



Polymer-Derived Ceramics Technology: Characteristics, Procedure, Product Structures, and Properties, and Development of the Technology in High-Entropy Ceramics

Jiabei He^{1,*}, Mengshan Song¹, Kaiyun Chen¹, Dongxiao Kan¹ and Miaomiao Zhu²

- ¹ Advanced Materials Research Central, Northwest Institute for Nonferrous Metal Research, Xi'an 710016, China
- ² Shaanxi Academy of Building Research Co., Ltd., No. 272 of West Huancheng Road, Xi'an 710082, China
- * Correspondence: hjb6260872008@hotmail.com

Abstract: Ceramics have become indispensable materials for a wide range of industrial applications due to their excellent properties. However, the traditional preparation of ceramic materials is often time-consuming and involves high sintering temperatures. These result in considerable energy consumption and high production costs, which limit the application of these materials in some industries. This paper focuses on the advent of polymer-derived ceramics (PDCs) technology, which enabled the application of ceramics to fibers, composites, coatings, and films, mainly due to the excellent design, process, and low-temperature ceramic properties. We review and evaluate the important research progress made in polymer-derived ceramics technology in recent years and discuss its recent development into high-entropy ceramics. The development of polymer-derived ceramics technology in the field of high-entropy ceramics has broad research prospects, which can greatly improve the understanding and design of high-entropy materials and accelerate their application in the industrial field.

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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Keywords: ceramics; polymer-derived ceramics technology; structure and properties; high-entropy ceramics

1. Introduction

In the 1960s, Ainger and Chanttrell obtained non-oxide ceramics for the first time by pyrolyzing polymer precursors [1,2]; this method laid the foundation for the development of polymer-derived ceramics (PDCs). Later, in the early 1970s, Verbeek and colleagues successfully produced Si₃N₄/SiC ceramic fibers from precursors, such as polycarbosilanes, polysilanes, and polysiloxanes [3,4]. Then, in the mid-1970s, Fritz and Yajima [5,6] pyrolyzed polycarbosilane to obtain SiC ceramics; this technique greatly promoted the development of PDCs. Since then, PDCs have gradually been employed by scientists and engineers due to their advantages, such as excellent oxidation, creep, ablation, and crystallization resistances, as well as high-temperature stability [7,8].

High-entropy ceramics (HECs) are a class of novel materials with high configurational entropy ($\Delta S_{\text{config}} > 1.5 R$) [9]. The first single-phase HECs were synthesized by Rost and co-workers in 2015 [9], and several HECs with different crystal structures have been produced to date [10–13]. Research on HECs has revealed their extraordinary properties, including mechanical, electrical, and corrosion resistance [14–16], which have expanded their application prospects. The process of preparing PDCs from polymer precursors is referred to as PDCs technology. In recent years, several attempts have been made to prepare high-entropy ceramics using PDCs technology, with some success [17–19]. These advances show a new way of understanding and discovering high-entropy ceramics. Therefore, in this paper, PDCs technology and the results that have been achieved in the field of high-entropy ceramics will be reviewed.

2. Polymer-Derived Ceramics Technology

At present, most of the precursors of commercial PDCs are silicon-based ceramics precursors and their modified products, and, as PDCs technology has attracted more attention, researchers have prepared precursors not only from polymers but also precursors containing a variety of organic and inorganic components that require chemical reactions to obtain ceramic products [20]. Although there are more and more types of precursors, the characteristics and preparation procedure via PDCs technology are the same.

