



1 INTRODUCTION, MOTIVATION AND OBJECTIVES

A great step in the technological development of civilizations was the combination of different materials to obtain the desired final properties. In this context, the development of coatings stands out, as they can modify substrates to change appearance, functionality and/or increase resistance against the environmental conditions. Due to their intrinsic properties, polymeric, metallic and ceramic coatings are suitable for different applications. However, not only the properties, but also the processing plays an important role in the choice of the coating materials. As a consequence, even though a given material may offer the best properties for the intended application, the processing of this material as a coating may be too difficult and expensive, or even impossible. Indeed, in more extreme conditions, like harsh environments and high temperature applications, the hall of materials with sufficient resistance is limited, and ceramic coatings are often the only suitable option. Contradictorily, the same properties – like high hardness and stability up to very high temperatures – make the processing of these coatings a great technological challenge, requiring generally expensive and/or time-consuming processes.

Another characteristic of the processing of ceramic coatings, which increase the difficulty of the processing, are the synergistic effects resulting from interactions between coating, substrate and environment. These effects become even more relevant when coatings are deposited onto non-ceramic substrates. Good examples of such systems are thermal barrier coatings (TBCs) [PaGJ2002]. These coatings provide the surface of metallic substrates – in general, with lower temperature resistance – properties of refractory ceramics. Due to the low thermal conductivity of these coatings, the temperature of the substrate is reduced, enabling the expansion of application limits of the metal and extension of the lifespan of metallic parts.

The predecessors of TBCs were enamel coatings developed for military engines in the 1950s. However, it was only two decades later that TBCs were successfully applied in gas turbine to protect parts against damages caused by the high temperatures [Mill1997]. This was an important technological improvement for aerospace and energy industries, as an enhanced temperature resistance of the parts enabled operation of turbines with higher inlet temperatures, resulting in a significant increase of turbine efficiency. Since then, application of TBCs has expanded significantly [KuKa2016]. In military and aerospace sectors, TBCs have also been used on wings and nose of rockets and missiles, in order to protect these parts against heat generated by dislocation at extreme velocities, and at the inside of combustion chambers. The automotive industry has been applying TBCs for two main reasons. The first relates to the performance of engines, where TBCs protect the combustion chambers and piston tops, enabling higher



combustion temperatures without damages to the engine. Higher combustion temperatures are associated with higher efficiency and reduction of emissions. The second application relates to the protection of parts surrounding hot components. In this case, TBCs deposited on the exterior side of hot components reduce heat transfer to the environment, protecting less temperature-resistant parts in the surroundings from excessive heat.

In aerospace, energy and military sectors, priority is to obtain effective, reliable and durable coatings, whereas processing cost is a secondary aspect. For automotive applications, however, processing cost is decisive and limits the range of application of TBCs. Hence, although very effective, the use of TBCs by the automotive industry is still limited to isolated branches, like racing and military vehicles, and to high-end segments.

A third possible automotive application aims the increase of efficiency of exhaust systems by depositing TBCs on the inside of exhaust pipes. The advent of internal combustion engines brought with it great concerns about air pollution, especially from the 1950s, when photochemical smog and acid rain have become frequent occurrences in large cities. Several technologies have been implemented – e.g. three-way catalytic converters – and automotive emissions reduced drastically since then. Nevertheless, legislations worldwide have been frequently reducing emission limits further, forcing the automotive industry to continuously search for ways to reduce these emissions. Catalytic converters are currently able to convert sufficiently gaseous pollutants during normal operation, in order to fulfill legislation requirements. However, the conversion rate in a catalytic converter is dependent on temperature. Hence, when the system is cold, catalytic converters are not able to convert gaseous pollutants sufficiently. Indeed, the so-called cold start behavior is responsible for the majority of automotive emissions [Reif2015]. The low thermal conductivity of a thermal barrier coating applied on the inside of pipes preceding the catalytic converter would reduce heat loss from the exhaust gas to the metallic pipes during the first seconds of operation. Thus, combustion gases would reach the catalytic converter with higher temperature and sufficient conversion rates would be achieved faster.

Together with high processing cost, feasibility of coating deposition onto the inside of pipes is a limiting factor, especially in the case of long pipes with small inner diameter. The APS method requires a plasma gun with much bigger dimensions than typical exhaust pipe diameters. EB-PVD, on the other hand, is a deposition technique in gas phase. Hence, only exposed surfaces can be coated homogeneously, which is not the case of the inside of pipes.



