

Processing of porous ceramics: Piezoelectric materials

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Abstract

The paper reviews processing techniques used to produce porous ceramics with tri-dimensionally interconnected porosity, in a wide range of pore volumes and pore size and distribution. Attention is focused on the development of porous electroceramics and especially piezoelectric PZT materials. The porosity can be introduced through dry or wet techniques. In the dry techniques, a fugitive phase is added to the perovskitic powder by mechanical mixing. Wet techniques involve the manipulation of suspensions and a better control of the final morphology and microstructure of the samples can be achieved by the colloidal approach. The whole spectrum of techniques for generation of porosity is surveyed; it includes burnout of volatile particles or thermally unstable sponge structures, generation of porosity by foaming, slip casting, tape casting, direct consolidation, solid freeform fabrication, die pressing. Porosities of up to 70% are obtained in aerogels by sol–gel processing. The pore size distribution and microstructural differences resulting from various processing parameters influence the physical properties, particularly the acoustic/piezoelectric response of PZT materials.

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1. Introduction

The interest in porous ceramics has grown rapidly in the recent years with the demands from new fields of applications; processing routes to develop unique structures are now under extensive investigation. The use of porous ceramics in thermal insulation, substrates for catalysts and filtration systems has been assessed for many years and the materials are still expanding into other areas.¹ Porous membranes are used for filtration of high temperature, high pressure gas streams to remove pollutants, or recover gases like methane from mines or hydrogen in petroleum refineries, for separation of metallic inclusions from hot metals such as cast iron, steel, aluminium. These all require improvements of membrane resistance to high temperature environments, abrasion and chemical attack. Membranes^{2,3} find application in biotechnology, food processing, pharmaceutical, petrochemical, electronics; improvement of the thermo-mechanical properties while lowering production costs is necessary for further expansion of the applications. In the biomedical field⁴ porous ceramics (hydroxyapatite) find use in bone replacement and drug delivery systems⁵; because of its

excellent biocompatibility, it enables the production of architectures similar to those of real bones, and has the potential to repair the defects through a complete penetration of the osseous tissue.

Porous ceramics are classified according to their pore size (from the order of nanometer to several millimeters) and basic pore structure (open cell structure, closed cell structure, membranes, tangle fiber network ceramics, functionally gradient pore-size distribution, etc.). Membranes⁶ are classified on the basis of their pore size into filtration membranes (pore size greater than 104 nm), micro filtration membranes (pore sizes in the range 102–104 nm) and ultra filtration membranes (pore size in the range 2–100 nm)⁷ and hyper filtration, reverse osmosis or gas separation membranes (pore sizes 1 nm or less).⁸ In the open cell structure, the pores are interconnected, while they are isolated in a continuous ceramic matrix in the closed cell structure; the former, due to their permeability to gas or liquids (depending on the pore size) are suitable for applications involving fluid transport while the latter are used in those applications, like thermal insulation, where no fluid flow is required. Open cell structures are also called reticulated ceramics when the porosity degree is very high (70–95%) with rather large voids (10 μm to 5 mm) and are usually formed by replicating a polymer sponge or by the polymer foam method⁹; they have low strength and fracture toughness because, upon burning of

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the organic matrix, very thin struts of ceramic remain that limit the mechanical properties.¹⁰ More complex structures are now developed, that combine closed and open porosity, alignment of continuous pores,^{11,12} anisotropic¹³ or functionally gradient porosity.¹⁴ Several new shaping methods convert natural templates, like coral skeletons or wood,¹⁵ into novel cellular ceramics with micro-, meso- and microstructure pseudomorphs of the initial porous tissue skeleton ranging from nanometers to millimeters. The control of pore size and morphology complexity can be achieved through the application of novel approaches to the powder processing, including direct casting methods and solid freeform fabrication.¹⁶ Electro ceramics with different porosity content and morphology are developed and the complexity of the interaction between the dominating factors like thermal and electrical conductivity, piezoelectricity, nonlinear phenomena of the grain boundaries, defects, impurities and domains means that the porosity property relationships are not completely understood.^{17,18} One of the applications of piezoelectric materials is in acoustic receiving systems. The dense PZT-type piezoceramic materials are not appropriate for hydrostatic sensing applications, due to their low hydrostatic figure of merit (FOM) (the product $d_h g_h^a$). Moreover, the stiff and dense PZT has also the disadvantage of poor acoustic coupling to water. Therefore, in the last few years, new piezoelectric porous materials with improved piezoelectric properties and good qualities for hydrophone applications, obtained by introducing soft material inhomogeneities into the perovskitic phase, have been investigated^{19,20,21} (in the case of tri-dimensionally interconnected pores they can be compared to composites with 3–3 connectivity). In porous piezoelectric materials, where the interconnected pores are filled with air, a partial decoupling between transverse and longitudinal effects avoids direct cancelation, therefore d_h increases. Moreover, due to the lower dielectric constant, g_h is further increased and consequently the hydrostatic FOM of porous piezoelectric materials can reach values a few orders of magnitude higher than in dense materials.

