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Porous polymer derived ceramics

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ABSTRACT

Porous ceramics, in particular cellular ceramics with open and closed porosity, are key enabling components in different demanding applications because of their favorable set of properties. The production of porous ceramics from preceramic polymers offers advantages in terms of simple processing methodology, low processing cost, and ease of control over porosity and other properties arising from the composition of the resultant ceramics. Therefore, a vast amount of research has been conducted, in the past decade, towards the fabrication and characterization of porous ceramics produced from different polymeric precursors, such as polysiloxane, polycarbosilane, polysilazane and borazine. The potential of polymer-derived-ceramics can only be fully achieved if the type of fabrication method used is tailored taking into account the specific application of interest. For brevity, this review deals specifically with the different processing strategies employed to obtain, from polymer precursors, ceramic foams, membranes, aerogels or porous ceramics for which porosity higher than 50 vol% has been deliberately introduced, including also components with high specific surface area or hierarchical porosity. The different processing strategies, such as replica, sacrificial template, direct foaming, etching, aerogel forming, fiber spinning and automated manufacturing, are explained and the published literature has been reviewed with particular concern for the critical issues that affect the pore size, the amount of porosity and strength of the ceramic components.

Contents

Abbreviations: ADA, azodicarbonamide; AHPCS, allylhydrido polycarbosilane; AM, automated manufacturing; APTE, 3-aminopropyltriethoxysilane; ATES, amyltriethoxysilane; BCN, boron carbon nitride; BN, boron nitride; BTEE, (bistriethoxysilyl)ethane; BTEM, (bistriethoxysilyl)methane; CDC, carbide derived carbon; CVI, chemical vapor infiltration; DDS, dimethyldicholorosilane; DVB, divinylbenzene; EB, electron beam; EPD, electrophoretic depositions; GPTMS, propyltrimethoxysilane; MCF, mesocellular siliceous foam; MCM, mesoporous silica; MTES, methyltriethoxysilane; MTMS, methyltrimethoxysilane; NaCMC, sodium carboxymethylcellulose; NiAc, nickel acetate; NWs, nanowires; OM, ordered mesoporous; PAA, polyacrylic acid; PAN, poly[B-(methylamino)borazine]; PB, polyborazylene; PCS, polycarbosilane; PDCs, polymer derived ceramics; PDMS, poly(dimethyl-siloxane); PE, polyethylene; PEIA, poly(ethyliminoalane); PEO, methylpropylethylene oxide siloxane; PEOc, poly(ether-co-octene); PHMS, poly(hydridomethylsiloxane); PHPS, poly(perhydropolysilazane); PMAB, polyacrylonitrile; PMMA, poly-methlymethacrylate; PMPHS, poly-methylphenylhydrogen-silsesquioxane; PMPS, poly(methyl-phenyl-siloxane); PMS, polymethylsiloxane; PMVS, poly(methylvinyl)silazane; POBSZ, polyorganoborosilazane; PP, preceramic polymer; PS, polystyrene; PSA, polysilane; PSD, pore size distribution; PSX, polysiloxane; PSZ, polysilazane; PTMS, phenyltrimethoxysilane; PTFE, polytetrafluoroethylene; PU, polyurethane; PVSZ, polyvinylsilazane; RT, room temperature; SBA, mesoporous silica; SEM, scanning electron microscope; SiBOC, silicon boronoxycarbide; SiBCN, silicon boroncarbonitride; SiC, silicon carbide; SiCN, silicon carbonitride; Si(HIPE), silicon high internal phase emulsions; SiOC, silicon oxycarbide; SiOCN, silicon oxycarbonitride; SiTiOC, silicon titaniumoxycarbide; SSA, specific surface area; TBA, tetra butyl alcohol; TBOT, titanium orthotitanate; TES, triethoxysilane; TEOS, tetraethylorthosilicate; THF, tetrahydrofluorane; TVTMS, tetravinyltetramethylcyclotetrasiloxane; VTES, vyniltriethoxysilane; μ-CT, micro computed tomography.