In this context, the development of a thermal barrier coating by polymer-derived ceramic (PDC) technique is proposed. The PDC route enables deposition of silicon-based polymeric coatings in liquid phase by simple lacquer techniques. After deposition, a thermal treatment induces cross-linking and transformation of preceramic polymers into ceramic materials [CMRS2010]. This strategy enables a simple and relatively cost-effective processing, and offers improved flexibility regarding substrate's geometry, which could open doors not only of the automotive industry, but also from other segments, to the use of TBCs in large scale.

To obtain a coating system with high thickness, strong adhesion, low thermal conductivity and high thermomechanical stability is the greatest challenge of this development, since most PDC-based coatings on metallic substrates are limited to a few microns in thickness and/or to application temperatures up to ~ 800 °C. The coatings developed in this work should have a thermal conductivity comparable to conventional TBCs, sufficient thermal stability for application in exhaust systems, and a large thickness obtained by a single deposition step to reduce processing time. The thermal conductivity must remain low up to temperatures sufficient for the catalytic converter to achieve full conversion of the pollutants, i.e. about 500 °C [YuKi2013, Reif2015]. Furthermore, to enable application in exhaust systems, deposition on the inside of exhaust pipes must be feasible.

In automotive exhaust systems, maximum temperatures of ~ 950 °C may occur. Thus, the developed coatings must be able to withstand such conditions. However, exhaust systems of conventional vehicles reach temperatures above 900 °C only sporadically and for a few seconds at a time. In fact, exhaust system developers consider average temperatures of 700-750 °C as typical for exhaust pipes located between manifold and catalytic converter. Thus, although the coating system must be able to withstand temperatures as high as 950 °C for short periods, they must resist long-term exposure to temperatures of at least 750 °C. Moreover, severe temperature variations occur in exhaust systems, especially during winter or rainy days, due to water splashes. Hence, the coatings must also withstand thermal shock of at least 700-800 °C, corresponding to the immediate cooling from normal operation conditions to negative ambient temperatures.



2 BACKGROUND AND LITERATURE OVERVIEW

This chapter presents a background for the development of thermal barrier coatings by PDC-processing with focus on application in automotive exhaust systems. The following sections offer an overview about PDC technology with emphasis on coatings, on conventional processing and properties of thermal barrier coatings, as well as on exhaust systems and automotive emissions.

2.1 General aspects of polymer-derived ceramics (PDCs)

The polymer-derived ceramic route is an alternative method for preparation of ceramic materials. It is based on the conversion of suitable molecular precursors, generally called preceramic polymers, into ceramics by a series of thermally and/or chemically-induced processes. The resulting ceramics may be binary materials like Si_3N_4 , SiC, BN, and AlN; ternary such as SiCN, SiCO, and BCN; or even quaternary like SiCNO, SiBCN, SiBCO, SiAlCN, and SiAlCO [CMRS2010]. In fact, some of these phases – e.g. SiCN – can only be synthesized homogeneously by PDC processing [PeVB1990].

In comparison to traditional methods for preparation of ceramics, like powder sintering, the PDC-route offers advantages such as lower processing temperature and time, better adjustment of properties, homogeneity in a molecular level, and chemical purity. Notwithstanding, the most interesting characteristic of this processing route is the large variety of shaping techniques, achieving in several cases near-net-shaped parts before any treatment at high temperatures. Preceramic polymers may be formed into complex and/or highly porous 3D parts [CoHe2002, Motz2006], coatings [ToBo2008b, GKDD2009] and fibers [MBCT2007, FBNK2014] through the most varied methods, including typical techniques for polymer processing.

The work of Fritz and Raabe in the 1950s [FrRa1956], reporting about conversion of polycarbosilanes into SiC-based ceramics, is considered the starting-point of the PDC technology. In the following decade, several other studies on the preparation of ceramic materials from molecular precursors were published, among which those of Ainger and Herbert [AiHe1960] and Chantrell and Popper [ChPo1964] stand out. In the beginning of the 1970s, first approaches combining the use of molecular precursors and shaping techniques were developed in Germany [Verb1973, VeWi1974, WiVM1974]. Short after, polymer-derived ceramic fibers were developed in Japan [YaHO1975, YHOO1976]. Since then, the PDC technique evolved and the number of applications increased tremendously.



