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Engineering porosity in polymer-derived ceramics

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Abstract

By employing carefully controlled processing methods, a large amount of porosity (>70 vol%) was introduced in ceramic materials derived from preceramic polymers (silicone resins) after pyrolysis at 1000–1200 °C in inert atmosphere. The resulting components have a bulk density ranging from ~250 to 950 kg/m^3. Three main fabrication methods have here been employed: (1) direct foaming of a solution of a thermosetting silicone resin in a suitable solvent (with or without the addition of polyurethane precursors), acting also as a blowing agent; (2) the use of sacrificial fillers that decompose during pyrolysis, consisting in polymeric microbeads; (3) the mixing of preceramic polymers possessing different characteristics, in particular ceramic yield, depending on their molecular structure. In addition to that, several methods for developing micro- or meso-pores within the resulting SiOC macro-porous ceramics were explored, with the aim of fabricating components with hierarchical porosity. These include a controlled thermal treatment, the addition of fillers with a high specific surface area (SSA), the deposition of zeolites or meso-porous silica coatings, the infiltration with aerogels, selective etching of the SiOC material and the in situ formation of C-based nanostructures. Depending on the fabrication procedure adopted, cells with an average size ranging from the micrometer to the millimeter were obtained. All these processes are simple, economical and versatile, and large bodies with various shapes (tubes, plates, blocks) can be produced, possessing a wide range of morphologies and properties. Compression strength, flexural strength and Young's modulus vary with the morphology and density of the porous components. It is also possible to add to the preceramic polymers some filler powders, for instance possessing electrical conductivity or magnetic properties, leading to the production of functional cellular ceramics.

Keywords: Shaping; Precursors-organic; Porosity; Functional applications; Foaming

1. Introduction

Highly porous ceramics (foams, honeycombs, fibers mats, etc.) find numerous applications in various engineering fields, including filtration (molten metals, particulate from diesel exhaust gases), radiant burners, catalyst supports, biomedical devices, kiln furniture, reinforcement for metal matrix composites, bioreactors, thermal protection systems, supports for space mirrors, components in solid oxide fuel cells, lightweight sandwich structures, heat exchangers (graphite foams), etc.[1] Different manufacturing processes for cellular ceramics have been proposed, including replica of a polyurethane foam, direct blowing of a ceramic suspension, the use of sacrificial fillers, extrusion or the bonding of fibers.[2]

In this paper, the main results concerning the fabrication of highly porous ceramics (mainly ceramic foams) from preceramic polymers will be discussed. Preceramic polymers, are organic–inorganic polymers whose backbone contains usually Si atoms, which give a ceramic residue through the elimination of organic moieties (by breaking of C–H bonds, and release of H_2 and CH_4 and other volatile compounds).[3] The polymer-to-ceramic conversion is achieved either thermally (pyrolysis, via conventional oven annealing, microwave or laser heating) or non-thermally (for instance by irradiation with ions), usually by processing in inert atmosphere. Nanostructured polymer-derived ceramics (PDC) in the systems Si–O–C, Si–N–C, Si–C, Si–E–N–C (with E = B, Al, Ti, etc.) can be thus produced[4]; the introduction of suitable fillers allows also to obtain engineering ceramics such as cordierite,[5] mullite[6] or SiAlON.[7] The production of ceramic materials from preceramic polymers offers unique opportunities, especially from a processing point of view. In fact, using preceramic polymers, it is possible to apply conventional plastic forming technologies (injection molding, extrusion, resin transfer molding, melt spinning, etc.), gener-

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ally with low processing costs, to the fabrication of ceramic products.

The first suggestion that porous ceramics could be produced from preceramic polymers can be found in the patent literature – by direct blowing[8–10] or by solvent extraction from a phase-separated polysilane gel[11] – albeit very limited processing information or data are reported. Several papers have been since then published in the scientific literature by the present author and various collaborators, detailing a range of processing procedures, reporting extensive characterization of the products and describing their testing for diverse applications.[12–33] Alternative processing methods for the production of open or closed cell (macro-)porous ceramics have also been proposed by different researchers as well. These include the infiltration of a porous salt preform using a molten preceramic polymer,[34] coating of a polyurethane foam with a preceramic polymer,[35,36] evaporation of silane oligomers,[37] decomposition of a siloxane polymer during pyrolysis,[38] self-foaming by in situ evaporation of volatile condensation products generated during silicone crosslinking reactions,[39] foaming of a molten silicone by thermal decomposition of a solid blowing agent,[40] the dissolution of CO_2 gas into a preceramic polymer under pressure followed by introducing of a thermodynamical instability,[40–44] the use of expandable sacrificial polymeric microspheres,[5,45–47] the use of already expanded sacrificial polymeric microspheres,[48–50] the infiltration and pyrolysis of organic porous templates (wood structures),[51] the dissolution of colloidal silica sub-micron spheres,[52,53] or freeze-drying using camphene.[54]

