity, controlled permeability, high surface area, low density, high specific strength and low dielectric constant. These properties can be influenced by their composition and microstructure; in particular, a not negligible role is played by the total porosity percentage, by the pore morphology as well as size distribution. Most microstructural features are also significantly influenced by powder properties and processing method [1, 2].

Pores and the related ceramic walls are often known as cells, while the ceramic network surrounding the voids is made of struts; a typical porous structure is reported in Figure 1.1.

Pores should be closed or open that is presenting openings (named cell windows) or interconnections.

![Figure 1.1 – Structure of porous materials](image)

The cellular ceramics can be classified in two groups [3, 4], as shown in Figure 1.2 [10]:

- honeycombs, in which cells form an ordered two-dimensional array (Figure 1.2a);

![Figure 1.2 – Commercial ceramic honeycombs (a) and foams (b) [10]](image)

- foams, characterized by a three – dimensional array of cells (Figure 1.2b).
Honeycomb monoliths present laminar flow patterns and generally lateral mixing between walls is not allowed. On the other hand, in ceramic foams, the porous network is very tortuous, so that laminar and turbulent flow and mixing are promoted [4]. Since a part of the experimental work detailed in the manuscript will be devoted to foam-like components, a deeper literature review on such a type of structures will be presented in the followings.

Generally ceramic foams are defined as materials having pore sizes ranging from 10 μm to 5 mm and percentage pore volume higher than 60% [11, 12]. If the cells are isolated and completely surrounded by ceramic walls, they are called closed – cells; on the contrary, a ceramic component which presents a three – dimensional network of interconnected cells, characterized by cell windows on the walls or larger interconnections, is named open – cell material [2 – 4, 12]. Figure 1.3 shows the porous structures of an open (a) and a closed (b) cell material [4]. Open – cell structures having very high porosity level (between 70% and 95%) are called reticulated ceramics [13]. Moreover, porous materials can be made of partly open or partly closed – cells [2, 3].

![Figure 1.3 – Open – (a) and closed – (b) cell materials [4]](image)

The nature of porous ceramics, in terms of open or closed cell, influences the final application of materials: in fact, the presence of open pores allows applications involving fluid transport (open – cell materials are permeable to gases and, if the mean cell size is high enough, to liquid), while closed – cell materials are suitable when fluid flow is not required, such as for thermal insulation [12]. Foams are also applied as thermal insulating materials for furnaces and for aerospace applications, because of their thermal stability, low thermal conductivity, low density, resistance to thermal cycling, thermal shock resistance and low specific heat.

The most common applications for open – cell ceramic foams are molten metal and Diesel engine exhaust filters. The former ones are employed for removing non metallic inclusions from molten alloy baths (such as aluminium, titanium, iron, copper, bronze, steel, zinc, etc.) and they must withstand corrosion at high temperature in contact to molten metals. Foams for Diesel engine soot filtration are competitors of the largely-used honeycomb components, but they can also successfully exploited in many high temperature industrial processes, for instance filters for waste incineration ashes, thanks to their thermal, chemical and mechanical stability, besides their long – term structural durability [3].

### 1.1 Forming techniques for ceramic foams

The production of a three-dimensional network of pores in a ceramic material can occur during the sintering treatment or during forming procedures, as schematically represented in Figure 1.4. The latter methods allow a more strict control of porosity, in terms of total volume, nature, morphology and dimensions, features that depend on the specific forming technique.
The simplest technique to produce 3D porous ceramics is the **partial sintering**. Powder compacts are submitted to suitable thermal treatments that imply a microstructural evolution with the development of a porous network among the necked particles. This method is quite versatile, since the powder particle size influences pore size distribution and porosity total volume [14].

The porosity degree can be also controlled through the powder agglomeration, the compaction pressure, the isothermal temperature or time [13]. To limit the densification mechanism it is possible to exploit sintering treatments under selected gas atmospheres (such as hydrochloric acid in the case of ZrO$_2$ [15, 16], TiO$_2$ and Fe$_2$O$_3$ [17]). In this way, a very limited or no shrinkage occurs, so that pore continuity is preserved and controlled grain growth takes place, as showed in Figure 1.5 [17].

![Figure 1.5 – Fe$_2$O$_3$ materials sintered at 1200°C for 5 h](image)

(a) in air and in (b) HCl atmosphere [17]

Partial sintering generally leads to materials having a total porosity of about 50%. Closed-pore materials having a porosity ranging between 5% and 15% were obtained, while open-pore components having about 10 – 20% porosity were produced [14].
Another method to produce 3D porous ceramics is the so-called **reactive pressureless sintering**. The initial powder mix contains compounds that undergo thermal decomposition yielding gaseous by-products and the subsequent development of a porous structure. For instance, porous CaZrO$_3$/MgO composites have been produced starting from a mixture of natural dolomite [CaMg(CO$_3$)$_2$] and ZrO$_2$. CaMg(CO$_3$)$_2$ decomposes in MgO and CaCO$_3$, which reacts with ZrO$_2$ yielding CaZrO$_3$; these reactions involve the production of gaseous CO$_2$ and the formation of a homogeneous open-pore structure, with pores of about 1 μm and a porosity percentage between 30% and 50% [18].

**Microwave sintering** was recently exploited by Oh et al. to produce porous composite ceramics, made of Al$_2$O$_3$ – ZrO$_2$ [19]. Since the pore size depends on the starting powder particle size as well as on the grain size in the intermediate stage of sintering, a thermal treatment at low temperature allows to obtain porous materials having nanometric pores.

![Figure 1.6](image1.png)

**Figure 1.6** – Conventionally (a) and microwave (b) sintered Al$_2$O$_3$ – ZrO$_2$ porous composites [19]

Moreover, the obtained microstructures, compared in Figure 1.6 [19] to a conventionally sintered material, are characterized by a large amount of necks among particles, promoted by the microwave treatment. In fact, due to a different absorbency of the microwaves between the matrix (Al$_2$O$_3$) and the second phase (ZrO$_2$), the localized heating induces a preferential, enhanced neck growth, with a consequent increase of the elastic modulus of the component [19].

Moreover, microwave sintering has been applied to obtain glass materials characterized by highly porous core and a denser outer layer, according to the scheme shown in Figure 1.7 [20].

![Figure 1.7](image2.png)

**Figure 1.7** – Layered structure of glass materials obtained by microwave sintering [20]

The inhomogeneous heating developed during microwave sintering in the sample implies a lower temperature at the surface respect to the core. In the central region gas evolution implies the formation of bubbles that are entrapped by the molten glass. At the same time, in
the outer layer glass sinters by viscous flow creating a shell that avoids sample deformation [20].

The forming techniques developed in order to produce porous ceramics can be classified in three main classes: replica, sacrificial template and direct foaming techniques, as schematically represented in Figure 1.8 [1].

![Figure 1.8 – Scheme of the possible processing routes for the production of porous ceramics [1]](image)

**Replica techniques** are based on the impregnation of a sacrificial porous structure with a ceramic suspension, so that, the final porous component presents strong morphological analogies to the original skeleton. The first attempt reported in literature is due to Schwartzwalder and Somers who in 1963 developed this method by using a polymeric sponge as template [1, 3, 21].