Due to several advantages, interest for PDC technology grows from year to year. Hence, the PDC technique has been subject of a large number of review papers and books throughout the last decades [WyRi1984, PeVB1990, BiAl1995, Grei2000, RMHK2006, CMRS2010, CRSK2010, Bern2012, BFPS2014]. Today, progress of the technology relies mainly on synthesis of tailored preceramic polymers, on understanding and modifying parameters for polymer-to-ceramic conversion and on the use of fillers, to enable preparation of complex shapes and to improve and/or modify properties of ceramic products. Thus, these three main topics are discussed with further details in the following sections.

2.1.1 *Preceramic polymers*

The characteristics of preceramic polymers have strong influence on the properties of resulting ceramics. Therefore, an extensive variety of ceramic materials can be prepared by PDC processing only by changing or tailoring precursors. Indeed, the modification and synthesis of new preceramic polymers is a recurrent topic of research in the last decades [Seyf1995, RKDR1996, AbGu2004, ZSMK2012, FSKH2013].

To the group of preceramic polymers belong metalorganic compounds, mostly based on silicon with additional elements (e.g. B, N, C, O) in the main chain, with side groups R = hydrogen, alkyl, vinyl, aryl, etc. [Grei2000, RMHK2006], as exemplified in Fig. 2.1.1. Composition of backbone as well as of side groups attached to it will dictate which ceramics may be obtained. They will determine, especially, phase composition and distribution of elements in the ceramic products, as well as the properties of the material as a polymer and as a ceramic. Indeed, properties like chemical and thermal stability, solubility, rheological behavior and optical characteristics may be tailored simply by changing side groups. Side groups also allow adjustment of physicochemical behavior related to cross-linking reactions and to polymer-to-ceramic conversion [BiAl1995, RMHK2006, CMRS2010].

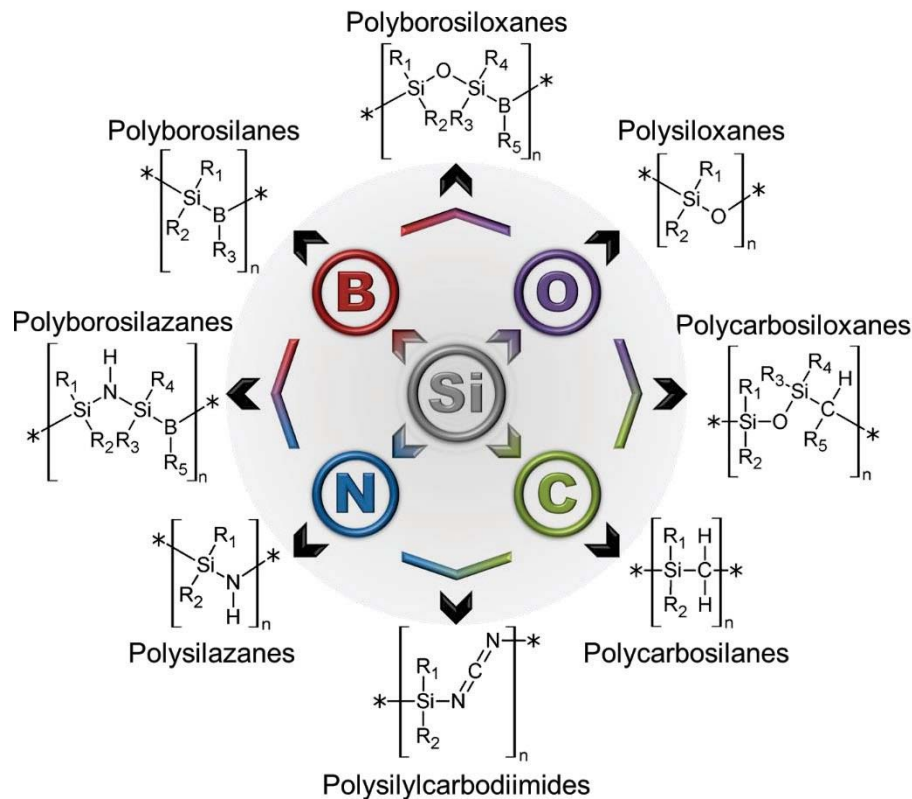


Fig. 2.1.1: Examples of basic units of usual silicon-based preceramic polymers.