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1. Introduction

Porous ceramics have been found to be key enabling components in various engineering applications, and this has resulted in extensive research into new processing routes that would enable to produce parts with an ever increasing range of morphologies and characteristics. Indeed, well controlled and diversified processing strategies are the key to the production of highly porous ceramic components that could be used in a wide range of applications, and therefore there is still the need for innovation in this area. Unique properties such as low density, high permeability, high thermal shock resistance, high chemical stability make porous ceramics of use in applications such as filtration (e.g. diesel particulate, molten metal and hot gas filtration), absorption, membrane supports (e.g. for hydrogen separation), separation membranes, light weight structural materials, porous bioimplants, sensors, etc. [1–8].

The potential application of porous ceramics is not only governed by the chemical composition of the porous scaffold material but also by the porosity characteristics, such as pore size distribution (PSD), tortuosity, specific surface area (SSA), closed/open (3D interconnectivity), aligned or graded porosity, etc., which all are determined by the selected manufacturing process. For example, while high surface area (provided by micro- (<2 nm) and meso- (2–50 nm) pores) gives the functionality to the component, macroporosity (50 nm to several mm) improves heat and mass transfer. Aligned porosity provides anisotropic properties, which can be advantageous when maximum axial permeability is desired. Graded porosity can be beneficial when a porous surface is intended to be coupled with another material, as for instance in the case of the integration of bio-implants with tissues [9]. Therefore, the combination of different pore morphologies and sizes in a single framework significantly extends the range of applications that can be pursued using porous ceramics.

Comprehensive reviews [3,10,11] and books [12,13] have been published on the topic of highly porous ceramics. However, in those publications the fabrication and characteristics of porous ceramics obtained from preceramic polymers (PPs) has not been covered in detail, or the focus was just given to specific polymer types [14]. Therefore, this review article will focus on the production of porous ceramics from the entire range of preceramic polymers available.

PPs can be converted into ceramics through a controlled heat treatment. In polymer derived ceramics (PDCs), the polymer is first shaped, followed by crosslinking or gelling, and finally converted into a ceramic component through pyrolysis at suitable temperatures (generally >800 °C). The elimination of organic moieties occurring during pyrolysis, by breaking of C-H bonds with release of H_2, CH_4 or other volatile compounds, results in the formation of an inorganic material. The ceramic material forms through a complex microstructural evolution, which depends on the thermal history and final heating temperature, leading to nano-sized crystalline phases embedded in an amorphous matrix containing a free-carbon phase [15].

The early, pioneering work conducted on polycarbosilane (PCS) prompted the synthesis and commercialization of several Si- or B-based polymeric precursors, such as polysiloxane (PSX), polysilazane (PSZ), PCS, polyborazylene (PB), etc. which allow to obtain a wide range of ceramic materials of different composition, such as silicon-oxycarbide (SiOC), silicon-oxycarbonitride (SiOCN), silicon-carbonitride (SiCN), silicon-boroncarbonitride (SiBCN), silicon-carbide (SiC), silicon nitride (Si_3N_4), boron nitride (BN), etc. [16,17]. Some of these ceramic materials possess advantageous characteristics, for instance in terms of oxidation resistance, refractoriness, low creep rate, chemical durability or functional properties (e.g. piezoresistivity), and cannot be produced by conventional ceramic powder-based processes. Moreover, the possibility of introducing nano- and micro-sized fillers widens the available compositions and properties of the resulting ceramic products [18,19].

The fabrication of porous ceramics using polymeric precursors offers various advantages over conventional sintering of ceramic powders. Such advantages include: (i) lower temperatures needed for the polymer to ceramic conversion [17,20–22]; (ii) shaping of polymer precursors can be performed using low-cost plastic-forming techniques, such as injection molding, extrusion, melt spinning, blowing, 3-D printing, etc. [2,4,23]; (iii) utilization of unique polymeric properties, such as plasticity, in situ gas evolution, CO_2 solubility, and solubility of PPs into organic solvents