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# Preparation of Ultra-High Temperature Ceramics–Based Materials by Sol-Gel Routes

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## Abstract

Ultra-high temperature ceramics (UHTCs) are a class of inorganic materials that have melting point over 3000°C and are typically borides, carbides, and nitrides of early transition metals. UHTCs are considered as the promising candidate used in the extreme environment involved with the hypersonic aviation thermal protective system. Synthesis of UHTC-based materials can be divided into solid-based and solution-based protocols according to the state of the raw materials. A sol-gel technique is one of the solution-based protocols for the preparation of UHTC-based materials, which involves the hydrolysis, condensation of the metal organic and/or metal inorganic compounds, gelation, and the posthigh temperature treatment of the dried gels. The sol-gel technique enables the synthesis of UHTC-based materials at 1300–1600°C. UHTC-based materials with desired shapes, such as nanopowders, fibers, and porous monoliths, can also be prepared via sol-gel routes.

**Keywords:** ultra-high temperature ceramic (UHTC), sol-gel, nanopowders, ceramic fibers, porous ceramics

## 1. Introduction

Temperature at 3000°C is not just hot, but it is extremely hot. It is just a baseline in the world of extreme environment engineering. Very few materials can meet this criterion due to the facts that most of the materials have already melted or decomposed below this temperature. Materials with melting temperatures above 3000°C are very limited, which are shown in **Figure 1** [1–4]. The borides, carbides, and nitrides of group IV and V elements have melting temperatures above 3000°C and are considered as ultra-high temperature ceramics (UHTCs), such as zirconium diboride ( $\text{ZrB}_2$ ), hafnium diboride ( $\text{HfB}_2$ ), tantalum diboride ( $\text{TaB}_2$ ), zirconium carbide ( $\text{ZrC}$ ), hafnium carbide ( $\text{HfC}$ ), tantalum carbide ( $\text{TaC}$ ), and hafnium nitride ( $\text{HfN}$ ) [1].

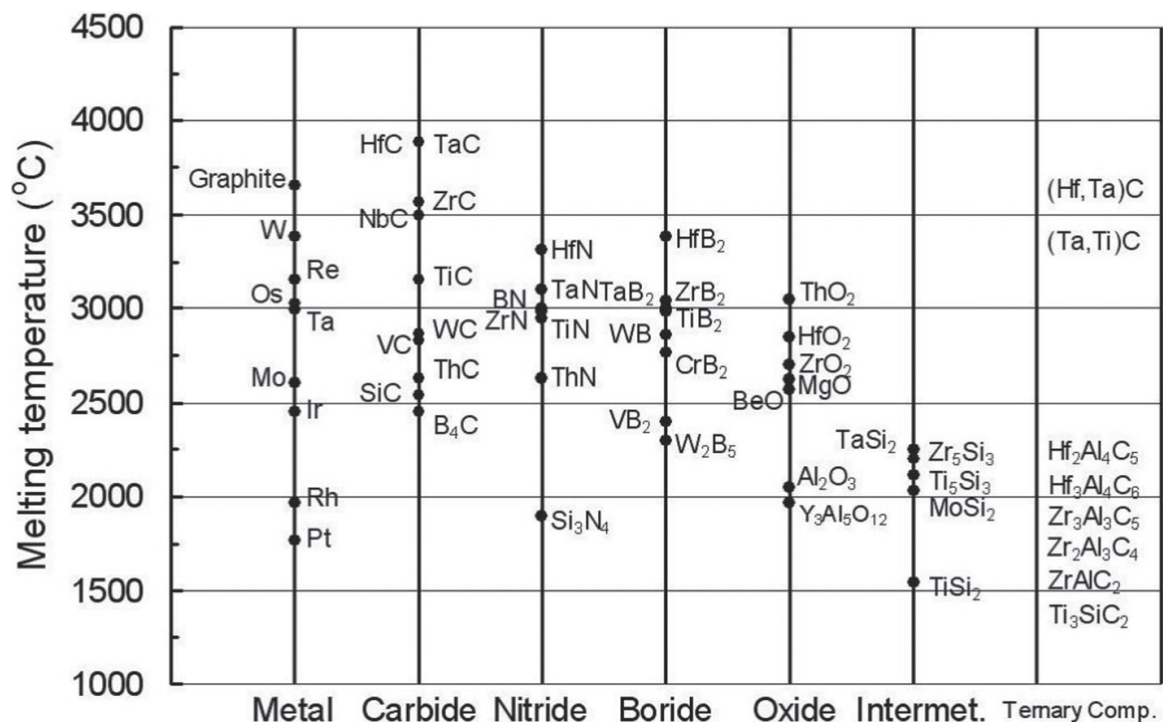


Figure 1. A comparison of the melting temperatures of the most refractory members of several classes of materials.

Recent interest in UHTCs has been motivated by the search for materials that can withstand extreme environments, such as extreme temperature, chemically aggressive environments, and rapid heating/cooling, etc. [5, 6]. Due to the combination of series of excellent physical and chemical properties, such as high hardness, good high temperature stability, and excellent solid-phase stability, UHTCs are considered as promising candidates for a variety of high-temperature structural applications, including engines, hypersonic vehicles, plasma arc electrode, cutting tools, furnace elements, and high temperature shielding. However, owing to the strong covalent bond and relatively low volume diffusion coefficient, UHTCs are difficult to get successfully sintered. Densification of these materials is typically performed by hot pressing and spark plasma sintering with or without sintering aids.

UHTCs can be synthesized by a variety of routes, which can be divided into solid phase protocols and solution based protocols based on the state of the starting materials [7, 8]. Among the solid-phase protocols, transition metal oxides, carbon black, boron oxide, and boron carbide are commonly used as the starting materials. After ball-milling and high temperature carbothermal reduction, the mixtures are converted into UHTC powders. Examples of the reactions used to synthesize borides and carbides are listed in Table 1 [7]. These reactions are written for ZrB<sub>2</sub> and ZrC, but analogous processes produce other borides and carbides. These solid phase protocols are very straightforward and simple and are used to produce UHTC powders commercially. However, due to the heterogeneity of the reactants, the reactions need to be performed at high temperatures for several hours to complete. Also, those synthesized UHTC powders are micron-sized particles.

Reactions	Category	Example	
1	Carbothermal	$\text{ZrO}_2 + 3\text{C} \rightarrow \text{ZrC} + 2\text{CO}$	(1)
2	Carbothermal	$\text{ZrO}_2 + \text{B}_2\text{O}_3 + 5\text{C} \rightarrow \text{ZrB}_2 + 5\text{CO}$	(2)
3	Borothermal	$\text{ZrO}_2 + 4\text{B} \rightarrow \text{ZrB}_2 + \text{B}_2\text{O}_2$	(3)
4	Boron carbide	$7\text{ZrO}_2 + 5\text{B}_4\text{C} \rightarrow 7\text{ZrB}_2 + 3\text{B}_2\text{O}_3 + 5\text{CO}$	(4)
5	Combined	$2\text{ZrO}_2 + \text{B}_4\text{C} + 3\text{C} \rightarrow 2\text{ZrB}_2 + 4\text{CO}$	(5)

**Table 1.** Examples of reduction reactions that can be used to synthesize borides and carbides [7].

In solution-based protocols, soluble transition metal containing precursors, boron precursors, and carbon sources are used as the raw materials to form homogeneous sols/solutions or polymers [8–10]. These sols/solutions or polymers can be converted into UHTC materials after hydrolysis, curing/drying, and pyrolysis at high temperatures. Actually, the formation of UHTCs via solution-based protocols is still based on the carbothermal or borothermal reactions of metal oxides with carbon. However, due to the homogeneous distribution of all the reactants at the molecular level, the following high temperature reduction reactions can proceed at much lower temperature and fine UHTC powders with particle sizes down to few hundred nanometers can be synthesized. Not only granular UHTC particles but also some other UHTC materials with different morphology can be synthesized through these solution-based routes.