2.1. Characteristics of Polymer-Derived Ceramics Technology

The characteristics of the preparation process of PDCs technology and the improvement of the material properties via this method can be summarized as follows:

- i. The designability of the organic precursor structure can be used to tune the microstructure of ceramics; in other words, the structure, composition, and preparation process of the organic polymer precursor are adjusted to control the phase composition and structure of the final ceramic product [21].
- ii. The polymer precursors have good moldability and can be used to achieve the preparation of ceramics with complex shapes, including one-dimensional ceramic fibers [6], two-dimensional coatings [22], as well as three-dimensional micro-electro-mechanical systems (MEMS) [23] and ceramic composites [24]. The preparation of fibers takes advantage of the fusible nature of precursors [6,25]; the synthesis of the coating exploits the fluidity of the precursor to achieve a two-dimensional uniform structure on the surface of the material [26–28]. Polymer-derived ceramics technology can be applied in semiconductor preparation techniques, such as lithography, and in the synthesis of ceramic micro–nano devices through the design of the functional groups of the polymer, which provides a good processing route for the manufacture of MEMS [23]. The solubility of the precursor can also be used to impregnate the fiber precast [29–31]; after impregnation, the polymer is crosslinked, cured, and pyrolyzed at high-temperature into the ceramic matrix to fill voids in the precast (this preparation process is called PIP); after repeating the PIP process, a dense fiber-reinforced ceramic matrix composite is obtained.
- iii. The process temperature is relatively low. Traditional non-oxide ceramics, such as SiC and Si₃N₄, require a high sintering temperature, usually above 1600 °C, while PDCs can be sintered at temperatures as low as 900 °C [32].
- iv. Sintering aids are not needed. Due to the slow atomic diffusion caused by the properties of covalent bonds, sintering additives are often required in the preparation of non-oxide ceramics [33]. These additives form a liquid phase at high temperatures and accelerate the diffusion of atoms, thereby promoting the sintering of non-oxide ceramics [34,35]. However, the sintering additive residues at grain boundaries will impair the oxidation resistance [36,37] and the high-temperature mechanical properties of non-oxide ceramics (such as the high-temperature creep resistance) [38]. In contrast, PDCs technology can achieve the sintering of ceramic materials without sintering additives [39,40], and the resulting materials exhibit good resistance to high-temperature oxidation [41], as well as high-temperature creep properties [42].
- Excellent high-temperature performance. Since no sintering additives are required in the preparation of polymer-derived ceramics, a high-purity matrix is obtained after sintering; thus, the prepared material has good high-temperature properties, such as creep [42–44], oxidation [41,45], and corrosion [46,47] resistances.

2.2. Procedure of Polymer-Derived Ceramics Technology

The most commonly used commercial precursors are silicon-based polymers, which include polycarbosilane, polysiloxane, polysilazane, and polyborosilazane and their modified products [20]. Thus, taking organosilicon as example, the processes of polymer-derived ceramics technology are as follows (Figure 1):

- i. Synthesis: various small organic molecules are used as raw materials to obtain precursors with specific molecular weights by organic synthesis methods [20]. The precursor can be varied by selecting suitable small molecules and optimizing the synthesis process. Ceramics with different microstructures can be obtained by using different precursors, as well as different curing and cracking systems [45–49].
- ii. Shaping: polymers can be shaped directly with a variety of methods, such as injection molding, blow molding, extrusion molding, coating, electrospinning, 3D printing, etc., which further enable one-step molding of polymer-derived ceramics [50].
- iii. Crosslinking/curing: the main purpose of crosslinking is to make the polymer backbone connected [20]. Crosslinking methods include light and thermal curing processes. Thermal-curing crosslinking generally relies on curing agents to polymerize polymer precursors into a mesh structure at a certain temperature, forming a non-molten polymer [51]. In light-curing crosslinking, a polymer is doped with a curing agent and polymerized under illumination at a specific wavelength to obtain a non-molten polymer [52].
- iv. Pyrolysis/caramelization: these processes complete the transformation of the material from organic to inorganic, inducing qualitative changes in its internal structure and properties [20]. During the process, the organic groups of the precursor gradually vanish, and the polymer transforms into amorphous ceramics, with a typical pyrolyzing temperature of 900–1000 °C [50]. The phase composition, structure, and properties of amorphous ceramics obtained by pyrolysis are strongly dependent on the caramelization process.
- v. Crystallization: typically, the polymer transforms into amorphous ceramics at a temperature between 900 and 1000 °C [38]. As the heat treatment temperature increases, the amorphous phase is gradually crystallized in the temperature range of 1200–1800 °C, and the crystalline ceramic material is finally obtained [20,38]. Several structural transformations are triggered by the amorphous \rightarrow crystalline transformations sition [20,29]: the amorphous disordered structure is rearranged with the relevant chemical bonds broken, and the structure gradually turns into crystalline as the temperature is increased; then, the rupture of chemical bonds and the atomic rearrangement cause the separation of the ceramic and carbon phases to form a multiphase ceramic system, which, in turn, promotes nucleation; the formed crystal nuclei gradually grow with increasing temperature and time. Take the C-enriched SiC produced by PDCs technology as an example; the amorphous \rightarrow crystalline transition can be schematically drawn in Figure 2 [53]. Meanwhile, the amorphous \rightarrow crystalline transition is usually accompanied by a decomposition reaction, along with the formation of a small amount of gaseous products.