Generally, the first process step consists in fully soaking a highly porous sponge into a ceramic suspension. When the sponge is totally impregnated, the excess suspension is eliminated (for instance by pressing or lamination) in order to retain just a thin ceramic coating over the sponge struts. After drying, the coated sponge is thermally treated to firstly pyrolyze the polymeric template and then sinter the ceramic coating [1]. A typical process flow-chart is reported in Figure 1.9 [22].
It was demonstrated that this method can be applied to any ceramic powder able to be well dispersed in suspension. Nevertheless, a crucial parameter is the rheological behaviour of the ceramic suspension. A shear-thinning slurry must be used; precisely, it must present a low viscosity when a high shear rate is applied and a high viscosity at low shear rate [23, 24]. In fact, a successful impregnation of the sponge requires a highly-fluid suspension, to completely fill also the inner pores [1]. Moreover, the sponge is compressed before plunging in the slurry, but it must then recover its original shape: its free expansion must not be avoided by a too high viscosity of the suspension [3]. After that, the removal of the suspension excess requires that the slurry recovers a suitable fluidity under the shearing conditions applied by rollers [1, 3, 24 – 26], wooden boards [3, 27] or centrifuging [3, 28, 29]. Finally, a high suspension viscosity must be reached under static conditions in order to retain the ceramic coating on the sponge structure [3].

Considering the removal of the suspension excess, Pu et al. underlined the different structure homogeneity obtained with roll – pressing or centrifuging. In the former case, porous materials can present struts having different thickness because of the slurry concentration at the joint points of the polymer sponge. On the other hand, the exploitation of a centrifugal force in the excess removal leads to a homogeneous distribution of the slurry on the organic skeleton [29].

The rheological behaviour of the ceramic suspensions can be modified by adding proper thixotropic and thickening additives such as clays, colloidal silica, carboxymethyl cellulose, polyethylene oxide and conventional dispersants [1, 3, 5, 30 – 32].

Another ticklish moment in the replica technique is to perform the pyrolysis of the template, avoiding crack and defect appearance on the ceramic coating. To limit such a risk, binders and plasticizers are often employed: typically colloidal aluminum orthophosphate, potassium and sodium silicates, magnesium orthoborate, hydratable alumina, colloidal silica, polyvinyl butyral with polyethylene glycol and polymerizable monomers are used [1, 3, 5, 25].

Other additives, such as antifoaming, flocculating or anti–setting agents can be added to the ceramic suspension in order to avoid foaming, to increase slurry adherence and to improve the strength of the ceramic coating after sponge pyrolysis during sintering [3, 22].

Moreover, in order to limit cracks, a second impregnation step should be performed to fill them [1, 25, 26, 29, 33] or even to add fibers or reactive compounds (such as in the case of the
reaction bonded Al₂O₃ (RBAO) in which Al powder is mixed to Al₂O₃ powder) able to enhance material strength [1, 34, 35].

The replica method presents another drawback able to drastically reduce the mechanical response of the porous materials. In fact, the polymeric skeleton implies the formation of triangular voids inside struts due to the burn out of the organic skeleton [3, 6, 23] which are retained even during sintering. This characteristic defect is shown in Figure 1.10 [32].

As reported in literature [1], the tricky impregnation of polymeric sponges having very small cell dimensions limits the possibility to lower the achievable final pore sizes. Porous ceramics from sponge replica method usually present a total open porosity ranging between 40% and 95%, with interconnected pores having dimensions between 200 µm and 3 mm. Most of the work performed on this technique refers to synthetic polymeric sponges, as poly(urethane), cellulose, poly(vinyl chloride), poly(styrene), latex, which were used since they volatilize at relatively low temperature, without inducing residual stresses in the ceramic network [3, 5]. However, environmental issues concerning the possible yielding of noxious by-products have not been frequently kept in mind [36].

On the other hand, natural cellular structures characterized by particular pore morphology as well as interconnected porosity can be used [1, 13]. For example, in the “replamineform technique” corals and other marine invertebrate skeletons have been employed in the production of scaffolds. In fact, a negative preform can be prepared by impregnating a natural foam with wax under vacuum and then leaching out using acidic solution. Then, the wax foam is coated with a ceramic suspension and a similar procedure as already described above is followed [37, 38]. This approach has employed wood cellular structures, obtaining macroporous ceramics with highly anisotropic aligned pores. Wood structures have been heated between 600°C and 1800°C under inert atmosphere to obtain a carbon cellular preform. Exploiting its open tracheidal cells, the carbon preform was infiltrated with gases or liquids at high temperature for producing macroporous ceramics or with liquid sols at room temperature to prepare cellular ceramics [1, 39 – 43]. These porous ceramics are characterized by cell sizes between 10 µm and 300 µm as a function of the starting wood microstructure. The total open porosity varies between 25% and 95%. Because of the highly oriented porous structures, the mechanical strength is anisotropic, being higher in the direction along the oriented pores. As in the porous materials obtained from synthetic template, the absolute strength values are low because of flaws and pores present in the walls and struts. Also in this case, this drawback can be limited if the carbon preform is totally converted into a ceramic phase [44].

**Sacrificial template methods** generally consist in preparing a starting composite structure in which ceramic particles or precursors create a continuous matrix containing a homogeneously dispersed sacrificial phase.
Ceramic powder and sacrificial phase can be dry mixed and pressed [1, 13, 45] or used to prepare a composite suspension and then cast [1, 13, 46]. Moreover, it is possible to employ a preform of the sacrificial material impregnated with a preceramic polymer or a ceramic slurry [1, 47]. It is important to underline that the dry mixing can be difficult in the case of a relevantly different density between the ceramic powders and the sacrificial phase [13]. The sacrificial templates, also called “pore formers” [1] or “pore makers” [13], can be natural or synthetic organics, salts, liquids, metals and ceramic compounds. In all cases, in order to avoid the collapse of the porous structure during their removal, setting agents and binders are employed, particularly in the case of composite suspensions. On the contrary, in the presence of preceramic polymers, consolidation is reached through a curing process during which macromolecules cross–link at a temperature lower than pyrolysis [1]. Sacrificial methods allow to obtain porous materials that present the negative morphology of the original porous template. On the other hand, in the replica techniques a positive morphology is obtained with polymeric sponge and porous ceramic having the same pores structure. This difference implies that porous materials obtained via a sacrificial template are characterized by struts unaffected by flaws. Consequently, these materials present higher compressive than the components obtained by the replica technique [1].

Another main advantage of the sacrificial template methods is the strict control of the porosity features, such as pore shape, size distribution, total volume, by a suitable choice of the pore former [1, 13]. The use of organic materials as template requires a well-stated thermal treatment, usually in the range 200°C – 600°C, in order to allow the pyrolysis of the sacrificial phase and consequent pore formation. The choice of the pore former influences the thermal cycle steps and its duration. Once again, it is important to keep in mind nature and toxicity of the by–products [1].

Materials having a tri – dimensionally interconnected porosity can be obtained by pressing mixtures of ceramic powders and organic pore makers, such as wax, polymer beads, starch or natural fugitive phases like graphite [1, 7, 13, 45]. Colloidal processes have been developed by using starch, graphite, polyethylene [1, 13, 8, 9], yeast [48] and polymer beads (PVC [49] and PMMA [45, 50 – 52]) as sacrificial phase. Finally, porous ceramics can be produced through the infiltration of organic preforms obtained by pressing polystyrene beads [53].

The use of polymer beads allows to obtain a uniform pore distribution and morphology. However, the large volume of gases developed during organic burn out can promote the presence of cell windows with a consequent, uncontrolled increase of the interconnection number [44].