A sol-gel technique is one of the solution-based processes, which enables processing of ceramics at low temperature in various desirable shapes, such as monoliths, films, fibers, or nano-sized powders, as shown in **Figure 2** [11, 12]. Typically, the sol-gel technique involves the hydrolysis, condensation of the metal organic and/or metal inorganic compounds, gelation, and the posttreatment of the dried gels to obtain final ceramic products. Small molecular compounds are used as the starting materials in sol-gel routes. The homogeneity of the starting compounds at molecular level facilitates the preparation of these materials at relatively low temperatures via the sol-gel technique. The sol-gel route is an old but an efficient way to produce high quality, fine UHTC powders under moderate conditions compared with other solution-based protocols [8, 10, 13]. Combined with various shaping techniques, UHTC-based materials in various desirable shapes, such as nanopowders, nanofibers, and porous ceramics can be prepared from similar starting materials and simple reactive processes via the sol-gel technique [8, 14–16].

In this chapter, we will present recent works covering the synthesis of nanopowders, nanofibers, and porous ceramics of UHTC-based materials via sol-gel routes. The discussions mainly focus on the synthesis of ZrC- and ZrB<sub>2</sub>-based materials, but analogous processes produce other borides and carbides. Meanwhile, numbers of publications discussing the utilization of UHTC sols to prepare fiber-reinforced ceramic composites via polymer infiltration pyrolysis routes will not be discussed here.

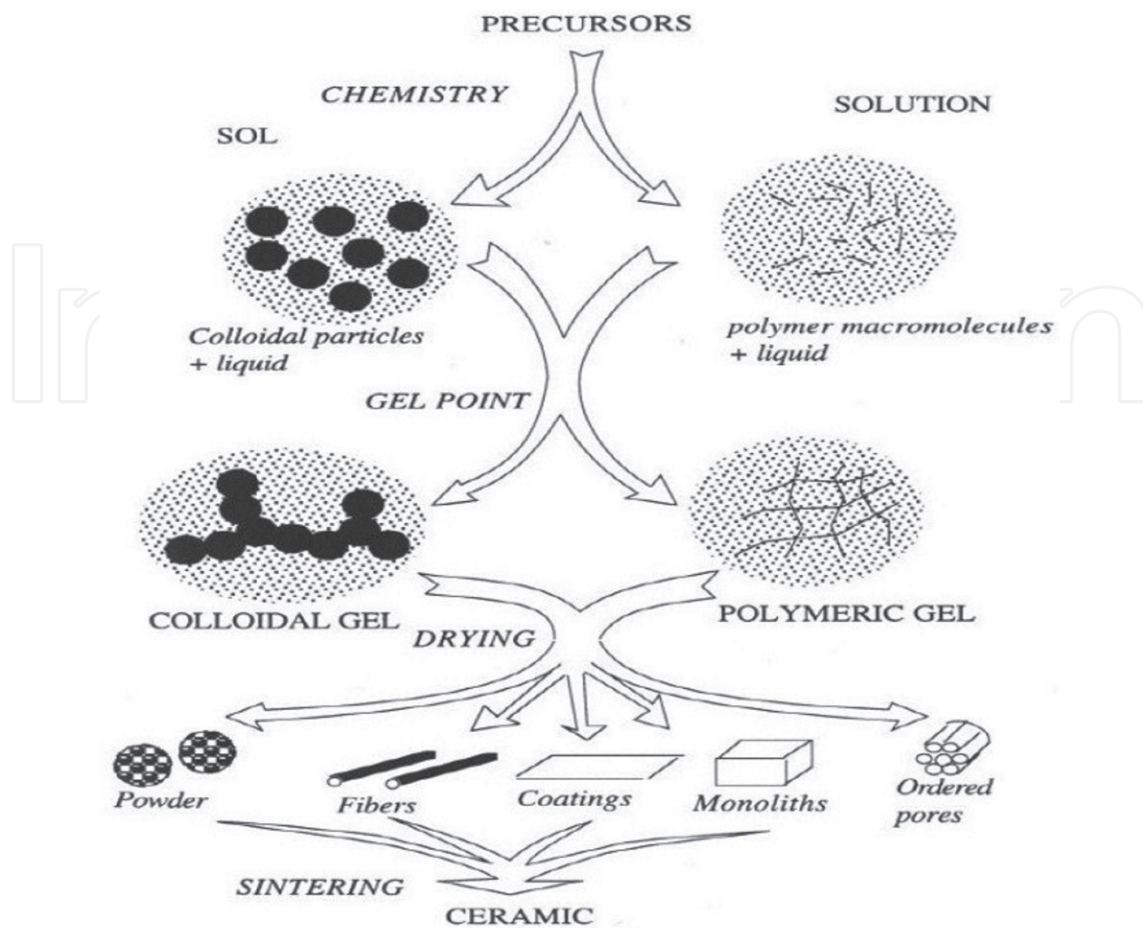
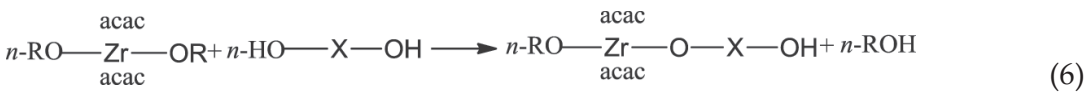


Figure 2. Simplified chart of sol-gel processes [12].

2. Synthesis of the precursors for UHTC

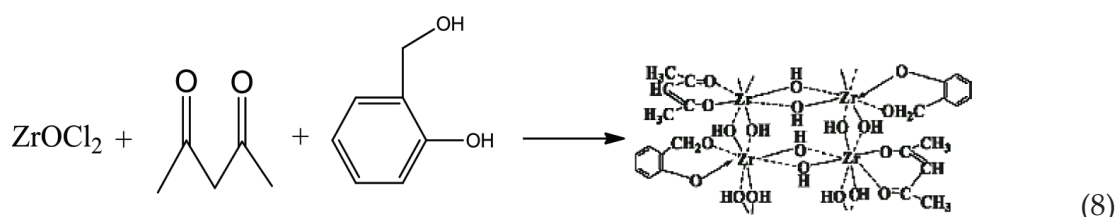
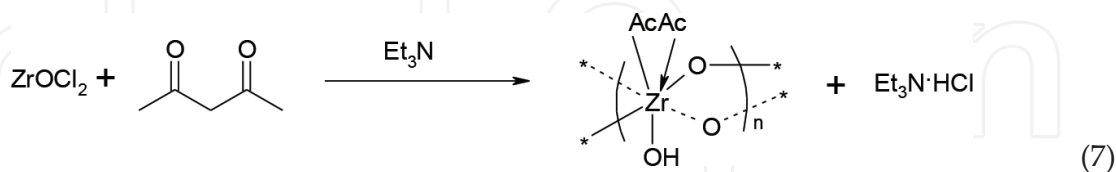
It is very straightforward and simple for the researchers to apply a sol-gel technique to prepare UHTC nanopowders. It seems simple to obtain the sols of the target materials by mixing the precursors of a transition metal with a carbon source and a boron source in liquid state. On drying and after high temperature ceramization, the UHTC nanopowders can be prepared [8, 10]. However, it is not always easy to get homogeneous precursor sols of UHTC materials without considering the chemical compatibility and stability of the precursors.