Figure 2. (a) Schematics of a detailed model describing the temperature-dependent evolution of nanodomains comprised of SiC, free carbon, and residual amorphous matrix in polymer-derived C-enriched SiC ceramics. (b) the average NC–SiC particle size varied with temperature, from 2 nm (1200 °C) to 15 nm (1500 °C). (c) the in-plane crystallite diameters (L_a) of the NC-G phase and the average defect distances of a single graphene sheet (L_d) grow trend varied with temperature, both remained nearly constant [54].

In addition, in order to introduce metallic elements into the backbone of the precursor to improve the thermal stability of PDCs, some researchers have also developed inorganic precursors [55]. For example, the most common inorganic precursor is metal chlorides, which are often used to synthesize polymetallosiloxanes with silicic acid and partially hydrolyzed tetraethoxysilanes [56]. After the synthesis of polymetallosiloxanes, taking the SiZrOC ceramics precursor as an example, the subsequent crosslinking process can retain the metal atoms in the backbone structure of the final product and then pyrolyze to obtain PDCs containing metal elements [57]. The formation of Si–O–Zr bonds occurs during crosslinking, as shown below [55]:

$$\begin{array}{l} \equiv Si-H+\equiv Zr-OPr\rightarrow \equiv Si-O-Zr\equiv +C_{3}H_{8}\\ \equiv Si-H+\equiv Zr-OH\rightarrow \equiv Si-O-Zr\equiv +H_{2} \end{array} \end{array}$$

Ceramics prepared by PDCs technology undergo a unique phase evolution process with increasing temperature, and the performance of the final product is directly affected by the pyrolyzing process, precursor composition, and molecular structure (a comparison with the traditional manufacturing procedures is displayed in Table 1). Therefore, PDCs technology can provide control of the ceramic microstructure and properties, and it represents an innovative preparation process that will play an important role in industrial applications of ceramics in the future.

 Table 1. Main processing parameters for manufacturing ceramics via conventional route and PDC route [58].

Processing Parameters	Conventional Route	PDC Route
Ceramic Raw Material	Ceramic powders, such as alumina, zirconia, silicon carbide, or aluminum nitride	Precursor polymers, such as polysiloxanes or polysilazanes, with passive or active fillers

Processing Parameters	Conventional Route	PDC Route
Mixing/Milling	Powders are mixed, generally in a ball mill, to liquid + dispersant for breaking up agglomerates; binders and plasticizers are added homogenized	Synthesis: solid or liquid are dissolved, with the aid of different equipment, in a solvent; fillers, crosslinkers, and others are added and homogenized
Shaping	Cutting or press into desired shapes	
Thermal Treatments	Debinding at middle temperatures and sintering at high temperatures are needed	Crosslinking at low temperatures (as low as room temperature) and pyrolysis at high temperatures are needed; eventually, crystallization at higher temperatures is accomplished; composite materials may be produced with partial pyrolysis of precursors
Ceramic Products	Dense parts with a residual porosity and controlled shrinkage, or, less often, macroporous parts; all kinds of oxide and non-oxide ceramics may be fabricated	Near net shape parts with the use of active/passive fillers, or controlled porosity with the aid of pore formers; mostly silicon-based ceramics are fabricated (SiC, SiOC, SiOCN)

Table 1. Cont.