In the case of preforms made of expandable polymer beads, the beads packing ability can influence the porosity structure. In fact, without pressure applied to the beads bed, the ceramic slurry is able to completely surround the polymeric spheres; on the other hand, the imposed pressure yields contacts among porogene spheres which will create windows on the pore walls [52]. Moreover, expandable polymer beads can be also exploited to produce closed – cell foams by using preceramic polymers (such as polyalkylsiloxane for silicon oxycarbide foams) [7]. Foaming was carried out at temperatures higher than the softening temperature of the preceramic polymer. When the fugitive phase expanded, the resin softened can completely fill the voids among beads, leading to a porous structure having highly homogeneous cell shapes and sizes.

To obtain a closed porosity and to control the pores structures the hetero-coagulation method was developed [50, 51], as schematically shown in Figure 1.11 [51].
Thanks to a surface modification, polymer beads and ceramic particles showed an opposite charge and when they were mixed, a core–shell structure was formed, since ceramic particles flocculated on the surface of polymer beads due to electrostatic attraction. Their densification during sintering allowed to obtain ordered and homogeneous porous structures. In the case of starch, the removal of sacrificial phase and the consequent pore formation is linked to its gelling ability in water. In fact, at room temperature starch is insoluble in water; on the other hand, at temperatures between 50°C and 80°C, a rapid and irreversible swelling takes place so that water is removed from the slurry and a solid body is produced.

To produce porous ceramics with uni–directionally–aligned, continuous pores, coating was performed with a slurry containing fugitive fibers (SCF). As shown in Figure 1.12 [54], a ceramic slurry was employed to coat cotton fibers, for example, that have been spooled forming green components [7, 54, 55]. After the burn out of the fugitive fibers, porous ceramics characterized by continuous, aligned pores having a fixed diameter were obtained.

The development of toxic gases can be avoided by exploiting liquid pore formers as water or suitable volatile oils, removable by evaporation or sublimation [1]. Moreover, the use of volatile oils as sacrificial phase shows the advantages of a simple incorporation in the ceramic suspensions by stirring. Finally immiscible liquids present a low interfacial energy so that smaller bubbles can be produced [1]. Freeze drying in presence of water or high–melting point oils was employed in the preparation of porous materials having peculiar morphology, precisely a highly oriented structure induced by the directional growth of ice or oil crystals [1]. Orientation in ice crystal growth can be induced by a temperature gradient in the mould. Moreover, an open–cell material can be produced with the formation of a dendritic structure characterized by the presence of micropores in the inner walls of the oriented macropores [13, 56].

In the case of salts, of ceramic or metallic particles as pore formers, their removal is carried out through chemical routes. In the former case, the starting composite structure is just washed with water, while ceramic and metallic templates require more aggressive agents such as an acidic leaching [1]. A ceramic pore former is NiO, used for the production of porous
nickel – yttria – stabilized zirconia for SOFCs applications. NiO oxide is reduced by H₂ to the metal state and then leached by nitric acid, leading to pore formation [13, 57]. On the basis of the nature of pore former and of its volume fraction, porous materials via the sacrificial template routes show a total porosity ranging between 20% and 90% with pore sizes from 1 μm to 700 μm [1].

The sacrificial template method was combined to the replica method to produce open-cell structure having a bimodal pore size distribution [58]. In fact, the immersion of a polymeric sponge in a ceramic suspension containing a pore former allows the formation of both large pores (due to the sponge skeleton) and small pores (formed by the burning out of the sacrificial compound).

**Direct foaming techniques** provide the incorporation of bubbles into ceramic suspensions by using blowing agents. A gaseous phase can be directly added or yielded by the reaction of suitable chemical mixtures [1, 3, 5, 12]. Porous materials via the foaming approach were firstly developed by adding propellants as calcium carbide, calcium hydroxide, aluminum sulfate, hydrogen peroxide, in a clay slurry [3, 5, 59]. Generally, the blowing agents can be liquids or solids: in the case of cement porous materials, metal blowing agents (such as magnesium, calcium, chromium, manganese, iron, cobalt) react with acids yielding hydrogen bubbles [60]. Aluminosilicate hydrogel can be employed as source of alkali which produces hydrogen gas reacting with metals such as aluminum [61]. In the presence of an aqueous solution of metal phosphate, polyvalent metal carbonates can evolve carbon dioxide gas [62].

A simpler foaming method consists in the “in situ” production of a polyurethane sponge: polyurethane precursors such as polyisocyanates and polyols, added in the ceramic suspension, react. The developed carbon dioxide induces the foam forming of the ceramic slurry and the production of the polymeric skeleton [1, 3, 63–66]. In particular, the nature of the isocyanate reactant can affect the structure of the PU foam (flexible or semi – rigid) and, consequently, the nature of the pore structure (fully or partially open), as well as the pore sizes and foam morphology [64, 65]. In the last years, “intrinsic” foaming agents [67] have been also studied in the case of silicone resins. Through condensation reactions between hydroxyl and ethoxy groups and the release of water and ethanol, at temperatures above 200°C, foaming takes place into the ceramic suspension [67, 68, 69]. In comparison with the replica method, in this way it is possible to avoid the ceramic coating of the polymeric skeleton and consequently to obtain dense struts with an improvement of the mechanical properties of the foam [64, 66].

The foam formation by using intrinsic agents is characterized by bubbles nucleation, growth and coalescence, as shown in Figure 1.13 [66, 69].

![Figure 1.13 – Process of the foam formation in the ceramic suspension](image)

The viscosity of the liquid phase is a very important parameter in foam stabilization. The polymer melt must present a low viscosity in the nucleation step, while the foam stabilization requires an increase of viscosity [67–69].

Finally, as previously reported, the gaseous phase can be directly added through the dispersion of Freon or air bubbles with the mechanical frothing with surfactants [1].

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The porosity obtained by foaming methods depends to the amount of gas added or produced in the ceramic suspension; moreover, in the case of wet foams, the bubbles stability and coalescence phenomena play a crucial role in the cell dimensions and their size distribution [1]. Several approaches have been developed in order to stabilize the bubble structure, as schematically resumed in the Figure 1.14.

![Figure 1.14 – Approaches to stabilize foams](image)

The foam structure can be fixed by the setting of polymeric (in gelcasting procedures) or inorganic (in sol-gel techniques) materials [1].

**Gelcasting** is a method based on “in situ” polymerization of organic monomers or more environmental – friendly gelling agents; the formation of a polymeric network allows to maintain the bubbles structure avoiding coalescence or growth phenomena [1]. Since the materials studied in this work have been produced by using a gelcasting procedure, the set-up of which represents a relevant part of the experimental part, a more detailed description of this method is reported in Chapter 2.

**Sol–gel** setting exploits the capability of some inorganic materials (particularly silica–based systems) to undergo sol-gel phase transitions in a liquid medium [1]. Generally, starting from metal salts or alkoxides as precursors, the gel formation takes place due to pH modifications, or hydrolysis and condensation reactions [1, 13, 70, 71]. Porous materials can be produced generating air or Freon bubbles directly in inorganic sols, and the foam is stabilized by pH modifications with the electrostatic control of the gel viscosity [72, 73], as shown in Figure 1.15 [73], or through an increase of temperature [74].
Figure 1.15 – A typical flow-chart of the foaming sol-gel method [72]

On the other hand, in the case of the addition of surfactant molecules or particles, the foam stabilization is due to electrostatic or steric repulsive forces. Generally, the liquid – gas interface of the bubbles in the slurry presents a high superficial energy that decreases if neighboring bubbles combine through Van der Waals attractive forces. The adsorption at liquid – gas interface of surfactant molecules or particles allows to decrease the superficial energy, avoiding the bubbles coalescence and the consequent presence of large pores in final materials [1].