Generally, transition metal alkoxides, oxychloride, and chloride are used as the starting metal oxide precursors. Bidentate ligands, such as  $\beta$ -diketones, acetic acid, and cellulose acetate, are used to modify the high reactivity of the metal alkoxide allowing a slow-down of the system's reactivity [17, 18]. The chemically modified metal alkoxide undergoes hydrolysis and condensation in a controlled manner to form preceramics, as illustrated in Eq. (6) [17].





Polyzirconoxane (PZO) can be synthesized by chelation of acetyl acetone to zirconium oxychloride and is widely used as the powdery and soluble zirconia precursor [19, 20]. The synthesis process of PZO is shown in Eq. (7) [20]. It is also possible for the synthesis of powdery preceramic polymers for ZrC through reactions of zirconium oxychloride with acetyl acetone and salicyl alcohol in a one-pot reaction procedure according to Eq. (8) [21]. The preceramic polymers can be converted into ZrC nanopowders after the high temperature treatment.



While sucrose, phenolic resin, and polyacrylonitrile are used as the carbon source; boron-containing compounds (e.g., boric acid and triethyl borate) are usually used as the boron source to synthesize metal borides. By mixing the modified metal precursors with carbon and boron sources in controlled molar ratios, the precursor sols for UHTC are prepared.

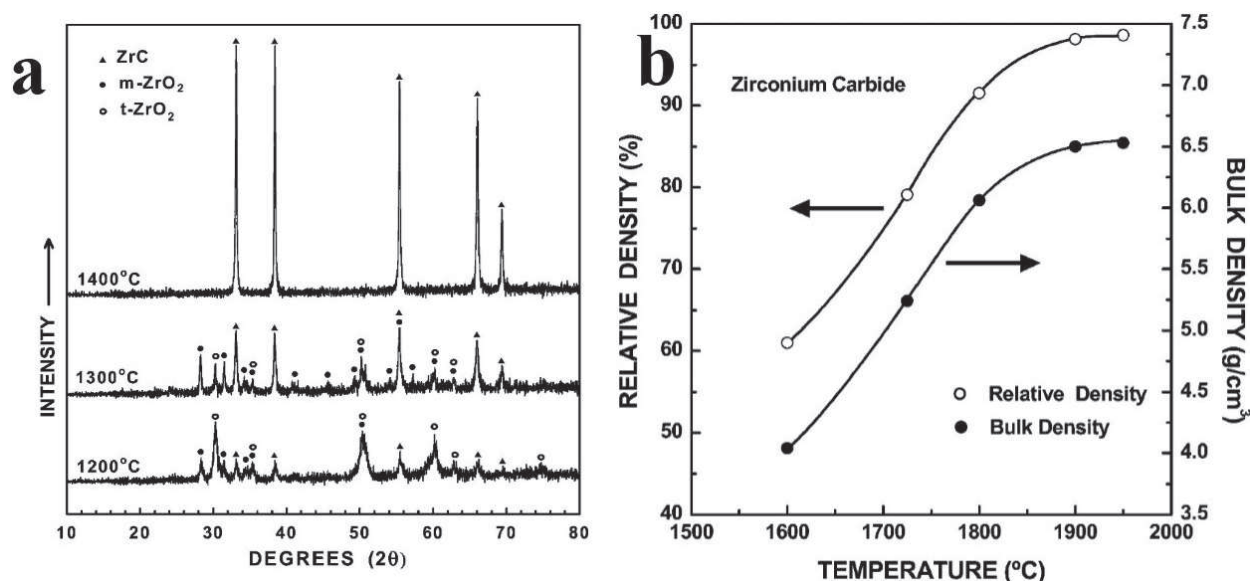
### 3. Synthesis of UHTC-based nanopowders

UHTC nanopowders can be synthesized by directly heating the dried gels in an inert atmosphere. By controlling the composition of the starting sols, unary UHTC nanopowders (e.g., ZrC, HfC, ZrB<sub>2</sub>, and HfB<sub>2</sub>) and composite nanopowders (e.g., ZrC-SiC, ZrB<sub>2</sub>-SiC, and ZrB<sub>2</sub>-ZrC-SiC) can be prepared.

#### 3.1. Synthesis of unary UHTC nanopowders

##### 3.1.1. Synthesis of metal carbide nanopowders

Sacks et al. [8] used zirconium and hafnium alkoxides as the metal precursors, acetylacetone as a chemical modifier, and phenolic resin and glycerol as the liquid carbon source. After controlled hydrolysis, condensation and drying of the precursor sol, the dried gel was obtained. The dried gel was heated at temperatures up to 1200–1600°C for carbothermal reduction reaction (Eq. (1)). During heating process, the organic components decompose and leave the fine-scale mixed metal oxide and amorphous carbon. The carbothermal reduction reaction begins at 1200°C is demonstrated by the appearance of ZrC diffraction peaks in the pyrolyzed products, as shown in **Figure 3a**. The carbothermal reduction reaction is completed after heat treatment at 1400°C for 2 h. After heated at 1475°C, the average crystallite size of