3. Structure and Properties of Polymer-Derived Ceramics

PDCs are prepared by pyrolysis of ceramic precursor polymers. At lower temperatures, the PDC lattice exhibits an amorphous structure, with many unique properties, such as high-temperature stability [20,49], excellent semiconducting [50] and piezoresistive [53,54] properties, oxidation and corrosion resistance [20], as well as light transmission and luminescence [4,59]. At higher heat treatment temperatures, PDCs are gradually crystallized, and single- or complex-phase crystalline nanoceramics can be obtained by controlling the process parameters. By taking advantage of the gradual structural evolution of PDCs at high temperatures, the structure and distribution of ceramic nanoparticles can be adjusted to effectively improve their mechanical properties, such as strength, modulus, and hardness [45].

3.1. High-Temperature Stability

Thermal stability is the ability of a material to resist thermal decomposition [60]. Traditional SiC materials have good strength and thermal stability in high-temperature environments; however, Si_3N_4 is usually decomposed into Si and N_2 above 1400 °C; decomposition leads to volatilization and weight loss, limiting the application of the material in high-temperature environments [61]. Additionally, the Si_3N_4 ceramic prepared by PDCs technology can remain in the amorphous state in the temperature range of 1000–1800 °C; hence, its lattice structure is stable, volatilization and weight loss are rare, and the material has outstanding high-temperature stability [61].

Riedel et al. [62] reported that polymer-derived SiCN ceramics remain amorphous at 1500 °C. The thermal weight loss curves of β -Si₃N₄, Si_{1.7}C_{1.0}N_{1.6}, and Si_{3.0}B_{1.0}C_{4.3}N_{2.0} in a 0.1 MPa helium environment were compared in a later study [63]; it was found that the thermal stability of Si_{1.7}C_{1.0}N_{1.6} is higher than that of Si₃N₄, whereas the lattice of Si_{3.0}B_{1.0}C_{4.3}N_{2.0} remains stable up to ~2000 °C without significant degradation. Riedel [64] and his team further investigated the relationship between the PDC's ability to retain its amorphous structure and its high-temperature stability. They found that the ability of PDCs to remain amorphous is closely related to the carbon content (Figure 3): when the carbon content in the system is high, the carbon phases are distributed in a continuous network structure, with the amorphous Si₃N₄ embedded in it, thus inhibiting the crystallization process. On the other hand, a continuous layer of graphite inhibits the outward diffusion of nitrogen and thus reduces volatilization. The combined effect of the two factors improves the high-temperature stability of SiCN. Studies have shown [20] that SiCN ceramics with higher carbon content have better high-temperature stability than their lower-carbon counterparts. Moreover, molecular dynamics simulations showed that the addition of boron can increase the activation energy for breaking Si–N bonds in the system so that Si–N bonds in SiBCN do not easily react with C to form SiC and N₂; at the same time, the added B reduces the diffusion coefficient of carbon and nitrogen in the material so that the SiBCN system shows enhanced high-temperature stability [65].



Figure 3. Thermogravimetric curves of polymers S1–S4 and S5–(SiMe₂–NCN)_n– up to 1400 °C [64]. S1–S4 represent polymers with the structures of –(PhSiR–NCN)_n–, R = Phenyl(S1), Methyl(S2), H(S3), and Vinyl(S4). The ceramic compositions of pyrolyzed S1–S4 are Si₁C_{12.14}N_{1.81}H_{10.07}Cl_{0.19}O_{0.14}, Si₁C_{7.93}N_{1.83}H_{8.71}Cl_{0.12}, Si₁C_{6.81}N_{1.96}H_{6.68}Cl_{0.03}O_{0.03}, and Si₁C_{8.75}N_{1.37}H_{8.63}Cl_{0.54}O_{0.08}, respectively.

