

Feature article

Multifunctional advanced ceramics from preceramic polymers and nano-sized active fillers

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Abstract

In this paper, the introduction of nano-sized active fillers into preceramic polymers for the realization of multifunctional ceramic components is discussed. Several silicate and oxynitride systems have been produced, by heat treatment in air or nitrogen, greatly widening the compositional range of ceramics made from preceramic polymers. Phase pure ceramics were obtained with very favorable reaction kinetics, and therefore at low temperature and for short heating times. Shaping of the components was carried out using several plastic forming technologies, such as warm pressing, extrusion, injection molding, foaming, machining, fused deposition and 3D printing. Some significant examples of this new methodology are described, ranging from relatively simple oxide systems (mullite, zircon, cordierite, fosterite, yttrium-silicates) to more complex oxynitride ceramics (SiAlONs, YSiONs). Some results concerning the potential application of these components, ranging from structural or thermo-structural functions (bulk components and environmental barrier coatings) to more functional purposes (bioactive ceramics and inorganic phosphors), are also reported.

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1. Introduction

Preceramic polymers have been successfully used for almost 40 years to fabricate advanced polymer-derived-ceramic components (PDCs) with some distinctive advantages over conventional (powder) synthesis procedures, such as the production of ceramics with a composition (e.g. in the ternary SiCO and SiCN systems) not obtainable from other non molecular processing routes, the fabrication of components using plastic-forming techniques (e.g. the spinning of fibers), the occurrence in the ceramic material of specific functional properties (e.g. piezo-resistivity), deriving directly from the microstructure at the nano-scale, based on the presence of distinct nano-domains (i.e. C, SiC, SiO₂, Si₃N₄).^{1,2}

An unavoidable feature of the polymer-to-ceramic transformation, that is of the heat treatment that leads, in the temperature

range of ~600–800 °C, to the elimination of the organic moieties typical of a polymer (e.g. –CH₃, –C₆H₅, ...) leaving a fully ceramic residue, is that this conversion occurs with gas release (in the form of methane, benzene and hydrogen) and a large shrinkage (due to the change in density from that of a polymer – ~0.8–1.2 g/cm³ – to that of an amorphous silicon-based ceramic – ~2.2 g/cm³).^{1,3} This, in turn, results in the formation of unwanted/uncontrolled porosity and cracks which prevent the direct conversion of a component of large size in the preceramic state to a dense ceramic part.^{3,4} Only when the dimension of the component is small (as in fibers), and therefore the diffusion path for the generated gases is limited, or when a preferential route for the elimination of the decomposition gases is present (as in bodies with a high amount of interconnected porosity, e.g. foams) it is possible to produce defect-free (dense) ceramic components.⁵

Early on, it was recognized that the addition of suitable filler materials to a preceramic polymer could lead to bulk components retaining their integrity after pyrolysis. The pioneering work of Greil^{3–10} demonstrated in particular that two types of fillers could be used for this purpose: (1) so-called “inert”, or passive, fillers, which are ceramic powders that do not react with

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the ceramic residue from the preceramic polymer, the decomposition gases or the heating atmosphere¹¹ and (2) so-called “active” fillers, which are metallic or intermetallic powders which react, during pyrolysis, with the decomposition gases generated during heating, or the heating atmosphere or (more rarely) with the ceramic residue from the preceramic polymer.^{3,12} The main difference between these two types of fillers, from the point of view of the shape retention of the component during firing, is that inert fillers simply dilute the preceramic polymer, therefore decreasing the amount of gas generated and the associated shrinkage, reducing the likelihood of forming macroscopic cracks during processing. On the other hand, active fillers, because of their ability to react, form carbides or nitrides or silicide phases which develop with a concurrent significant volume increase (due to the change in density from that of a metal to that of a ceramic material). This volume increase counteracts the shrinkage, the presence of solid particles reduces the amount of gas generated and the in situ reaction with the filler reduces the local gas pressure in the part, therefore enabling the fabrication of near-net shape, bulk, uncracked ceramic components.³ Some residual porosity (~5–15 vol.%) is typically retained in the pyrolyzed parts, but their typically good mechanical properties, associated with the near-net shaping capabilities, make these components suitable for a variety of applications.⁴ In these papers, the amount of fillers introduced varies from a few percent to several tens of a percent, but the amount of preceramic polymer present is always sufficiently high to enable the use of plastic forming technologies (e.g. warm pressing, extrusion, injection molding or resin transfer molding). The dimension of the fillers is always in the (several) micron range, as metallic particles of smaller size are difficult to handle for safety reasons (pyrophoricity). It should be mentioned that, in a separate and partly related development, preceramic polymers can also be used as (reactive), low loss binders for metal¹³ or ceramic particles,^{14–18} providing the intergranular phase after high temperature processing.

