Chapter 51
Polymer-Derived Ceramics (PDCs): Materials Design towards Applications at Ultrahigh-Temperatures and in Extreme Environments

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ABSTRACT
Polymer-derived ceramics (PDCs) represent a rather novel class of ceramics which can be synthesized via cross-linking and pyrolysis of suitable polymeric precursors. In the last decades, PDCs have been attaining increased attention due to their outstanding ultrahigh-temperature properties, such as stability with respect to decomposition and crystallization processes as well as resistance in oxidative and corrosive environments. Moreover, their creep resistance is excellent at temperatures far beyond 1000 °C. The properties of PDCs were shown to be strongly related to their microstructure (network topology) and phase composition, which are determined by the chemistry and molecular structure of the polymeric precursor used and by the conditions of the polymer-to-ceramic transformation.

Within this chapter, synthesis approaches, the nano/microstructure, as well as the behavior of PDCs at ultrahigh temperatures and in harsh environments will be presented. The emphasis of the highlighted and discussed results will focus on the intimate relationship between the precursors (molecular structure/architecture) and the resulting PDCs (phase composition, nano/microstructure, and UHT properties).

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SYNTHESIS APPROACHES FOR PDCs

Polymer derived ceramics (PDCs) are defined as intrinsically complex nanostructured materials produced by the controlled pyrolysis of polymers in an inert or reactive atmosphere; their synthesis cannot be achieved by any other techniques (Riedel, 2006; Colombo, 2010a; Colombo, 2010b; Mera, 2012a; Ionescu, 2012b; Riedel, 2010a). Thus, ternary and quaternary ceramics such as SiOC, SiCN, SiMOC and SiMCN, (M = B, Al, Hf, Zr, Ti, etc.) become accessible only by this simple and inexpensive additive-free polymer-to-ceramic route. Due to their excellent properties such as resistance to crystallization and creep up to very high temperatures, corrosion resistance, high oxidation and thermal shock resistance, low thermal conductivity, semiconduction, photoluminescence, piezoresistivity, piezoelectricity, and Li-storage capability, PDCs won a lot of attention in the last years in the field of materials science, chemistry and engineering science. (Colombo, 2010a; Colombo, 2010b; Mera, 2012a; Saha, 2006; Widgeon, 2012a; Widgeon, 2010) These investigations help to clarify their extraordinary high resistance against crystallization and decomposition up to extreme temperatures.

Due to the low solubility of carbon in silica or silicon nitride, the synthesis of ternary ceramics such as SiOC or SiCN is possible only from suitable precursors (organosilicon preceramic polymers). Thus, ceramic materials synthesized upon pyrolysis of preceramic polymers in inert gas atmosphere are capable to incorporate relatively large amounts of free carbon in their structure. (Blum, 2005; Gregori, 2006; Kleebe, 2006; Kleebe, 2008; Mera, 2009) Depending on the carbon content, PDCs can have diverse structural and functional properties such as electrical conductivity, porosity, high specific surface area, piezoresistivity, Li-storage capability, optical properties, etc. (Graczyk-Zajac, 2010; Kaspar, 2010; Prasad, 2012; Reinold, 2012; Riedel, 2010b; Terauds, 2010; Zhang, 2008). Moreover, carbon-rich PDCs were shown to have a higher resistance against crystallization and a higher ceramic yield than their low-carbon containing analogues (Blum, 2005; Mera, 2009).

In order to be suitable for the synthesis of ceramics, the precursors should have a high molecular weight in order to avoid volatilization of low molecular components, appropriate rheological properties and solubility for the shaping process as well as latent reactivity (presence of functional groups) for the curing and cross-linking step.