3.2. Semiconducting and Electrical Properties

Yajima [66] found that the conductivity of amorphous SiC ceramics derived from polycarbosilane varies with the pyrolyzing temperature. Specifically, the ceramic exhibits a DC conductivity of less than $10^{-10} \Omega^{-1} \cdot \text{cm}^{-1}$, as well as electrical conductivity properties similar to that of an insulator when the heat treatment temperature is below 600 °C; then, when the temperature exceeds 800 °C, the polymer precursor is fully transformed into an inorganic amorphous ceramic whose conductivity increases with the heat treatment temperature, resulting in semiconducting electrical properties [66]. In addition to the pyrolyzing temperature, the DC conductance of PDCs varies with the series, composition, and sintering atmosphere of the precursor and usually ranges from approximately 10^{-10} to $1 \Omega^{-1} \cdot \text{cm}^{-1}$ [67]. For example, when the carbon phase content in the ceramic is high under high-temperature conditions, the continuous phase formed by carbon induces a tunneling effect, which increases the conductivity (from 0.1 to $1 \Omega^{-1} \cdot \text{cm}^{-1}$) and results in electrical properties similar to those of a conductor [67].

The current research on the electrical properties of amorphous PDCs is mainly focused on SiCN and SiCO systems. Wang et al. [68] studied the relationship between DC conductance and carbon phase structure in SiCO ceramics and found that the DC conductivity activation energy of the material is similar to that of various carbon phases. This indicated that the DC conductance of SiCO ceramics is affected by the evolution of the carbon phase; moreover, the DC conductance and heat treatment temperature of the material are consistent with the Arrhenius equation. Furthermore, the authors studied the effect of the carbon phase evolution on the conductivity of SiCO ceramics under different heat treatment temperatures and found that the conductivity of the material increases with the pyrolyzing time; however, the trend changes around 1200 $^{\circ}$ C, indicating that the conductivity mechanism changes as the carbon phase structure varies at different temperatures: at 1100 $^{\circ}$ C, the carbon phase is rearranged in the matrix, new carbon clusters are formed, and the spacing between the carbon phases is reduced, resulting in an increase in the hopping conductivity and in the overall conductivity of the material. At 1300 °C, the amorphous carbon phase nucleates and transforms into a microcrystalline phase whose continuous growth results in an increasing conductance [69].

Another electrical property of amorphous PDCs is the change in piezoresistive resistivity with applied pressure, see Figure 4 [53,70]. The reported piezoresistive coefficient of polymer-derived SiCN ceramics ranges from 1000 to 4000 [20], which is much higher than that of any existing ceramic material. Some researchers have pointed out that the piezoresistivity of PDCs is affected by the structure and content of free carbon; under applied pressure, the continuous phase formed by the carbon phase in the ceramic matrix triggers a local tunneling effect, which, in turn, causes a change in resistance [53].



Figure 4. Experimental data of piezoresistivity response of (a) SiCN [53] and (b) SiCO [70].

3.3. Oxidation and Corrosion Resistance

Several comprehensive and in-depth studies have focused on the oxidation behavior of SiC, SiCO, SiCN, and SiBCN. For crystalline SiC, the oxidation behavior in the temperature range of 800 to 1400 °C shows a parabolic trend; the activation energy remains at ~120 kJ·mol⁻¹ and the oxidation rate is very low, close to or slightly higher than that of pure silicon carbide or silicon nitride ceramics [38]. Reidel et al. [71] studied the relationship between the silica protective layer on the surface of SiCN ceramics and the solid-state reaction of the matrix and found that the latter is inhibited by the very low diffusion coefficient of nitrogen in the SiO₂ protective layer. In addition, the diffusion coefficient of oxygen atoms in the dense silica layer is also very low, with values around 10^{-11} – 10^{-16} cm²/s in the temperature range of 900–1400 °C, which effectively inhibits the further oxidation of the SiCN matrix [41]. The combination of the above two mechanisms leads to good oxidation resistance of SiCN ceramics. An [47] and Wang [72] prepared SiCN-based SiAlCN ceramics in which Al atoms were doped to form an effective blocking structure in the oxidized SiO₂ layer and greatly improved the oxidation resistance.