Besides using inert or active fillers for their merely volumetric/geometrical effect, they can be added also to modify the composition of the produced ceramic material, therefore introducing another level of functional design into the process. For instance, the use of tungsten, niobium or molybdenum particles leads to the formation of carbide inclusions affording high hardness to the component,^{19–21} iron alloy particles are suited to produce wear resisting linear bearings by injection molding,²² the introduction of iron silicide powders enables the fabrication of ceramics possessing magnetic properties²³ while that of MoSi₂ powders gives electrically conductive ceramics.^{24,25}

Most processing has been conducted in inert atmosphere, to produce carbide or nitride phases thereby taking full advantage of the filler volume change, and oxide particles have been rarely used as fillers. Metal oxide particles, such as Cu₂O, were used to form metallic Cu clusters (by reduction because of reaction with the carbon species developing from the preceramic polymer during pyrolysis in inert atmosphere) affording electrical conductivity.²⁶ Corundum (or Al alloy) particles were added to a siloxane to produce mullite after firing in air, but phase pure components could be obtained only after heating at very high temperatures.^{27,28}

Recently, we conducted a series of experiments with the aim of producing oxygen-containing advanced engineering ceramics from preceramic polymers and nano-sized oxide fillers.^{29–37} The oxide fillers react with the decomposition products of the preceramic polymer (pure silica, when processing in air) producing the desired new phases, and their small dimension allows for very favorable reaction kinetics with the formation, in selected conditions, of phase pure ceramics at low temperature.^{29,30} This can therefore be considered a novel direction for filler-containing preceramic polymer components, in which the fillers react to give a single phase ceramic material at the same time enabling the production of crack-free bulk components, while retaining (at least to a certain extent) the processability characteristics of preceramic polymers. In comparison to the sol–gel method, which has similarly favorable reaction kinetics and also allows for the fabrication of phase pure ceramics,³⁸ this approach does not require a strict control of the synthesis conditions (e.g. amount of water and catalyst in solution, reaction rate of the different precursors), does not need, in principle, the use of flammable solvents or precursors, and enables the use of plastic-forming technologies (extrusion, injection molding, spinning, fused deposition, foaming, printing, . . .) for the shaping of the component. An alternative to the use of nano-sized fillers, is the chemical modification of preceramic polymers using alkoxides, which has been explored recently by Ionescu et al.^{39,40} In this case, the added alkoxide provides a well dispersed oxide phase capable of reacting with the polysiloxane matrix, which retains the possibility of plastic forming. However, it is still to be demonstrated that this important feature can be retained in the material when the added alkoxide exceeds a certain amount, as it would be necessary for producing ceramics in which Si is not the main element in the composition. A very recent paper⁴¹ reported on the addition of nano-sized metal particles (Al) to a silicone resin, followed by heat treatment in inert atmosphere. However, the amount of filler introduced was too limited to give phase-pure mullite and the results indicate that at temperatures as high as 1300 °C, some residual alpha-alumina and Si crystals were present. For the sake of completeness, we should also mention that a few papers have been published dealing with the production of ceramics from preceramic polymers containing unreactive nano-sized fillers, such as carbon nanotubes,^{42–44} carbon nanofibers⁴⁵ or graphene (via graphite oxide).⁴⁶ These findings are not discussed in this paper, which summarizes the main past research in the field of preceramic polymers plus (reactive) nano-sized fillers, and introduces new results which demonstrate how, with this approach, it is possible to further widen the applicability of the preceramic polymer technology to develop different ceramic systems (oxides and oxynitrides) and different components of engineering interest.

2. Processing and characterization

Various commercially available preceramic polymers with different characteristics in terms of composition (oxygen, nitrogen and carbon content), rheological characteristics (liquid/solid, glass transition temperature) and ceramic yield (>70 wt%) were used. The selection of the type of preceramic

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