Industrial production of silicon-based polymers only became possible in the 1940s after development of the Müller-Rochow process by E. G. Rochow (USA) and R. Müller (Germany) to produce organochlorosilanes. Today, a great variety of these compounds is produced from chlorosilanes, including polycarbosilanes, polysilazanes and polysiloxanes. However, in order to be suitable as precursor for PDC processing, polymers must fulfill some requirements. The first requirement is a sufficiently high molecular weight, to prevent volatilization of light compounds during thermal treatment, enhancing the ceramic yield α_{pc} (defined as the mass residue in percent after polymer-to-ceramic transition related to the initial mass of precursor) [CMRS2010]. During the last years, a great amount of novel polymers were developed, which can provide ceramic yields of 90% or more [Grei2000]. The second requirement is a latent reactivity. The presence of specific chemical groups, which upon curing and cross-linking form branched structures, ensure such reactivity, turning fusible or liquid polymers into thermoset materials. This latent reactivity is normally related to unsaturated organic groups (e.g. vinyl) or to highly reactive bonds such as Si-H or N-H [WyRi1984]. The third requirement is an appropriate and controllable rheology and/or solubility to allow shaping of the polymer for the respective application (bulk parts, fibers, coatings, porous materials, etc.). Precursors are liquid or solid, depending on their structure and molecular weight. If they are solid, they must be soluble or meltable at low temperatures, usually below 150 °C, in order to be suitable for PDC processing. Processing in liquid phase



enables application of polymer shaping methods to obtain near-net-shaped parts, reducing finishing work in comparison to powder technology [Grei1998].

The most famous materials among preceramic polymers are the silicones, which belong in the class of polyorganosiloxanes. These polymers – backbone composed of Si and O atoms, with hydrogen and organic substituents – have been studied and synthesized since beginning of the 20th century [KiL1901]. Additionally to outstanding properties in polymeric state, polyorganosiloxanes may also be used as precursors for preparation of ceramics in the system SiCO by PDC processing [BlMK2005]. Another well-known class of preceramic polymers is that of polycarbosilanes, with -Si-C- backbone. Polycarbosilanes are usual precursors for SiC-based ceramics by means of a pyrolytic process [RRBB1997]. Indeed, the precursor used by Yajima and coworkers in their breakthrough study published from 1975 [YaHO1975] about development of polymer-derived ceramic SiC fibers was a polycarbosilane.

Polymers with Si and N in the backbone – called polysilazanes – or with Si, C and N, like polycarbosilazanes and polysilylcarbodiimides are interesting precursors for PDC processing, especially to prepare SiCN-based materials [SeWi1984, DrRi1997, RGMD1997, GRSM1997, RKG1998, ZKMM1999, Motz2006, Luka2007]. In fact, the pioneering work of Verbeek and co-workers in the 1970s proposed the use of polycarbosilazanes to obtain small diameter SiCN ceramic fibers [Verb1973, VeWi1974, WiVM1974].

Other molecular precursors have been studied and used for preparation of ceramic materials by PDC processing. Among them, polysilazanes, polysilylcarbodiimides and polysilanes modified with boron or aluminum stand out and were used for preparation of SiBCN [RKDR1996, BKMW2001], SiAlCN [BWAM2004, MUKS2006] and SiAlON [SRCB1991, PBCL2014] ceramics. Furthermore, preparation of ceramics from preceramic polymers modified with transition metals has been carried out as well. Especially tailoring with late transition metals (e.g. Fe, Co, Ni, Pd, Pt, Cu, Ag and Au) is of utmost relevance due to enhanced magnetic properties and potential applications in catalytic systems [YIYO1981, BaSo1991, GSKH2010, ZaMK2011, ZSMK2012].

2.1.2 *Polymer-to-ceramic conversion*

Polymer-to-ceramic conversion is a complex process, which involves a series of transformations responsible for drastic structural changes in precursors. As mentioned earlier, one of the fundamental requirements of preceramic polymers is to have a latent reactivity. Products of precursor syntheses – reactions of halogenosilanes by hydrolysis, ammonolysis, etc. – are usually mixtures of oligomers and low molecular weight polymers, which may easily volatilize and depolymerize, resulting in low ceramic yields.



To avoid volatilization, precursors must undergo cross-linking reactions, which increase the molecular weight prior to ceramization [SeWi1984, BLSL1989]. Cross-linking occurs through thermally- or catalytic-induced condensation and/or addition reactions of certain functional groups, such as Si-H, Si-OH, Si-vinyl [IcTI1987, CMRS2010, MSTK2012]. Although in some extent necessary, an excessive cross-linking might prevent further shaping [WWPK2004]. Therefore, control of cross-linking reactions must be taken carefully into consideration during PDC processing. When complete, cross-linking of a suitable precursor results in a solid thermoset polymer, which will not decompose or deform significantly during ceramization [LaBa1993, BiAl1995]. This enables machining of parts before ceramization, reducing wear of tools and avoiding damage of products during finishing process [RGG2005, Motz2006]. Aside from thermic/catalytic methods, cross-linking may be carried out by several other processes, including UV [SBGH2004, PKKS2007], laser [FTNS2005], electron or γ -ray radiation curing [INOS2001, ISTN2004, FSKH2013], plasma [Lipo1988] and other reactive environments [RaLL1990, Hase1992, PGDM2008].