Two reactions occur when silicon-based ceramics are exposed to high-temperature aqueous vapors [38]: (1) silica is generated (oxidation), and (2) it continues to react with water vapor to form volatile products (corrosion), such as $Si(OH)_4$. Oxidation causes thickening and mass increase in the oxide layer, but corrosion causes the oxide layer to become thinner and reduces its mass. When oxidation and volatilization occur at the same time, the stability of the silica layer formed by oxidation determines the corrosion rate of the material. Wang et al. [73] compared the corrosion resistances of SiCN and SiAlCN ceramics (Figure 5) and found that a small amount of doped aluminum reduces the activity of silica in Al_2O_3 –SiO₂, resulting in the SiAlCN ceramics exhibiting higher corrosion resistance. Moreover, He et al. [74] reported that $Y_2Si_2O_7$ is formed when SiC is doped with Y atoms under a high-temperature air atmosphere; the Y-containing compounds cover the whole samples, resulting in a lower oxidation resistance compared with Al-doped SiC.



Figure 5. A plot of the square of oxide scale thickness as a function of annealing time for SiCN and SiAlCN ceramics at 1200 °C [72].

3.4. Light Transmission and Luminescence

Owing to the presence of a network-structured absorbing layer formed by carbon atoms in the structure of PDCs [75], their optical properties are difficult to measure and use in applications. Thus, Soraru et al. [59,76,77] used precursors with higher amounts of Si-H functional groups to design and control the content of free carbon in SiCO; in this way, the elemental content of the SiCO ceramics was closer to the stoichiometric ratio, and the prepared ceramics exhibited good transparency. The higher content of Si-H functional groups in polymers has two effects [78]: (i) they can reduce the C content in the precursor; (ii) the formation of new Si-C bonds enables more Si to be incorporated with C into the inorganic structure, reducing the final free carbon content. Fluorescence spectroscopy measurements of the SiCO ceramic show a wide luminescence band at ~500 nm, originating from sp^2 carbon clusters contained in the matrix [20]; when the content of these clusters is low, their presence does not affect the transparency of the SiCO glass, which is evidenced in Figure 6. Based on this phenomenon, the luminescence of amorphous PDCs can also be improved by introducing additional elements into the precursors through the solgel process. For example, Zhang et al. [59] introduced Eu ions into SiCO ceramics by adding $Eu(NO_3)_3$ to the precursors. When the ceramic containing Eu^{3+} is pyrolyzed at a higher temperature, the $Eu^{3+} \rightarrow Eu^{2+}$ reduction results in a wide blue luminescence band at ~450 nm. These photoluminescent properties of PDCs make them very promising materials for the manufacture of optical amplifier components.



Figure 6. Experimental proof of visible luminescence of the Si-rich SiCO thin films pyrolyzed from 800 °C to 1250 °C under UV laser excitation [79].

3.5. Mechanical Properties

Polymers usually shrink during pyrolysis, so it is very difficult to prepare dense bulk ceramics through PDCs technology at the early stage [21]. Previous research on their mechanical properties mainly focuses on fiber preparation and modification [20]. Taking polymer-derived SiC fibers as an example, in 1976, Yajima et al. [80] reported a preparation method for silicon carbide fibers, which showed a tensile strength and Young's modulus of 6.2 and 440 GPa, respectively. Then, PDCs technology was used to prepare the first generation of commercial Nicalon fibers. Subsequently, as the temperature and strength requirements of SiC fibers for practical applications gradually increased, improved and optimized processes [81–83] enabled SiC fibers to reach a tensile strength and Young's modulus of 3 and 220 GPa [84] at 1200 °C, respectively. SiC fibers containing Al and Zr have also been studied; the mechanical strength of Al-containing fibers can be maintained at high levels even at a temperature of 1900 °C [85].