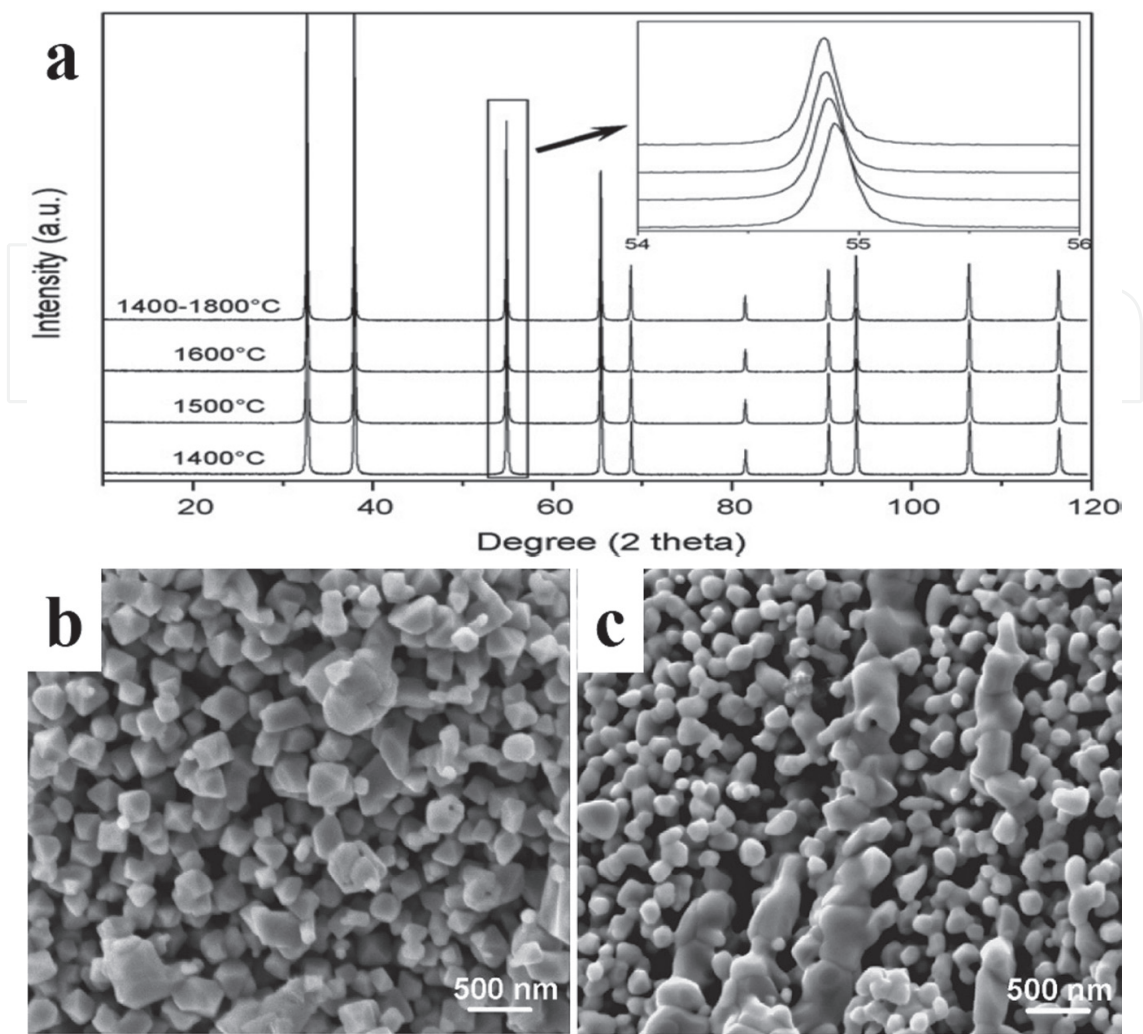


**Figure 3.** (a) X-ray diffraction patterns for heat treated samples prepared from a (zirconium n-propoxide/phenolic resin)-based sol. (b) Plots of relative density and bulk density versus sintering temperature for dry-pressed ZrC powder compacts [8].

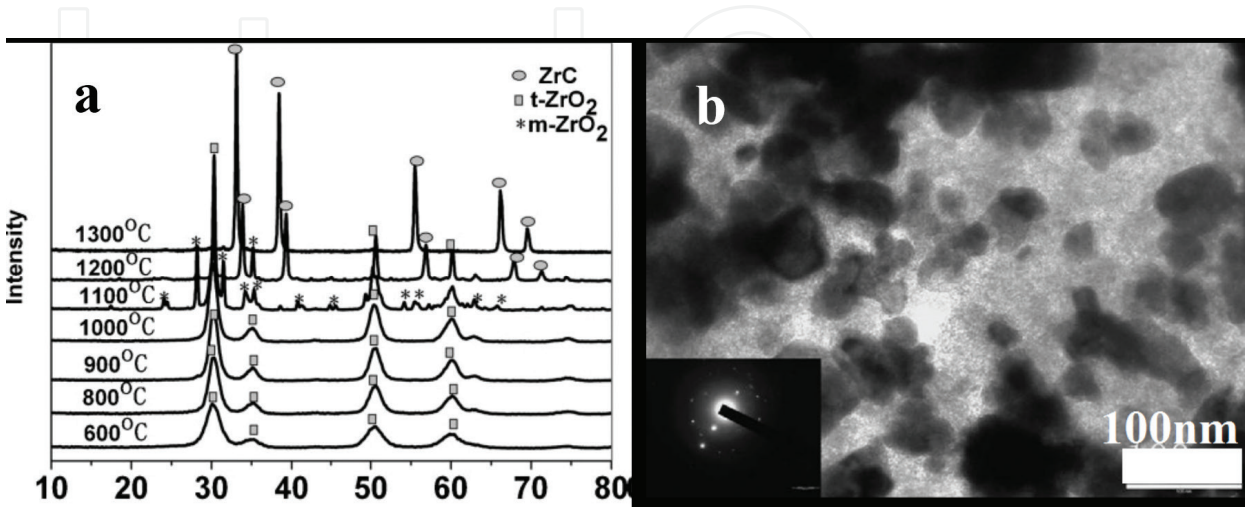
the ZrC nanoparticles is 100 nm. The oxygen content within ZrC nanopowders decreases with the increasing heating temperatures, from 3.3 wt% at 1475°C to 0.1 wt% at 1800°C. The ZrC nanopowders show good sinterability and can reach 98% of relative density after sintering at 1900°C with no pressure, as shown in **Figure 3b**.

High pyrolyzing temperatures are effective to synthesize metal carbide nanopowders with low impurity content. However, it causes the increase of the average crystallite size of the products. Dollé et al. [10] developed a two-step heat treatment approach to realize the purification of ZrC nanopowders with no significant increase in the average crystallite size by using metal alkoxide, sucrose, and acetic acid as the starting materials. Only diffraction peaks of ZrC can be observed when the precursor was heated at 1400°C for 3 h in argon. Only a slight shift of the peaks to the low angles with the increase of heating temperatures indicated an increase in the lattice parameter with temperature. The average crystallite sizes increase from 93 to 150 nm with the temperatures increase from 1400 to 1600°C. During the two-step heat treatment process, the precursor was first heated at 1400°C for 150 min and then at 1800°C for 6 min maintaining the heating rate at 20°C/min. The average crystallite size came out to be 110 nm, a slight increase as compared to the one heated at 1400°C (**Figure 4**).

Tao et al. [21] developed a preceramic route to synthesize ZrC nanopowders by using zirconium oxychloride, acetylacetone, and salicyl alcohol as the raw materials (Eq. (8)). ZrC nanopowders can be prepared by directly heating the powdery precursor in argon. Only diffraction peaks of ZrC can be detected when the precursor was pyrolyzed at 1300°C for 2 h (**Figure 5a**). Such low temperature indicated a fine contact between the metal precursor and the carbon precursor. Disadvantage of the technique is the presence of the residual carbon in the final ZrC products, as can be observed in **Figure 5b**. ZrC nanoparticles seem embedded in the matrix of amorphous carbon. This might be ascribed to the reason that it is not easy to control the degree of the polymerization during the synthesis process.



**Figure 4.** (a) Evolution of the XRD patterns of the different samples as a function of their respective heat treatment under argon flow. (b) SEM image of an agglomerate microstructure of a sample heat treated at 1600°C for 3 h. (c) SEM image of an agglomerate microstructure of a sample heat treated at 1400°C for 150 min then at 1800°C for 6 min [10].