The next transition is called ceramization and involves thermolysis (generally called pyrolysis) and evaporation of organic groups, which cause the organic-to-inorganic transformation of precursors, resulting in amorphous ceramics [SoBM1988]. Rearrangement and radical reactions initiate at temperatures above 300 °C, resulting in cleavage of chemical bonds and release of organic functional groups (CH_4 , C_6H_6 , CH_3NH_2 , NH_3 , etc.) [Grei2000, MSTK2012]. Also pyrolysis may be carried out by different methods, like hot pressing [IGBA2002], spark plasma sintering (SPS) [SSKM2015], chemical vapor deposition (CVD) [BSMH2001], plasma spraying [KrUI2006], radiation pyrolysis [ChMa1991], laser [MHTA2003], microwave [DSCP2000], ion irradiation [PiCS2000], and others. Some of these methods even combine shaping and pyrolysis processes in one single step. Nevertheless, pyrolysis in furnace using a suitable atmosphere is still the most common method.

The polymer-to-ceramic conversion is usually completed below 1100 °C [CMRS2010]. However, ideal conditions for cross-linking and ceramization processes depend strongly on the chemical structure of the precursor. Furthermore, by changing conditions for cross-linking and/or ceramization (temperature, heating rate, atmosphere, etc.), different materials may be obtained [BPGC1993].

Amorphous PDCs may be further treated to originate crystalline ceramics. For a great number of applications, crystallization is not necessary, frequently even avoided, and processing is terminated in amorphous stage. Indeed, some PDCs have the capability of avoiding crystallization at temperatures up to 1700 °C [RKDR1996], whereas others – especially ceramics containing oxygen – may crystallize at temperatures as low as 1000-



1200 °C [Grei2000]. One example of a desired crystallization is the preparation of polycrystalline Si₃N₄/SiC nanocomposites from preceramic polymers, which show better properties than mixtures of the individual ceramics [WKSM1990, Niih1991, RKSA1995, RGMD1997]. Fig. 2.1.2 summarizes the general correlation between PDC processing stages [CMRS2010] and precursor's mass change with the temperature.

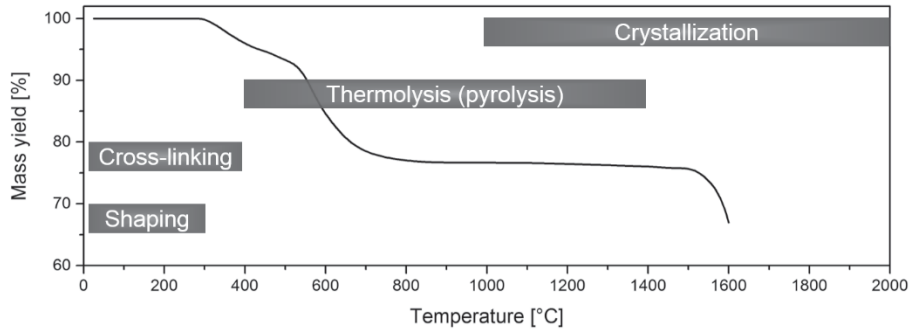


Fig. 2.1.2: Temperature range of the transformations during PDC processing and example of mass change with temperature (polycarbosilazane under inert atmosphere).

The PDC route enables preparation of different ceramics at lower temperatures compared to powder sintering process. However, the polymer-to-ceramic transition is associated to major changes in the materials. To evaluate these changes, two important parameters are used as references:

$$\alpha_{pc} = \frac{m_c}{m_p} \quad (\text{Eq. 2.1.1})$$

where α_{pc} is the ceramic yield (m_c and m_p are the masses of ceramic and polymer, respectively), and