The adsorption of solid particles at liquid – gas interface is energetically favored because the solid – liquid interface is characterized by a free higher energy with respect to the solid – gas area. Moreover, the presence of particles at the liquid – gas interface implies the hindrance of bubbles shrinkage and expansion and a longer stabilization of foams. The ceramic suspensions contain amphiphiles (such as valeric acid, propyl gallate, butyl gallate, hexyl amine). These molecules are characterized by a polar anchoring group that adsorbs on the surface of the ceramic particles, while a short hydrophobic tail is in contact with the aqueous phase. After the particles surface modification, air bubbles have been added into the ceramic suspension; then, modified particles are able to attach the air bubbles forming a slightly coagulated network implying an increase of suspension viscosity that improves the foam stability. Porous materials obtained by this method present porosity levels between 40% and 93%, with cells having diameters from 10 to 300 μm; it is possible to produce open – cell components with low concentrations of stabilizing particles [1].

In the case of surfactants, the stabilization is due to the reduction of the liquid – gas interfacial energy through the adsorption of these molecules; but these phenomena are reversible so that the foams present stability times lower than the particles – stabilized ones [1]. Moreover, surfactant features (such as type and amount) can affect the density, the porosity and the cell features of the porous materials [5, 12]. Generally long – chain amphiphilic molecules, lipids and proteins can be employed as surfactants, with different behaviour in the foam stabilization [1]. Materials obtained by surfactant – based foaming are characterized by porosity volumes from 40% to 97%, pores having generally spherical shape and diameters between 35 μm and
1.2 mm; through the control of gas content, surfactant concentration and setting kinetics it is possible to produce open or closed cells [1].

Finally, it is important to underline that the foaming methods allow to obtain closed – cell foams having smaller pores than those made by the sponge techniques [5].

### 1.2 Mechanical models for describing porous body behaviour

Most properties of porous ceramics (such as conductivity, specific strength, permeability, thermal shock resistance, specific area surface, hardness, wear and chemical resistance) can be affected by [12]:

- their relative density, \( \frac{\rho^*}{\rho_s} \) (given by the density of the porous material, \( \rho^* \), divided by that of the fully dense solid, \( \rho_s \));
- cell morphology;
- pore size distribution;
- the nature of ceramic material.

In order to investigate the influence of the above parameters on the mechanical behaviour of porous materials, several micromechanical models were developed. Among them, the Gibson and Ashby (GA) approach is the most realistic, especially for explaining the strut bending [75, 76]. Moreover, while other models have supposed that the overall mechanical behaviour is mainly controlled by relative density, the GA approach also highlights the influence of the cell size [76, 77].

The Gibson – Ashby model considers the foam structure as made of unit cells, having a cubic geometry, as reported in Figure 1.16 [4, 76, 78 – 80].

A typical compressive stress – strain curve for a brittle material having a relative density lower than 0.3 [78] is showed in Figure 1.17 [4].
The axes are the nominal stress $\sigma$ and the nominal compressive strain $\varepsilon$ defined as:

$$\sigma = \frac{F}{A_0}$$  \hspace{1cm} (1.1)  

$$\varepsilon = \frac{h_0 - h}{h_0}$$  \hspace{1cm} (1.2) 

where $F$ is the applied load, and $A_0$, $h_0$, $h$ are geometric parameters of the sample (the initial section, the initial height and the height after a strain $\varepsilon$, respectively).

The curve reported in Figure 1.17 presents:
- a linear elastic region at low stresses;
- a collapse plateau in which the stress is constant while the sample starts crushing because of the struts breakage and the consequent, progressive damage layer by layer;
- a densification regime with an steep increase of the stress after that the cell walls touch each other [4, 77, 78].

In the linear elastic regime (generally for strains lower to 5%), according to the Hooke law, the slope of the stress – strain curve is the Young’s modulus of the porous ceramic, $E^*$. This parameter depends on the cell wall modulus, $E_s$, and the relative density. In the second regime, the stress – strain curve presents a plateau at brittle collapse stress $\sigma_{cr}^*$; this response is due to the collapse of the cells associated with brittle crushing.

When opposing cell walls are in contact, the solid undergoes a further compression that implies a rapid increase in the stress. Then, it is evident that the mechanical response of a porous material depends on the behaviour of the dense cell walls. The cell wall moduli cannot be directly measured using tensile or bending tests [80] because of the small size of samples and the different cross section along the length. An evaluation of the strut strength can be carried out by using mechanical tests or fractography of broken cell walls [76]; both methods are approximate, but the latter turned out more accurate. Another method to evaluate the struts properties is the micro-indentation tests: Tulliani et al. demonstrated that this technique allows to obtain reproducible values, comparable to the data reported in literature [32].

The mechanism of linear elasticity is influenced by the nature of porosity: in the case of open – cell samples the mechanical behaviour is controlled by cell wall bending, whose contribution increases with a relative density higher of 0.1. On the other hand, for closed – cell components cell face stretching must be considered in addition to the cell wall bending: in fact, while the cell edges bend contracting, the cell faces stretch and the elastic moduli depends on the axial – wall stiffness too.
An open – cell porous material can be represented by a cubic array of members having length $\ell$ and a square cross section with side $t$, as reported in Figure 1.16a [4]; real cells present more complex shape, but this approximation allows to simplify the deformation and failure mechanisms.

If a beam of length $\ell$ is loaded at its midpoint by a load $F$, at low stress it undergoes a linear elastic deflection $\delta$ given by:

$$\delta \propto \frac{F\ell^3}{E_s I}$$

that is the linear elastic deflection underwent by the foam structure uniaxially stressed with consequent bending of cell edges, as showed in Figure 1.18 [4].

![Figure 1.18 – Cell edge bending during elastic deformation of a brittle open-cell foam [4]](image)

In particular, applying a compressive stress $\sigma$ on the foam, each cell edge transmits a force $F$ such as:

$$F \propto \sigma \ell^2$$

while the strain $\varepsilon$ depends on the displacement $\delta$ according to the equation:

$$\varepsilon \propto \frac{\delta}{\ell}$$

Then the Young’s modulus of the open – cell porous material is given by:

$$E^* = \frac{\sigma}{\varepsilon} = \frac{C_1 E_s I}{\ell^4}$$

and considering that $\frac{\rho^*}{\rho_s} \propto \left(\frac{t}{\ell}\right)^2$ and $I \propto \ell^4$ it is possible to conclude that:

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

with $C_f$ that includes the constants related to the cell shape. This parameter is generally equal to 1; in the case of porous materials prepared through replica technique, it is equal to 0.3 because of the voids present in the struts due to the polymeric skeleton burning out.
In open–cell materials the failure of the cell walls, showed in Figure 1.19 [4], takes place when it is subjected to a moment $M_f$ higher than:

$$M_f = \frac{1}{6} \sigma_{fs} t^3$$  \hspace{1cm} (1.8)

where $\sigma_{fs}$ is the modulus of rupture of the cell wall material.

Since $\sigma_{cr}^* \propto \frac{M_f}{\ell^3}$ (considering that $\sigma_{cr}^* \propto \frac{F}{\ell^2}$ and $F \propto \frac{M_f}{\ell}$), using $\rho^* \propto \left(\frac{t}{\ell}\right)^2$ it is possible to conclude that:

$$\frac{\sigma_{cr}^*}{\sigma_{fs}} = C_0 \left(\frac{\rho^*}{\rho_s}\right)^\frac{3}{2}$$  \hspace{1cm} (1.9)

considering the modulus of rupture of the strut constant [4, 78, 80].

