

Chapter 51

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

Emanuel Ionescu

Technische Universität Darmstadt, Institut für Materialwissenschaft, Germany

Gabriela Mera

Technische Universität Darmstadt, Institut für Materialwissenschaft, Germany

Ralf Riedel

Technische Universität Darmstadt, Institut für Materialwissenschaft, Germany

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) The possibility to shape these ceramics into components by using standard forming methods known from the plastic industry facilitates the application of PDCs in several fields of interest.

One of the most important characteristics of PDCs is the possibility to design new ceramic materials by changing the chemistry of the precursors. (Colombo, 2010a; Mera, 2010a; Riedel, 2006) The solid state structure of PDCs is predominately influenced by the molecular structure of the polymer precursors, their composition and chemical bonding. Moreover, parameters such as temperature of pyrolysis, heating rate, dwelling time, gas atmosphere used for decomposition are also playing a critical role on the final ceramic structure. Any changes of these parameters can be used for the tuning of the nanostructure and properties of PDCs.

The presence of nanodomains of 1-3 nm in size in amorphous PDCs was reported eight years

ago (Saha, 2005). PDCs are X-ray amorphous up to temperatures far beyond 1000 °C. However, they are heterogeneous materials with complex microstructures, as revealed by means of SAXS and solid-state NMR techniques. Recently, studies concerning the nature, size and shape of nanodomains in SiCN- and SiOC-based PDCs were reported and discussed in correlation with the molecular structure of the preceramic polymers and the temperature of pyrolysis. (Mera, 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.

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