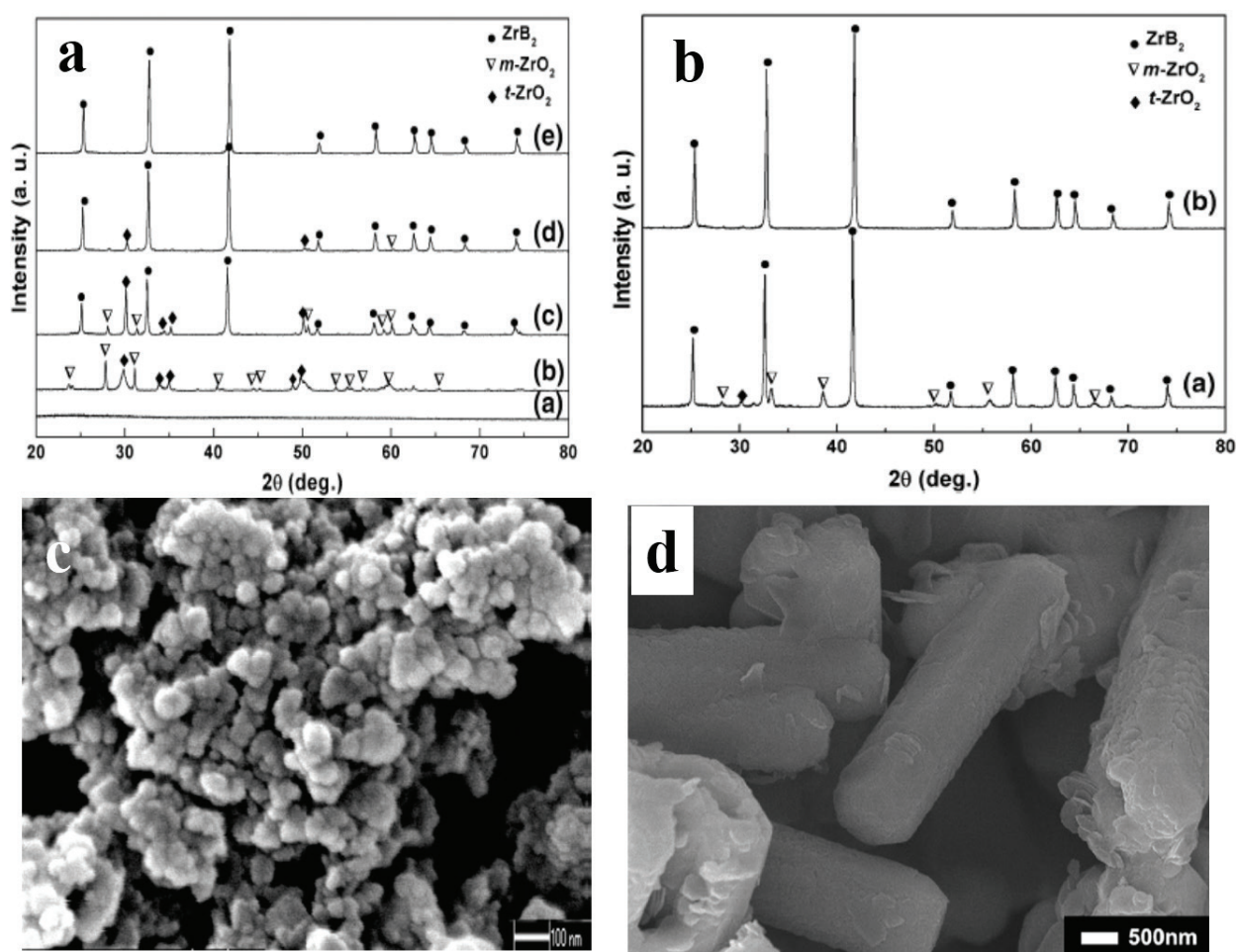


**Figure 5.** (a) XRD patterns of the ceramic products obtained at different temperatures. (b) TEM image of the ZrC powders pyrolyzed at 1300°C for 2 h [21].



### 3.1.2. Synthesis of metal diboride nanopowders

Boric acid is the commonly used boron source for the synthesis of metal diboride nanopowders via sol-gel routes. Li et al. [22, 23] prepared  $\text{ZrB}_2$  nanopowders by using zirconium n-propoxide as the zirconia source, sucrose as the carbon source, and boric acid as the boron source. By mixing the acetylacetone-modified zirconium n-propoxide with methanol solution of boric acid and sucrose, the precursor sol was obtained.  $\text{ZrB}_2$  nanopowder was obtained by heating the dried gels at high temperatures in an inert atmosphere (Eq. (2)). The B/Zr molar ratio plays a significant role in the formation of pure  $\text{ZrB}_2$  during the carbothermal reduction reaction. Boron loss due to the high vapor pressure of boron oxide at high temperature must be compensated during the high temperature carbothermal reduction. Pure  $\text{ZrB}_2$  nanopowders with particle sizes down to 100 nm can be prepared by tailoring the composition of the starting precursor sols (a B/Zr molar ratio of 2.3) and heat treatment temperature (1550°C) (**Figure 6**). Rod-like structure can also be synthesized by controlling the gelation temperature of the precursor sols.

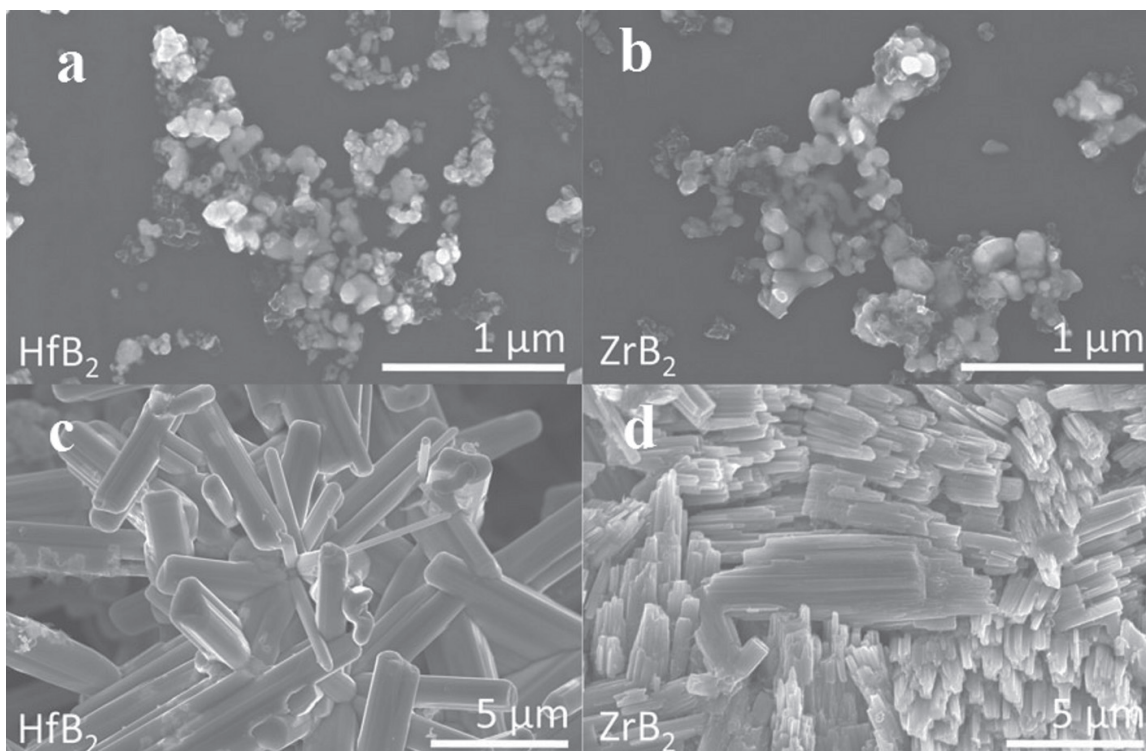


**Figure 6.** (a) XRD patterns of precursor and precursors pyrolyzed at various temperatures for B/Zr = 2.3. From bottom to top, precursor, 1100, 1300, 1400, 1550°C [22]. (b) XRD patterns of precursors pyrolyzed at 1550°C for 2 h with molar ratios of B/Zr 2.0 (bottom) and 2.3 (top) [22]. (c) SEM image of  $\text{ZrB}_2$  nanoparticles pyrolyzed at 1550°C for 2 h with B/Zr = 2.3. The scale bar in the SEM is 100 nm [22]. (d) SEM image of  $\text{ZrB}_2$  nanoparticles pyrolyzed at 1550°C for 2 h with a gelation temperature of 85°C [23].