The cell unit for closed–cell porous materials are shown in Figure 1.16b [4]: the cell of length $\ell$ presents a fraction $\phi$ of the solid in the cell edges of thickness $t_e$ and the remaining fraction $(1 - \phi)$ in the cell faces of thickness $t_f$.

In the case of closed–cell materials, Young’s modulus depends on the cell edge bending, as for open–cell specimens but with a factor of $(0.86\phi)^2$. In addition, it is necessary to consider the contribution of the membrane stresses in the cell faces. In fact, when a closed–cell porous component is submitted to a compressive load, the cell edges bend, deflecting of $\delta$, and consequently the cell faces stretch, as shown in Figure 1.20 [4].
The restoring force caused by face stretching is proportional to \( \frac{1}{2} E_s \varepsilon^2 V_f \), where \( \varepsilon \) is the strain associated to this mechanism and \( V_f \) is the solid volume of cell face. Moreover, the restoring force due to the cell edge bending is proportional to \( \frac{1}{2} S \delta^2 \), where \( S \) is the stiffness of the cell edge such as:

\[
S \propto \frac{E_s l}{\ell^3}
\]  

Owing to its linear elasticity, the structure opposes the work \( \frac{1}{2} F \delta \) to the cell forces so that:

\[
\frac{1}{2} F \delta = \frac{\alpha E_s l \delta^2}{\ell^3} + \beta E_s \left(\frac{\delta}{\ell}\right)^2 l^2 t_f
\]  

Considering that \( I \propto t^4 \) and \( E^* \propto \frac{E}{\ell} \)

\[
\frac{E^*}{E_s} = \alpha' \frac{t^4}{\ell^4} + \beta' \frac{t_f}{\ell}
\]  

and with \( \frac{t_f}{\ell} \propto (1 - \phi) \frac{\rho^*}{\rho_s} \) and \( \frac{t_e}{\ell} \propto \phi^2 \left(\frac{\rho^*}{\rho_s}\right)^{\frac{1}{2}} \) it is possible to conclude that:

\[
\frac{E^*}{E_s} = C_1 \phi^2 \left(\frac{\rho^*}{\rho_s}\right)^{\frac{1}{2}} + C_1' (1 - \phi) \frac{\rho^*}{\rho_s}
\]  

where \( \alpha, \beta, \alpha', \beta', C_1 \) and \( C_1' \) are constants and the last two are generally equal to 1.

When a closed – cell porous material undergoes a brittle crushing, the structure opposes a work \( F \delta \) to the plastic work of cell edges, that is proportional to \( M_f \delta \), and to the stretching work of the cell faces, that is proportional to \( \sigma_{fs} \delta t_f \ell \).

Then:

\[
F \delta = \alpha M_f \delta \frac{\ell}{\ell} + \beta \sigma_{fs} \delta t_f \ell
\] 

with \( \alpha \) and \( \beta \) constants; replacing \( F \) by \( \sigma \ell^2 \) and considering the equation (1.8):

\[
\frac{\sigma_{cs}^*}{\sigma_{fs}^*} = \alpha' \frac{t^3}{\ell^3} + \beta' \frac{t_f}{\ell}
\]  

and with \( \frac{t_f}{\ell} \propto (1 - \phi) \frac{\rho^*}{\rho_s} \) and \( \frac{t_e}{\ell} \propto \phi \frac{\rho^*}{\rho_s} \) it is possible to conclude that:

\[
\frac{\sigma_{cs}^*}{\sigma_{fs}^*} = C_6 \phi \left(\frac{\rho^*}{\rho_s}\right)^{\frac{3}{2}} + C_6' (1 - \phi) \frac{\rho^*}{\rho_s}
\]  

where \( C_6 \) and \( C_6' \) are constants that depend on strut size [4, 75].

As solid fraction in the cell faces increases, the strength dependence on density can become linear.

In summary, in the case of brittle crushing, the equations used to describe the mechanical compressive behaviour are:
\[
\frac{\sigma^{*}}{\sigma_{f_s}} = C_6 \left( \frac{\rho^*}{\rho_s} \right)^{\frac{3}{2}} 
\]  
for the open – cell materials

(1.17)

\[
\frac{\sigma^{*}}{\sigma_{f_s}} = C_6 \left( \phi \frac{\rho^*}{\rho_s} \right)^{\frac{3}{2}} + C_6' (1 - \phi) \frac{\rho^*}{\rho_s} 
\]  
for closed – cell ceramics

(1.18)

with \( C_6 = 0.65 \) and \( C_6' = 1 \).

Concluding, the GA model is an instrument to understand the deformation mode of the cellular microstructure of porous ceramics. The agreement between experimental and calculated data in terms of density exponent and constants states that the failure catastrophically occurs with a collapse of cells at a critical value of stress \([4, 75]\).

First of all, the discrepancy between experimental and theoretical values of the constants \( C \) can depend on the geometry of the unit cell. Moreover, this difference can be related to the strut strength. In fact, the GA model is based on the assumption that the modulus of rupture of the strut is constant \([4]\). But it is possible that strut walls contain microscopic or macroscopic flaws (such as pores, cracks or triangular voids in the materials obtained by replica) that imply a lower modulus of rupture \([81]\).

Generally, for a brittle material the modulus of rupture of the strut varies according to the Weibull distribution. This function describes the probability of failure, \( P_f \), in a brittle material of volume \( V \) and subjected to a uniform stress \( \sigma \) such as

\[
P_f = 1 - \exp \left[ -V \left( \frac{\sigma - \sigma_u}{\sigma_0} \right)^{m_w} \right] \quad \text{for } \sigma > \sigma_u
\]  
(1.19)

\[
\text{and } \quad P_f = 0 \quad \text{for } \sigma < \sigma_u
\]  
(1.20)

with \( \sigma_u \) (generally equal to 0 for ceramics), \( \sigma_0 \) and \( m_w \) (Weibull modulus) material properties characterizing the flaw size population in the material.

The Weibull modulus can be evaluated measuring the modulus of rupture of the cell walls of brittle porous materials through direct mechanical testing or fractography; for instance, the Weibull modulus of alumina foams is ranged between 1 and 3.

As a consequence of the Weibull distribution, the sample volume can influence the failure stress because of the higher probability of flaw presence in a larger volume.

Sammis and Ashby demonstrated that brittle solids containing closed, spherical pores fail in compression by a progressive micro-fracture \([82]\). According to the Griffith theory, under compressive stress tensile wing cracks can nucleate at the tips of flaws in brittle solids \([83]\). When compressive load increases, crack grows until to failure \([82]\). The pore dimensions influence the crack development: in fact, with larger holes crack initiates earlier, grows quickly and slows down later. On the other hand, materials having smaller pores present cracks at higher stresses and they fail with a higher rate at higher load \([83, 84]\), as reported in Figure 1.21 \([83]\).
The nucleation and the growth of the cracks are faster with a higher number of pores. In figure 1.22 [83] it is possible to note that, at the same stress (for instance 20 MPa), in the case of the array of holes, many cracks are present in comparison to materials having a single hole.

Moreover, Tang et al. demonstrated that the influence of nearby pores depends on their arrangement, as shown in Figure 1.23 [83]. In fact, in the case of holes arranged in diagonal lines, cracks propagate with a higher rate at lower compressive strengths.
In the case of multi-holes materials, different behaviours have been recorded depending on the distribution: the behaviour of a randomly and uniformly pores distribution is compared in Figure 1.24 [83].