With the development of techniques to prepare dense bulk ceramics, the mechanical properties of polymer-derived block materials have also started to be investigated. For amorphous bulk ceramics, the density, modulus of elasticity, hardness, and other properties increase with the pyrolyzing temperature [20,86]:

- i. Density and modulus: as the pyrolyzing temperature increases, the Si–H and C–H bonds in the system are broken, more Si–C network connections are formed by eliminating the hydrogen content in the system, and the density and elastic modulus increase accordingly [87].
- ii. Hardness and fracture toughness: similar to the modulus of elasticity, the increase in the heat treatment temperature and the formation of more Si–C network links after dehydrogenation will increase the hardness. The fracture toughness exhibits a more complicated trend: many studies have shown that cracks in Si–C–N ceramics extend along regions of the material that have not yet been dehydrogenated. These regions exhibit lower strength compared to regions that have been dehydrogenated to form Si–C bonds [86]. As the temperature increases, the areas with lower strength gradually decrease, resulting in a tortuous crack propagation path at a certain scale, and the overall fracture toughness of the material increases.

For crystalline ceramics, the main way to transform from an amorphous network into a crystalline structure is the rearrangement of chemical bonds, which causes phase separation and eventually leads to the formation of nanocrystalline nuclei and crystal growth. Some studies of the shape and size of nanoparticles present in the structure of PDCs after heat treatment at higher temperatures showed that these nanoparticles remain stable even at very high temperatures [20]. Therefore, the preparation of a fully crystallized ceramic containing such nanostructures by the polymer-derived method can achieve the purpose of controlling the structure and composition of nanoceramics.

Kodama et al. [88] prepared single-phase silicon carbide ceramics using polycarbosilane and controlled the grain size of SiC in the range of 0.2 to 1.4 μm by varying the sintering temperature; they found that grain size is directly related to fracture toughness. Moreover, the fracture toughness of the nanosized SiC reaches a maximum of 5.1 MPa·m^{1/2} for a grain size of $0.7 \,\mu$ m, which is much higher than the fracture toughness of microscale silicon carbide ceramics (\sim 3 MPa \cdot m^{1/2}). In addition to single-phase ceramics, multi-phase ceramics can also be obtained by varying the precursor components. Taking Si-C-N ceramics as an example, the amorphous SiCN undergoes phase separation at 1000 $^{\circ}$ C, as well as a carbothermal reaction at a higher temperature, yielding β -SiC and Si₃N₄ products after complete crystallization at 1500 °C [20]. Several studies found that, when the temperature is continually increased to 1800 °C, the powder particle size can be maintained below 200 nm [89–91]; this feature can be used to obtain a multi-phase ceramic powder (Figure 7). In summary, the phase separation process of PDCs at high temperatures can be used to prepare single-, bi-, or even multi-phase nanocomposites and improve the mechanical properties of materials. Therefore, this process has great application prospects in the field of functional and structural materials.



Figure 7. Experimental results for polymer-derived multi-phase nano ceramic: (**a**) selected-area electron diffraction pattern after annealing at 1800 °C; (**b**) bright-field image [91].

4. Development of PDCs Technology in the Field of High-Entropy Ceramics

The above discussion shows that the advantages of polymer-derived ceramics technology are mainly related to the designability and fluidity of the precursors, which is very suitable for the preparation of ceramics of any kind and their components, including high-entropy ceramics. However, the preparation of these systems using PDCs technology has rarely been reported.

High-entropy ceramics are defined as a new type of high-entropy materials consisting of four or more main components in near-equiatomic ratios, with each atomic percentage being between 5 and 35 at.% in a single-phase structure [9,92]. The complete mixing of multiple elements at the atomic scale is a key factor in triggering the properties of high-entropy ceramics [16–19], such as superionic conductivity [93], specific capacitive properties [94], water splitting resistance [95], low thermal conductivity [96], and good mechanical properties [97]. Because the PDC process starts from polymers or a mixture of inorganic and organic components, it can be expected that the first challenge to preparing high-entropy ceramics via PDCs technology is the preparation of high-entropy polymers or precursors. Several studies have focused on high-entropy polymers/precursors; for example, some researchers have studied the crystallization and mechanical behavior of multi-quaternary ammonium mixtures and found that the ternary and quaternary blending mixtures exhibit restricted crystallization behavior and high elongation at break; these characteristics are not observed in the reacted binary or unreacted quaternary blends [98]. It has also been reported that simply changing the state of some ethylene valence bonds in ternary copolymers, such as converting single to double bonds, can significantly improve their thermoelectric properties [99]. It must be noted that, in the current literature currently claiming to work on high-entropy polymers, the polymers used are actually mixtures [98] (blending multiple polymers together) and copolymers [99] (specific polymers formed by two or more polymer segments of different properties connected together). These forms of products do not achieve either atomic-level mixing or the concept of a single-phase structure. Hence, these polymers are strictly unable to meet the concept of high-entropy materials.