Walker and Corral [24] applied the metal oxychloride hydrates, triethyl borate, and phenolic resin as the starting materials to synthesize  $\text{HfB}_2$  and  $\text{ZrB}_2$ , as shown in **Figure 7**. The starting materials were mixed by high-energy ultrasonication to form precipitate-free sols which turn into stable gels without any addition of catalysts. They pointed out that the conversion process to  $\text{ZrB}_2$  involved the formation of  $\text{ZrC}$  subsequently reacting with boron oxide to form  $\text{ZrB}_2$ . Both  $\text{HfB}_2$  and  $\text{ZrB}_2$  prepared by optimizing the chemistry, processing, and heat treatment conditions can result in the desired final ceramic products.

### 3.2. Synthesis of UHTC composite nanopowders

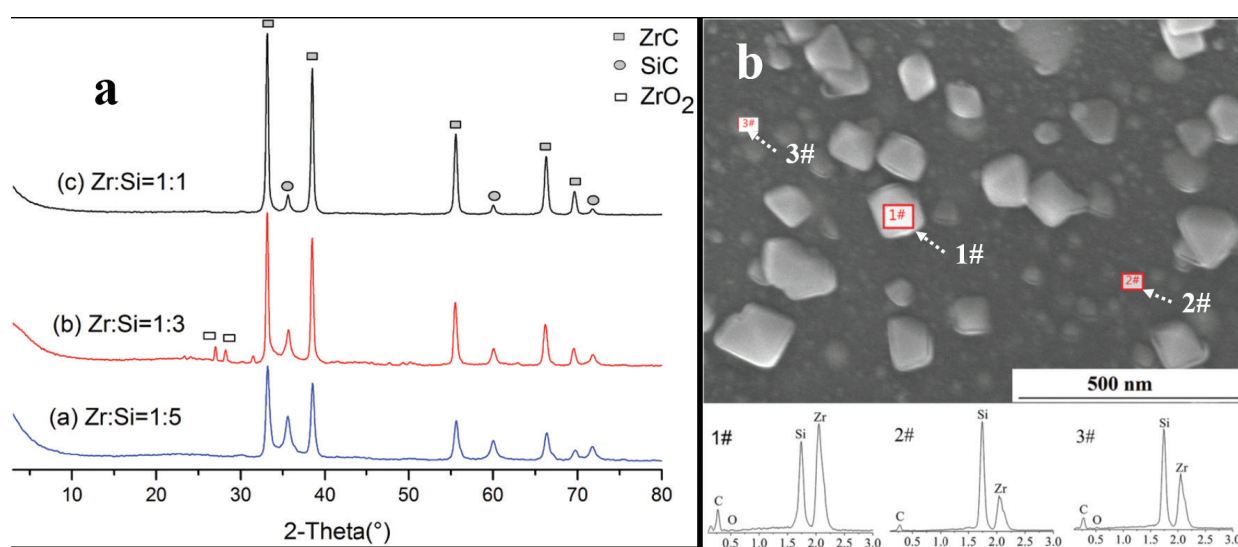
It is not easy to sinter phase-pure UHTC materials due to their strong covalent bonds. Sintering aids (e.g., silicon carbide-SiC) are commonly introduced to the UHTC matrix to improve their sinterability and properties of the corresponding ceramic materials [7]. It is one of the advantages of sol-gel techniques to obtain homogenous distribution of all reactants at molecular level. Precursors of UHTC-SiC composite powders can be synthesized by introducing independent precursors of UHTCs and SiC into a solvent (ethanol, toluene, and tetrahydrofuran, etc.) with the liquid precursor itself acting as a mutual solvent. The precursors are dried and cured at relatively low temperatures and then heated at high temperatures to complete the carbothermal reduction reaction to form HTC-SiC composite powders, such as  $\text{ZrC-SiC}$ ,  $\text{ZrB}_2\text{-SiC}$ , and  $\text{HfB}_2\text{-SiC}$ , etc. [25–30].



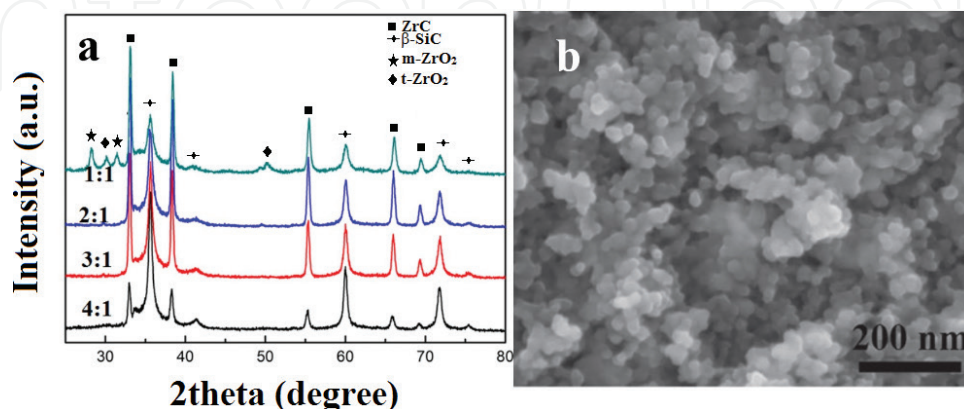
**Figure 7.** SEM images of heat-treated (a)  $\text{HfB}_2$  and (b)  $\text{ZrB}_2$  precursor with fine spherical particle morphology and extreme localized particle growth for (c)  $\text{HfB}_2$  and (d)  $\text{ZrB}_2$  that forms rod-like particles within the powder [24].

Cai et al. [28] used methylphenyldichlorosilane ( $\text{MePhSiCl}_2$ ) as a SiC precursor to react with zirconocene dichloride ( $\text{Cp}_2\text{ZrCl}_2$ ) to form organometallic polymers. ZrC-SiC composite powders with controlled Zr/Si molar ratios can be synthesized by pyrolyzing the polymers at  $1400^\circ\text{C}$  for 2 h. The particles seen in the SEM image are composed of three parts: large grains, the smaller grains, and the black matrix (**Figure 8b**). It is not easy to precisely control the residue carbon in this reaction system.

Wang et al. [31] prepared ZrC-SiC hybrid precursors by dissolving acetylacetonate-modified zirconium alkoxide (PZC) into liquid polycarbosilane (LPCS). In their reaction system, LPCS simultaneously played the role of a solvent, carbon source, and silicon source. ZrC-SiC composite powders with spherical morphology and grain sizes less than 60 nm can be synthesized by heating the hybrid precursors at  $1550^\circ\text{C}$  in argon (**Figure 9**). The constituent of the final ZrC-SiC composite powders can be controlled by tailoring the mass ratios of LPCS/PZC. The synthesized ZrC-SiC nanopowders exhibit improved oxidation resistance compare to ZrC nanopowders.