Moreover, several papers have been published dealing with the use of preceramic polymers to fabricate porous membranes (see for instance[55] and references therein), with pores sizes in the micro- and meso-range, and very recently the preparation of meso-porous ceramics via self-assembly of a preceramic polymer,[56] or via infiltration into meso-porous templates,[57,58] or via synthesis of an inorganic–organic diblock copolymer[59] has been reported.

All these proposed processing methods allow to produce ceramics with engineered porosity affording varied and tailored characteristics, which are of interest for a wide range of applications.

2. Experimental details

A silicone resin (SR) preceramic polymer (polymethylsiloxane (MK, Wacker-Chemie GmbH, Munchen, Germany) was used to form a Si–O–C amorphous ceramic material upon heat treatment at temperatures >800 °C in an amorphous atmosphere. Three different typologies of porous ceramics were produced: (a) macro-cellular ceramic foams; (b) micro-cellular ceramic foams; (c) high porosity ceramic components. Different processing procedures were followed to obtain the samples with different morphology (see Fig. 1).

Samples (a) were obtained by dissolving the silicone SR into a suitable solvent with a low boiling point (pentane, freon, etc.) and adding a surfactant (and a catalyst – zirconium acetylacetonate – if necessary). If desired, fillers (ceramic or metal powders, ceramic fibers, etc.) can also be added at this stage to tailor the composition and properties of the resulting porous ceramic material. Additionally, polyurethane precursors (PU) can also be added (up to 50 wt%) in order to use their expansion capability to better control the morphology of the foam (production of open cells or of closed cells). Expansion was achieved by high speed mixing (introduction of bubbles in the solution) and heat treatment at 25–40 °C. Samples (b) were obtained by dry mixing the SR powder with a sacrificial template constituted by PMMA microbeads of different size. Fillers and if necessary a crosslinking catalyst for the SR can also be added at this stage. After uniaxial pressing (cold or warm—$T < 180$ °C), the PMMA beads were eliminated by heat treatment in air at

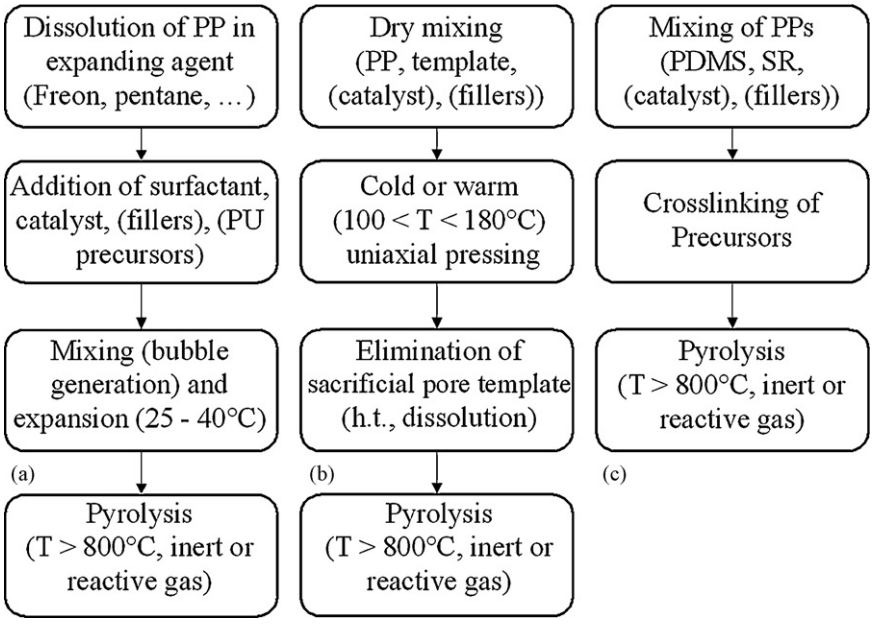

Fig. 1. Processing procedures for the fabrication of porous ceramic components from preceramic polymers.