$$\beta_{pc} = \frac{\rho_p}{\rho_c} \quad (\text{Eq. 2.1.2})$$

where β_{pc} is called density ratio (ρ_c and ρ_p are the densities of ceramic and polymer, respectively). A mass loss of typically 10-30% [Grei2000] occurs during polymer-to-ceramic transformation ($\alpha_{pc} < 1$). Furthermore, a drastic densification of the material (from about 1 g cm⁻³ as precursor to 2-3.5 g cm⁻³ as ceramic) takes place ($\beta_{pc} < 1$). Hence, $\alpha_{pc}\beta_{pc} < 1$ for all PDC systems known. This means that the volume of material reduces during the polymer-to-ceramic transition and this volume change results either in formation of porosity or in shrinkage of the shaped part, most commonly both. In early stages of ceramization, a series of open-pore channels is formed, which might close again during thermal treatment – in this case, called transient porosity [Grei2000] – or might be partially retained in the final product as residual porosity. Shrinkage is the greatest drawback of the PDC technology. Assuming isotropic behavior, let the linear shrinkage during polymer-to-ceramic transition ε_{pc}^l be considered as a function of $\alpha_{pc}\beta_{pc}$ and of the volume fraction of voids V_v as follows:

$$\varepsilon_{pc}^l = 1 - \left(\frac{\alpha_{pc}\beta_{pc}}{1 - V_v} \right)^{1/3} \quad (\text{Eq. 2.1.3})$$

By plotting the linear shrinkage as a function of α_{pc} and β_{pc} , and $\alpha_{pc}\beta_{pc}$ (Fig. 2.1.3), it becomes clear that a linear shrinkage comparable with powder sintering of a fully dense ceramic (~20%) can only be obtained if $\alpha_{pc}\beta_{pc} > 0.5$, which is rarely the case for PDC systems [GrSe1992].

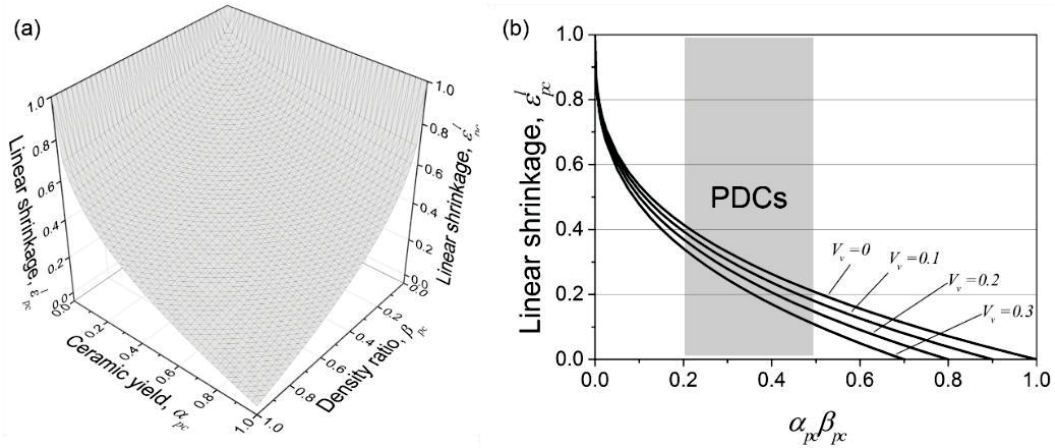


Fig. 2.1.3: Variation of linear shrinkage during polymer-to-ceramic transition (ε_{pc}^l) with the ceramic yield (α_{pc}) and the density ratio (β_{pc}): (a) for a fully dense PDC ($V_v = 0$), and (b) ε_{pc}^l vs. $\alpha_{pc}\beta_{pc}$ for different volume fractions of voids (V_v) in the PDC.

If the material is not able to sufficiently dissipate stresses by viscous flow or diffusional material transport, excessive shrinkage will lead to cracking, which reduces mechanical stability and may cause collapse of the part [Grei1995, RMHK2006]. For these reasons, the preparation of ceramic materials by PDC processing using only preceramic polymers is mostly suitable for shapes with small dimensions like fibers, thin coatings, and cellular ceramics (thin cell wall), which can relieve stresses smoothly [CMRS2010]. Notwithstanding, shrinkage might be reduced or compensated by using suitable fillers, enabling preparation of dense bulk parts and thicker coatings as well.

2.1.3 PDC processing with fillers

The use of fillers in PDC processing is a way to overcome shrinkage of precursors during the polymer-to-ceramic transition, enabling near-net-shape manufacturing of dense ceramics virtually without geometric limitations. This strategy offers, in addition, the possibility of modifying properties of the final material, either by introducing new phases or by modifying the microstructure of the PDC.

Fillers may be polymers, ceramics, glasses or metals, and are usually added in form of particles (nano-, submicron-, or micrometric), but also as flakes, nanotubes and fibers. They may be subdivided in four basic types, according to their behavior in the system: passive, active, meltable or sacrificial fillers.