2. Processing

2.1. Dry methods

The simplest method to obtain porous ceramics is by partially sintering the cold compacted powders, when the thermal treatments involve only microstructure evolution and no chemical change of phase. In this way, a porous network is formed by the spaces between the necked powders; the stability of the pores is achieved by controlling the sizes of the particles. The degree of porosity is controlled by the degree of partial sintering, which, in turn, is controlled by sintering at different temperatures and/or different times, but the final body suffers from poor mechanical strength and low stability. Porous ZrO₂ ceramics²² were produced with pore volume as high as 50% by firing die pressed bodies in the temperature range 1100–1150 °C. Different com-

paction pressures and the agglomeration of the fine powder influences the flaws and voids that are reduced by using a higher compaction pressure, thus improving the mechanical properties. By sintering at 1000 °C to 1100 °C PZT samples, obtained²³ by uniaxial pressing into pellets the as-calcined powder, the sintered density was in the range 66.3–93.0%. Very small pores with a narrow size distribution were found for samples sintered at the lower temperature whilst a small number of large pores together with micro and meso porosity was found after sintering at 1100 °C.

Tri-dimensionally-interconnected porous ceramics are usually obtained by mixing appropriate amounts of a particulate organic substances with the ceramic powder followed by die pressing^{23–27}; the pore maker can be wax, polymer beads, starch or a fugitive phase material like graphite. The process involves burning off the organics. This preferentially occurs at the surface region during the early stages of pyrolysis and is greatly accelerated by the developing porosity,²⁸ as the cavities formed by the burning of the organics during sintering act as sites for pore generation, leading to an increase in the porosity. Pore fraction, size, morphology and distribution are controlled by the amount of the added volatile phase. Homogenization of the organics with the ceramic powders by dry mixing may be a critical step as the difference in the density is high and the ceramic powders may be agglomerated. Kim et al.²⁵ added various amounts of corn starch to (Ba, Sr) TiO₃ powder and obtained 21–44% pore volume; the PTCR effect for the ceramic was 1–2 orders of magnitude higher than that of samples without corn starch. Porous Al₂O₃ ceramics with high surface area were fabricated²⁹ by adding Al(OH)₃ to the Al₂O₃ starting powder followed by sintering at a temperature higher than 1100 °C. The decomposition of Al(OH)₃ produces 60% volume contraction and material with pore volume as high as 60% and a bimodal size distribution was obtained; the material still retaining superior mechanical properties. This is method specific for the production of alumina as the pore structure is derived from the decomposition of the precursor hydroxide and the phase transformation from θ - to α -Al₂O₃. Similarly, other specific porous structures can be designed when intermediate products undergo significant volume change.

2.2. Wet methods

2.2.1. Colloidal processing

Most of the cold consolidation procedures to fabricate porous ceramics are based on the colloidal processing approach that allows the development of designed, ordered mixtures of several components through the manipulation of interparticle forces. It involves the preparation of a suspension where the ceramic powder is dispersed in a liquid or a polymer precursor, a dispersant and other organic additives like binders, plasticizers, pore-forming or foaming agents, precursors of secondary phases, so as to enhance homogenization and stability during time, and tailor the rheological properties to the adopted shaping technique. Most of the novel approaches¹⁶ developed to optimise powder processing can be applied to the production of porous materials. They enable the design of microstructure in advanced ceramics, characterized by high reliability, sufficient strength, near net

^a The piezoelectric charge constant d_h is given by: $d_h = g_h / \epsilon_{33} \epsilon_0$. The piezoelectric charge constant d_{31} ($=d_{32}$) is given by: $d_{31} = (d_{33} - d_H) / 2$.

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