In the case of randomly arranged pores having different diameters, cracks involve only some holes, particularly the largest ones, those closer to boundary and those arranged in diagonal
lines. On the other hand, a regular distribution of pores implies a more homogeneous nucleation of cracks and a higher maximum strength. These results have been obtained with a two-dimensional model, that allows to underline that the failure mechanism depends on several factors, such as the dimensions, the size distribution and the arrangement of pores.

To confirm the above statements, studies carried out on concrete materials demonstrated the influence of the pores size and arrangement on the compressive behaviour. In fact, materials having a regular pores structure, as shown in Figure 1.25 [85], present a compressive strength independent of the cell size [85].

![Figure 1.25 – Failure of a material having a regular porous structure [85]](image)

On the other hand, if pores are randomly arranged, the lower the cell size, the higher the compressive strength, for the same total volume porosity [86]. It is also important to underline the role of the porosity amount: in fact, the pore size effect is significant for low porosity percentages and become negligible in highly porous materials.

A two-phase mechanism is hypothesized for the failure of brittle porous materials: on one hand, the micro-crack initiation takes place at the end of the elastic behaviour, on the other, there is a competition between micro-cracking and macro-cracking propagation. For this reason the normalized compressive strength \( \frac{\sigma(p, \phi)}{\sigma_{\text{matrix}}} \) at the failure can be expressed as:

\[
\sigma_N(p, \phi) = \sigma_{\text{init}}^N(p) + \sigma_{\text{ad}}^N(p, \beta_m)
\]

where

- \( \sigma(p, \phi) \) is the compressive strength for a given porosity \( p \) and pore size \( \phi \)
- \( \sigma_{\text{matrix}} \) is the compressive strength for the relative dense material
- \( \sigma_{\text{init}}^N(p) \) is the stress required for the micro-crack initiation
- \( \sigma_{\text{ad}}^N(p, \beta_m) \) is the additional required stress for cracks propagation
- \( \beta_m \) is the mesoscopic brittleness number.

The micro-crack initiation is influenced by the total porosity; in fact, the elastic modulus is independent of cell size. On the other hand, the propagation phase can occur with or without the coalescence of micro-cracks to form macro-cracks.

The parameter \( \beta_m \) and the propagation mechanism depends on the geometric length \( \ell_s(p, \phi) \) and the characteristic length \( \ell_c \) according the equation:

\[
\beta_m = \frac{\ell_s(p, \phi)}{\ell_c}
\]

The characteristic length \( \ell_c \) is the width of the fracture process zone and it has been fixed at three times the maximum size of the matrix (that is the sand grains in the case of the concrete). The geometric length \( \ell_s(p, \phi) \) is related to the microstructure of the porous
material. It depends on the total porosity \((p)\) and the pore size \((\phi)\) and it controls the coalescence or the propagation of micro-cracks.

At low porosity, the material presents only few pores, with large, dense areas among them. The failure occurs through the propagation of few macro-cracks originated from pores. In this case, as already stated, the failure behaviour is influenced by the pore size \([83, 86]\).

At very high porosity, the failure takes place through the propagation of micro-cracks, the size of which depends on the average pores spacing \(e(p, \phi)\).

![Figure 1.26 – The average pores spacing \(e(p, \phi)\)](image)

This parameter, identified in Figure 1.26 \([86]\), is related to the total porosity \((p)\) and the pore size \((\phi)\) according the equation:

\[
e(p, \phi) = \phi \times \left( \left( \frac{p_{\text{max}}}{p} \right)^{\frac{1}{3}} - 1 \right)
\]

(1.23)

with \(p_{\text{max}}\) the maximum packing density of an ordered spheres arrangement (equal to 0.74 in the case of mono-sized spheres, considering the packing density of a face-centered cubic arrangement).

When the porosity amount is very high, the average pores spacing \(e(p, \phi)\) corresponds to the fracture process zone and \(\beta_m\) becomes negligible. In this case, the failure behaviour is only influenced by the total porosity.

The influence of the cell size on the compressive strength is also explained by the GA model in the case of the open-cell brittle foams \([4, 87, 88]\).

In fact, considering two cells having length \(\ell_1\) and \(\ell_2\) and strut thickness \(t_1\) and \(t_2\), it is possible to conclude that for materials characterized by same relative density the crushing strength decreases when cell size increases

\[
\frac{\sigma_{cr,1}}{\sigma_{cr,2}} = \left( \frac{\ell_2}{\ell_1} \right)^{\frac{3}{m_w}} \left( \frac{\rho_2^{*}}{\rho_1} \right)^{\frac{1}{m_w}}^{\frac{3}{2}}
\]

(1.24)

In this case the influence of the cell size is only related to the different thickness of the struts and consequently to the different failure probability (related to the different strut volume) \([87]\).
1.3 Industrial applications of porous ceramics

Porous materials are exploited for many technological and industrial aims. In this paragraph two specific applications will be further discussed, since the present PhD thesis was mostly focused to the exploitation of foamed ceramics for environmental and biomedical aims. Thanks to the financial support from Regione Piemonte, the production of porous materials was addressed to environmental applications. In particular, ceramic foams were developed in view of the filtration of extra-fine particulate matter present in exhaust gases from automotive, urban or industrial sources. In the frame of the European Integrated Project Nanoker, the study concerned the production of scaffolds, that is porous materials for bone substitution.

1.3.1. Environmental application of porous materials: filters

1.3.1.1. Air pollution: an introduction

Air pollution derives from the emission of substances such as sulphur dioxide (SO₂), hydrogen sulfide (H₂S), nitrogen oxides (NOₓ), ammonia (NH₃), carbon monoxide and dioxide, non-methane volatile organic compounds (NMVOC) and particulate matter (PM). In the atmosphere, they can react yielding further particulate matter, acidifying or eutrophying (that imply an oversupply of nutrients in soil and water bodies) substances, or even increasing the ozone level. The effects of these emissions are schematically proposed in Figure 1.27 [89].

![Figure 1.27 – Effect of air pollutant emissions [89]](image)

Air pollution can be due to natural sources, such as volcano eruption (particulate matter, SO₂, H₂S, methane) or accidental fires (source of smoke, unburned hydrocarbons, carbon monoxide and dioxide, nitrogen oxides and ash). Nevertheless, in civilized Countries the pollutants due to the human activities, called anthropogenic sources, are the main cause of air pollution [90]. Among these, there are the industry activities, with their waste products and emissions, combustion processes and utilities, such as energy, and the urban activities, such as energy, heating systems and automotive sources [89, 90]. The contributions of the principal anthropogenic sources on the air pollution in the Europe from 1990 to 2004 are resumed in Figure 1.28 [89].

The air pollution implies:
a human health impact (due to particulate matter, heavy metals and persistent organic pollutants, ozone);
- damage to ecosystems and crops (due to heavy metals and persistent organic pollutants, acidification and eutrophication, ozone);
- damage to materials and cultural heritage (due to acidification and ozone) [89].

Figure 1.28 – Main anthropogenic sources of air pollution in Europe in the period 1990 – 2004 [89]

1.3.1.2. **PM10: origin and effects on human health**

The particulate air pollution, called particulate matter PM, is a complex aerosol made of finely divided condensed matter and a gaseous suspending medium [91]. Particulate sources can be natural (fires and volcano eruptions) or anthropogenic; the latter ones can be divided in mobile sources (cars, trucks, planes, ships, trains) and stationary sources (electric power plants, factories, mines, farms, homes and waste – disposal sites) [90]. Figure 1.29 [92] presents the polluting substances for the main stationary and mobile urban sources. It is possible to note that PM in the urban area is due to power generation and domestic utilities, besides diesel car exhaust gases.