On the other hand, some studies skip the step of high-entropy polymer preparation and focus on the preparation of high-entropy ceramics by PDCs technology, in which polymers or raw mixtures are used to prepare high-entropy ceramics as precursors [100–106] and the polymer itself does not necessarily meet the concept of high entropy. Tseng et al. [100] used polymeric steric entrapment, with which cations are trapped in the long chain polyvinyl alcohol structure after stirring at room temperature and evaporating at 200 °C, and then a metal oxide is generated after heat treatment to form $Gd_{0.4}Tb_{0.4}Dy_{0.4}Ho_{0.4}Er_{0.4}O_3$ material. Sun et al. [101,102] successfully prepared a series of high-entropy nano-carbide powders with mixed rare-earth acetylacetonates and metal acetylacetonate alkoxides via co-hydrolysis and a subsequent polycondensation reaction (Figure 8). Moreover, the reaction between the M-OR alkoxide (M: metal, R: alkyl group) and a metal salt (MNO₃ or MCl) was used to produce various high-entropy ceramics, such as (Yb_{0.2}Y_{0.2}Lu_{0.2}Sc_{0.2}Gd_{0.2})₂Si₂O₇ [103], 4.5SiO₂–3Al₂O₃–1.5P₂O₅–4CaO–1CaF₂ [104], and 43SiO₂–24.5CaO–24.5Na₂O–6P₂O₅–2Fe₂O₃ [105]. Li et al. [106] and Du et al. [107] obtained high-entropy nano-carbide powders (Ti_{0.2}Zr_{0.2}Hf_{0.2}Nb_{0.2}Ta_{0.2})C and (Hf0.25Nb0.25Zr0.25Ti0.25)C by a hydrothermal reduction reaction at 2000–2200 °C using transition metal halides (TiCl₄, ZrCl₄, HfCl₄, NbCl₅, TaCl₅) and organic materials as a source of carbon.





These studies open a new research avenue for the fabrication of high-entropy ceramics or ceramic–matrix composites via PDCs technology.

5. Conclusions and Outlook

Polymer-derived ceramics technology provides designability and manufacturability, overcoming the shortcomings of traditional ceramic processes, such as high preparation temperatures and molding and processing difficulties, and has rapidly become a research hotspot since its development in the 1960s. The current research on polymer-derived ceramics and the corresponding technology has extended to various areas in the field of materials, including synthesis and modification of precursors, structural evolution during transformation, as well as electrical, optical, chemical, and mechanical properties. These studies confirm that the preparation of ceramics using precursors can allow tuning the

phase structure and enable the preparation of complex-phase nanoceramics, which may improve the brittleness and overall properties of the ceramics.

Moreover, the main advantages of PDCs technology lie in the designability and fluidity of its precursors, allowing structural designs at multiple scales to further meet the application requirements in the industrial field. Therefore, this technology has very good application prospects in the field of high-entropy ceramics, whose remarkable characteristics are closely related to the position and arrangement of atoms. However, studies exploring the use of PDCs technology in high-entropy ceramics are scarce and mainly focus on the synthesis of high-entropy polymers, pyrolyzing processes, and phase analysis.

Overall, we expect that PDCs technology will greatly support future studies in the field of high-entropy ceramics, expanding the scope and promoting the application of these systems.

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