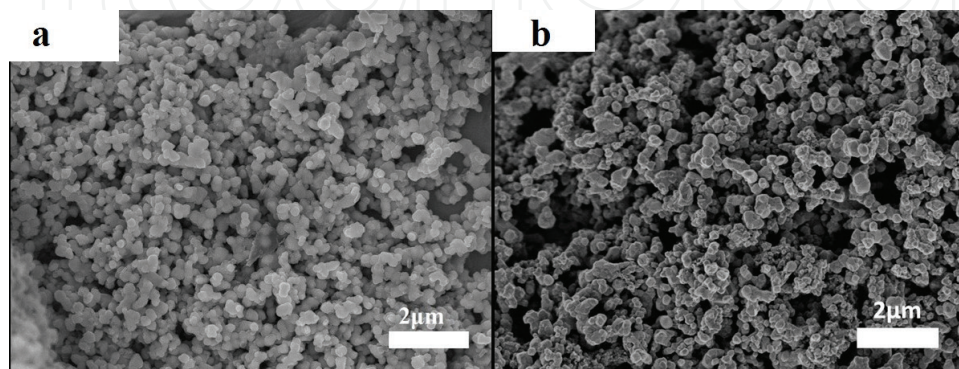
**Figure 8.** (a) XRD patterns of the poly-yne polymers pyrolyzed at  $1400^\circ\text{C}$  and (b) EDS spectra of the ceramic sample from the Zr:Si = 1:1 precursor [28].



**Figure 9.** (a) XRD patterns of samples derived from hybrid precursors with various LPCS/PZC mass ratios after pyrolysis at  $1550^\circ\text{C}$  in argon and (b) SEM image of the ZrC-SiC powders derived from a hybrid precursor with LPCS/PZC = 1 in mass ratio [31].



Liang et al. [32] used zirconia sol, tetraethylorthosilicate (TEOS) and sucrose as the independent zirconium-, silicon- and carbon-containing source. Hybrid sol can be prepared by introducing TEOS and sucrose into zirconia sol. ZrC-SiC composite powders with controlled constituent are obtained by pyrolyzing the hybrid gels at 1500°C for 1 h in vacuum (**Figure 10**). It is possible to precisely control both the residue carbon content and SiC content in the final composite powders by using these independent carbon sources and silicon sources as the starting materials. However, no sintering behavior of the as-synthesized ZrC-SiC nanopowders is examined.



**Figure 10.** ZrC-SiC composite powders with different SiC volume percentage. (a) ZrC-10 vol% SiC and (b) ZrC-90 vol% SiC [32].

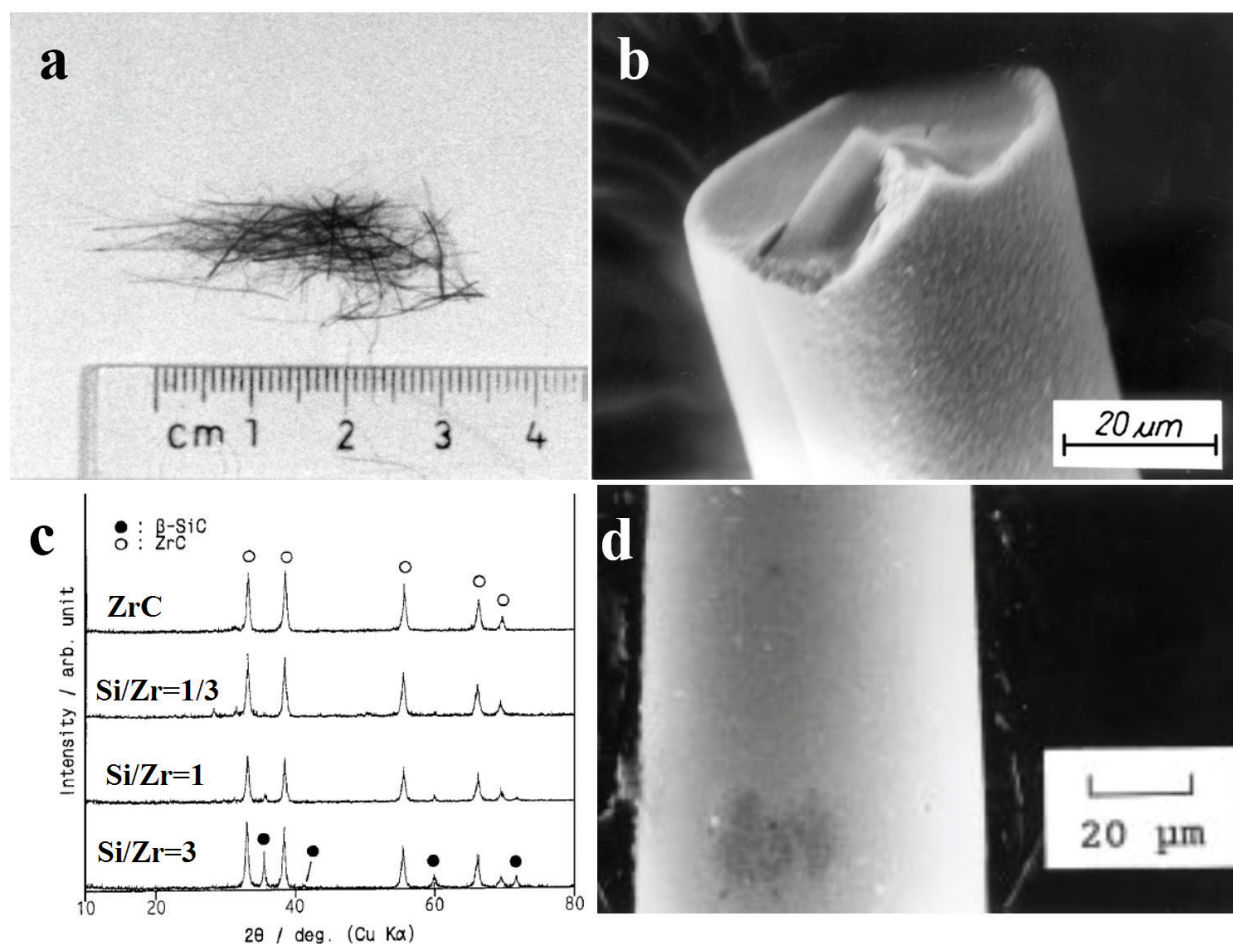
## 4. Synthesis of UHTC-based ceramic fibers

The sol-gel technique enables the processing of ceramics in various desirable shapes, such as monoliths, films, fibers, etc. [33]. The viscosity of the liquid precursors of UHTCs can be tuned by condensation polymerization of the sols themselves or by adding viscous polymers into the mixed solution. These viscous precursors can be drawn into fibrous shapes, dried, cured, and heated at high temperatures for the carbothermal reduction reaction to form UHTC ceramic fibers. Combined with different spinning techniques, such as dry spinning and electrospinning, UHTC fibers can be successfully synthesized [16, 17, 34–39].

### 4.1. UHTC fibers prepared by a hand-drawing method

Hand-drawing is a simple but effective method to estimate the spinnability of the spinning solution. Fibers are hand-drawn by extracting a glass rod from the viscous solutions. Spinnability can be estimated by the length of the drawn fibers. Preiss et al. [17] prepared polymeric precursors for carbothermal reactions from the chelate derivatives of zirconium alkoxides in alcohols by reaction with organic compounds having two or more reactive OH groups. These organic groups act as bridging ligands in transesterification and condensation polymerization yielding either spinnable viscous solutions or elastic gels. The spinnability of these polymeric precursors was estimated by hand-drawing fibers from the solutions. ZrC-based fibers with a diameter about 20 μm can be obtained by heating the hand-drawn precursor fibers in an argon atmosphere at 1550°C (**Figure 11a and b**).