Figure 1.29 – Pollutants from urban stationary (a) and mobile (b) sources [92]

The particles present in this aerosol are characterized by sizes between 100 μm and 0.001 μm: larger particles are unable to remain suspended in the air for long times, while smaller particles tend to evaporate in the air or to aggregate. Particularly, it is possible to distinguish PM$_{10}$ and PM$_{2.5}$ fractions, made of particles having diameters under 10 μm and 2.5 μm, respectively [91, 93]. The former is defined as the “inhalable coarse particle” size fraction, the latter as the “fine fraction” [94]. In Figure 1.30 PM$_{10}$ and PM$_{2.5}$ are compared with an human hair [95].
Concerning the effect on human health, in the case of particulate matter it is important to consider the number, the surface, the mass and the composition of the particles [91, 93]; on the other hand, the particles size determines the site in respiratory system where they deposit [93].

The human respiratory system, shown in Figure 1.31, is divided in nasal, tracheobronchial and pulmonary regions; the first includes nose, mouth cavities and throat; in the second there is trachea, bronchial tubes and alveolar sacs; the latter is made by terminal bronchi and alveolar sacs [90].

Particles deposition in human respiratory system depends on the region in which it is and on their size according to the relationship reported in Figure 1.32 [90].
Large particle generally deposit in the nasal region due to the presence of hairs in the nose or the bends of the nasal passages; on the other hand, smaller particles are able to reach the tracheobronchial and pulmonary regions [90, 93]. Smaller particles are removed from the air by impact with bronchi walls and, at the terminal bronchi smallest particles are eliminated by Brownian motion collecting on alveolar membrane [90].

The particles removal from respiratory system occurs through different mechanisms depending on the region: in fact, it is due to mucous fluid in the nasal and tracheobronchial regions, with the assistance of fiber cilia (called mucociliary escalator) in the latter one. In the pulmonary region, particles can move across the epithelial lining of the alveolar sac to the lymph or blood systems, or they may be removed by scavenger cells called alveolar macrophages.

The main effect of the PM on human health is related to their accumulation in the upper airways of the respiratory system [94].

As showed in Figure 1.33 [89], Regione Piemonte presents a high annual average value of the PM$_{10}$ concentration in the air, considering that the fixed limit in the European Countries is 40 $\mu$g/m$^3$. Figure 26 also allows to note that the PM$_{10}$ pollution is a relevant problem for many European Countries.

**Filtration mechanism**

Filtration can be defined as “the operation of separating a dispersed phase of solid particles from a fluid by means of a filter medium which permits the passage of the fluid but retains the particles [96].” For the investigated application, filtration consists in the removal of the particulate from the exhaust gases that pass through the porous structures; this phenomenon can occur according to two mechanisms, the cake (or surface) filtration and the depth filtration [97, 98].

In the surface filtration mechanism, schematically reported in Figure 1.34 [99], the flow impacts the filter perpendicularly and the particulate is collected on the surface of the porous structure [97, 98]. In this case the filtration ability depends on the pore size of the filter and the dimensions of the particles to remove. Moreover, the efficiency of filters decreases since the deposited particles induce a lowering of the mean pore size.
In the depth filtration mechanism, schematically shown in Figure 1.34 [99], the flow impacts the filter perpendicularly, but the particulate penetrates the wall surface and is collected inside the filter, along the thickness of the porous body [97, 98]. In this case particles are removed from gas flow by collision on the pore walls; for this reason, the filtration ability is related to the tortuosity of the porous network.

1.3.1.4. Present types of filters: advantages and drawbacks

At the end of 1980s, several researches were carried out in order to study porous ceramics for environmental applications [97, 100]. These components are able to remove the particle matter present in exhaust gases by filtration and catalytic combustion. This application involves the fluid transport and requires an open – cell structure [12, 99] with a high filtration efficiency [101], that depends on porosity, interconnections and mean pore size [102]. Moreover durability, back – pressures and regeneration are very important features. In particular, the durability depends on the ceramic material: it must present thermal, chemical and mechanical stability [3, 101, 103].

During the last years, particulate filtration was carried out by employing ceramic wall – flow monolith filters, multi – layer yarn – like fiber tubes and foam – like porous materials [97, 101, 103, 104].

The wall – flow monoliths are two – dimensional cellular structures characterized by parallel channels, having triangular, hexagonal or square shape, alternatively open and closed, in order to force the flow to pass through porous walls [101 ,104, 105, 106]. They utilize the cake filtration mechanism [97], as shown in Figure 1.35a [107].

The wall – flow monoliths are characterized by good mechanical strength [101], an effective compromise between pressure drop and filtration efficiency, but they present a drawback: the particulate deposited on the porous walls can imply a decrease of filtration capability and an increase of counter-pressure [97, 101, 103, 105].

The multi – layer yarn – like fiber tubes are fibers filters having high porosities; there are two types of ceramic fiber filters (reported in Figure 1.36 [103]), fabricated into cartridges with
fibers wound onto a support or forming a sheet [103]; the exhaust gas is forced to flow inside the tube through the fibers layer [101].

Figure 1.36 – Ceramic fiber filters [101]

They are economic and present low pressure drop; but the particulate deposited on the porous walls can imply a decrease of filtration capability and an increase of counter-pressure [104]. The cellular materials, particularly foams, used for this application exploit a depth filtration mechanism. In this case, the filtered particulate deposits on porous walls without limitations in filter actions [97], as shown in Figure 36b [107]. In the case of ceramic foams some parameters can influence the filtration capability, such as cell size, interconnections dimensions, the internal surface. It is important to underline that small pores allow a higher filtration efficiency but imply a higher pressure drop [104]. The cellular materials obtained by replica method present the drawback of the weakness due to the struts voids left by polymeric skeleton [107].

1.3.2. Biomedical application: scaffolds

1.3.2.1. Human bone tissue: an example of reference

Bone is a complex living tissue and it was composed of an organic phase (in amount of 20 - 30 wt%, made of collagen and proteins) with embedded calcium-containing inorganic crystals (about 60 - 69 wt%) [108, 109]. These mineral crystals are made of human apatitic calcium phosphates having cationic and monovalent anionic vacancies. It is important to underline that the bone composition can change with age, site and history [110]. Collagen is in the form of microfibers with diameters between 100 nm and 2000 nm; the inorganic crystals, having the form of plates or needles, are 40 – 60 nm long, 20 nm wide and 1.5 – 5 nm thick [109], as shown in Figure 1.37 [109].

Figure 1.37 – Structure of human bone [109]

In the mammalian skeletal system acts as a support, but it is also important for locomotion and protection of the vital organs [108, 111]. Moreover, bone is the production site of bone marrow and a mineral reservoir used by endocrine system in the control of calcium and phosphate homeostasis in the circulating body fluids [108].
Bone presents a dual structure: an external layer, or cortical bone, made of smooth, continuous and dense material (with a density of about 1.80 g/cm$^3$); an inner zone, called cancellous bone, characterized by high porosity (75 – 95%, with pores size between 200 µm and 400 µm [112]) and an average density of 0.2 g/cm$^3$ [108].

These different structures imply different mechanical properties: in fact, the former presents tensile strength of 50 – 150 MPa, compressive strength of 100 – 230 MPa, strain to failure of 1 – 3 % and Young’s modulus of 7 – 30 GPa. The latter is characterized by a tensile strength of 10 – 20 MPa, compressive strength of 2 – 12 MPa, strain to failure of 5 – 7 % and Young modulus of 0.5 – 0.05 GPa. These values also depend on the composition of human bones: collagen presents a tensile strength of 50 – 1000 MPa with a Young’s modulus of 1 – 2 GPa, while hydroxyapatite component shows a tensile strength of about 100 MPa and a Young’s modulus of about 130 GPa [113]. Then, it is important to consider the anisotropy of the bone: the cortical structure presents a tensile strength ranged from 79 MPa to 151 MPa in longitudinal direction and from 51 MPa to 56 MPa in transversal direction, with Young’s modulus of the order of 17 – 20 GPa in longitudinal direction and of 6 – 13 GPa in transversal direction. These mechanical properties are due to the composite structure of the bone, in which the calcium phosphate apatite crystals are longitudinally oriented in the collagen matrix [108, 113].

Figure 1.38 [109] reports the stress – strain curve of the human bone: it shows a linear elastic region up to 0.8% strain, followed by a flat plastic region up to failure at 3% strain. It is important to underline that bone is considered a tough material at low strain rates, but it presents a brittle behaviour at high strain rates.

![Stress-strain curve of the human bone](image)

**Figure 1.38 – Stress – strain curve of the human bone [109]**

1.3.2.2. Materials used for ceramic scaffolds

Ceramic materials used for scaffolds are hard, brittle materials that present excellent compressive strength, high resistance to wear, but their tensile properties are poor [113]. They must present biofunctionality; in particular, it is necessary to consider as main features
- the mechanical properties: tensile and compressive strength, fracture toughness, elongation to failure, fatigue strength and Young’s modulus;
- the physical properties: density, porosity, pore size distribution;
- the chemical properties: degradation resistance, corrosion and bone bonding ability.

The first two features classes are closely dependent on scaffold structure, whereas the latter is led by the choice of the material. Moreover, in scaffolds application it is important to consider the biocompatibility, which is the ability of a material to perform an appropriate response in a specific application [108].

On the basis of the biological response, implant materials can be divided in:
- Toxic, when the material causes the death of the cells and tissues releasing soluble detrimental products (lead oxide, arsenic oxide);
Nearly inert, when no direct chemical bond was created between the material and the tissue, with the formation of a fibrous layer (alumina, zirconia);

Bioactive, when the material participates in dynamic surface exchange bonding directly with tissue (calcium carbonates, calcium sulfates, calcium phosphates, bioactive glasses and glass-ceramics);

Resorbable, when material undergoes biodegradation producing nontoxic species (calcium sulfates, β-tricalcium phosphate, bioactive glasses) [110].

The development of materials in order to repair human tissues is related to the Vietnam War. In fact, the high number of casualties induced Larry Hench to design biomaterials for the production of an implant containing calcium and phosphate in proportions similar to bone mineral to avoid rejection by the body. This innovative material, based on a Na2O-CaO-P2O5-SiO2 system with B2O3 and CaF2 additions, is known as Bioglass® [108,111].

In the early 1980s, apatite – wollastonite (A-W) glass-ceramic material was developed; it was based on wollastonite (CaO-SiO2), oxyfluoroapatite (Ca10(PO4)6 (O,F2) and glass (MgO 17 wt%, CaO 24 wt%, SiO2 59 wt%). This material presented higher bending strength, fracture toughness and Young’s modulus than bioactive glass and glass ceramics so that it was more suitable for bioapplications with high compression load [106].

In the last years medical implants for orthopedic, cardiac, oral, maxillofacial and plastic surgery applications grew with a subsequent increase of the biomaterials development, concerning the optimization of the structure or the control of the biomaterial chemistry in biological environment [108, 110].

Besides bioactive glasses and glass ceramics, on the basis of mineral composition of human bone, ceramic scaffolds can be produced by using calcium phosphates compounds; according to the proportions of calcium to phosphorus ions, there are hydroxyapatite (HA, Ca10(PO4)6(OH)2, with theoretical composition of 39.68 wt% Ca, 18.45 wt% P, Ca/P wt ratio of 2.15 and Ca/P molar ratio of 1.67), tricalcium phosphate (TCP, Ca3(PO4)2, with four polymorphs, including α and β forms) [108, 111]. As bone graft materials silicate – substituted hydroxyapatites has been synthesized, in order to increase the rate and the amount of the bone apposition [111].

In contact with biological fluids, calcium phosphate ceramics undergo degradation through dissolution – reprecipitation mechanism. Surface hydration of calcium phosphates and possible impurities (for example, carbonate, fluoride and chloride species) implies ionic transfers from the solid phase to the liquid phase and vice versa. This process depends on the nature and the thermodynamic stability of the calcium phosphates: for instance, TCP presents a higher solubility than HA (with degradation rate of β-TCP of 3-12 times higher than that of HA) [108, 113, 114].

In order to exploit the reactivity of β-TCP and the stability of HA, biphasic calcium phosphates (BCP) are developed; their drawback is the brittleness and the susceptibility to fractures [111, 113]

Calcium phosphates are used for spinal fusion, cranio-maxillofacial reconstruction, treatments of bone defects, fracture treatment, total joint replacement and revision surgery [111].

The choice of the material depends on the application, also considering the mechanical properties: for instance, the use of calcium phosphates materials is limited by the fragile failure undergone by high porous scaffolds [111, 113, 115].

1.3.2.3. Properties of scaffolds

An ideal scaffold would mimic the matrix of the tissue to replace acting as a three – dimensional template onto which cells attach, grow, migrate and function [116, 117]. Particularly, it:

must be made of biocompatible material (preferably bioactive or resorbable material) [117];
must present interconnected macro-porous network with pores having diameters above 100 μm so that cell penetration, tissue ingrowth and vascularisation occur [108, 110, 113, 115, 117];

must degrade at the same rate as the new tissue is created [117];

must show mechanical behaviour suitable for application [117];

must be economic and speed to be realized [113].

The mechanical properties are closely related to the porosity volume, pore geometry and connectivity, considering both macropores and micropores present in the struts, as shown in Figure 1.39 [110].

![Figure 1.39 – Porous materials features](image)

The rate and the quality of bone integration are influenced by pore size, total porosity volume, interconnection size and amount, pore geometry and struts microstructure. Besides a minimum pores size of about 100 μm, pore sizes higher than 300 μm are recommended [108, 110, 113]. Moreover, an interconnection dimension of about 50 mm is necessary for bone ingrowth [110]. The interconnectivity and the porosity volume play a key role since, before the new bone formation, the development of a vascular network is necessary for an efficient transport of oxygen and nutrients [108, 110, 111, 114, 116, 118]; their influence on scaffold efficiency is stated particularly in the case of non-resorbable materials. In the case of a porous structure having spherical pores, the size and the amount of the interconnections increase when the porosity overcomes 60 vol%; this threshold is lower in the case of resorbable materials [110]. Then, the struts microstructure, and particularly the level of microporosity, can influence the biological response of the scaffold, because of the cell attachment and/or the selective sequestering and binding of adhesion proteins [110, 118].

As a conclusion, the total porosity volume and the pore (macro and micro) size influence the mechanical behaviour of the scaffolds; for this reason, their upper limits have been often chosen on the basis of mechanical and biological responses [108, 113, 114].