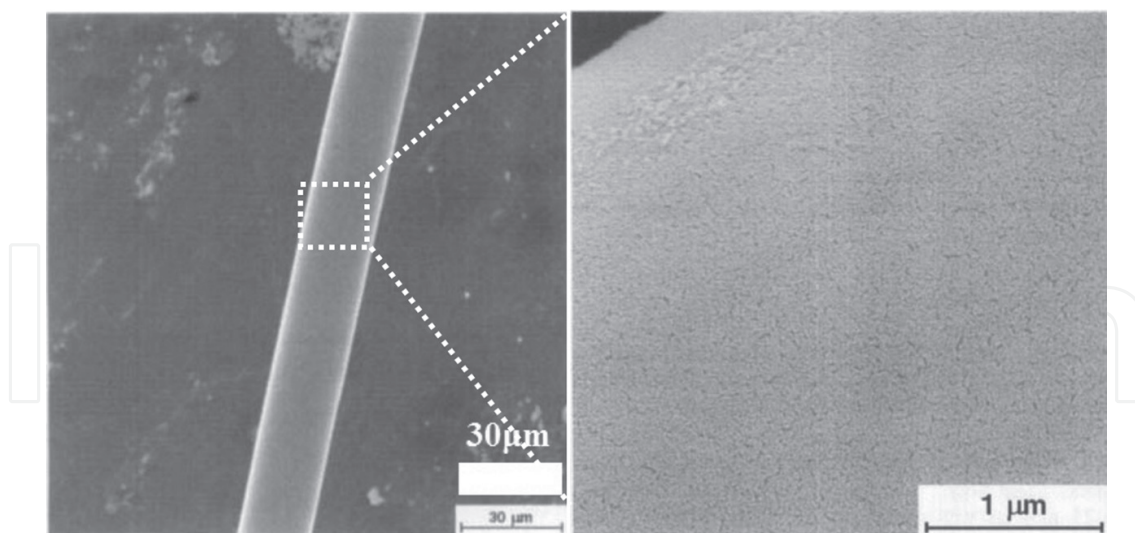


**Figure 11.** Photograph (a) and SEM, (b) image of ZrC fibers treated at 1550°C [17], (c) XRD patterns of fibrous products obtained by heat treatment at 1500°C in argon and (d) SEM image of ZrC-SiC fiber with a Si/Zr molar ratio of 0.92 [34].

Hasegawa et al. [34] prepared ZrC-SiC fibers by using zirconium tetrakis(2,4-pentanedionate) (ZTP), TEOS, and phenolic resin as raw materials via a hand-drawing method. The composition of the final ZrC-SiC fibers can be controlled by tailoring the Si/Zr molar ratios of the starting sols. The preceramic fibers were converted into ZrC or ZrC-SiC ceramic fibers after pyrolysis at 1500°C for 4 h under argon flow (**Figure 11c**). The diameter of the as-prepared ZrC fibers is about 40 μm (**Figure 11d**).

#### 4.2. UHTC fibers prepared by a dry spinning method

A continuous dry spinning process was applied to prepare ZrC-based fibers by Hu et al. [14]. In their works, ZTP and phenolic resin were used as the starting precursors to form a highly viscous mixed sol. Phenolic resin played the role of a carbon source and the spinning aid. ZrC-based fibers with fine-diameter (~20 μm) and relatively smooth surfaces were obtained by dry spinning the mixed sols and heating at 1450°C. The SEM images of the as-synthesized ZrC fiber show that the fiber has a porous, extremely fine-grained microstructure (**Figure 12**).



**Figure 12.** SEM images of a single ZrC fiber after carbothermal reduction at 1450°C [14].

However, very few studies were reported on the synthesis of UHTC fibers by the dry spinning process due to the brittleness of the ceramic fibers caused by the massive weight loss during carbothermal reduction. The state-of-the-art technique is not mature enough to apply this kind of scalable synthesis process of UHTC-based fibers.

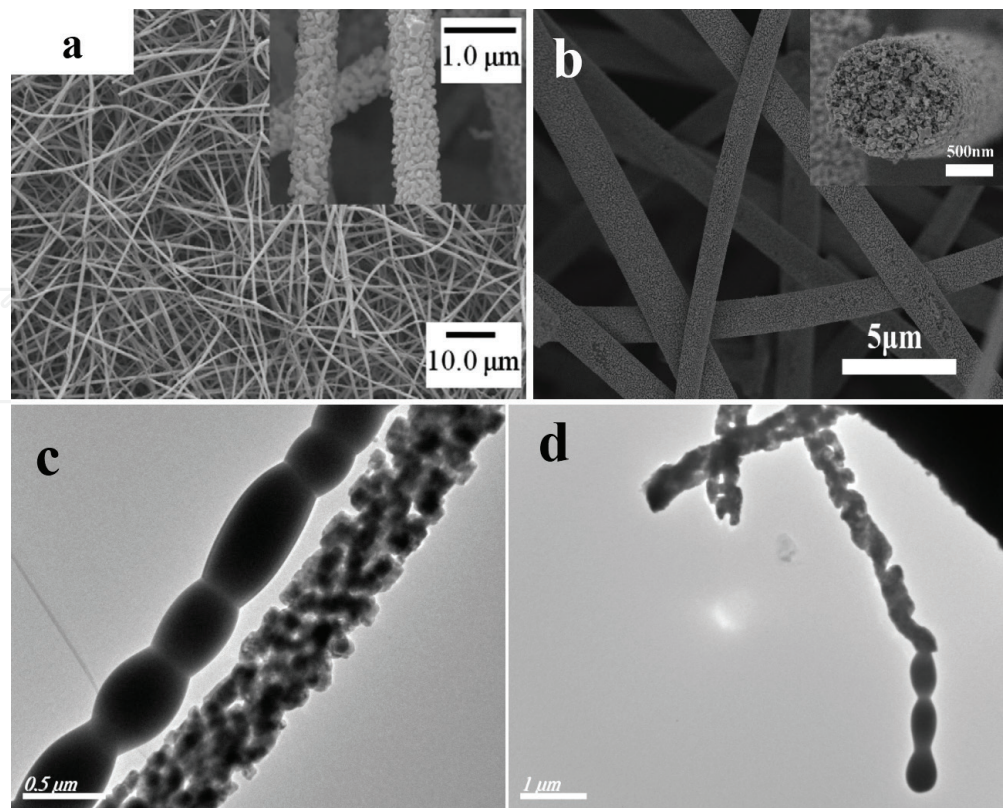
#### 4.3. UHTC fibers prepared by an electrospinning method

Electrospinning is a simple and versatile method for generating nanofibers of polymers and ceramics [40, 41]. The typical procedure for the preparation of ceramic nanofibers by electrospinning includes the preparation of precursor solution, the electrospinning of the precursor solution to get inorganic/polymer composite nanofibers, and the postheat treatment to get ceramic nanofibers based on the carbothermal reduction reaction. Generally, high molecular polymers such as polyvinylpyrrolidone (PVP), polyvinyl alcohol (PVA), polyacrylonitrile (PAN), and cellulose acetate are used as the spinning aids to facilitate the spinning process. The parameters including applied voltage, flow rate, and working distance influence the microstructure of the final ceramic nanofibers.

Using ZTP as the zirconia source, cellulose acetate as the carbon source and spinning aids, ZrC-based nanofibers were prepared. ZrC was initially formed at 1400°C and became the major phase at 1600°C. The fibrous structures of the electrospun green nanofibers could be well retained after high temperature ceramization.

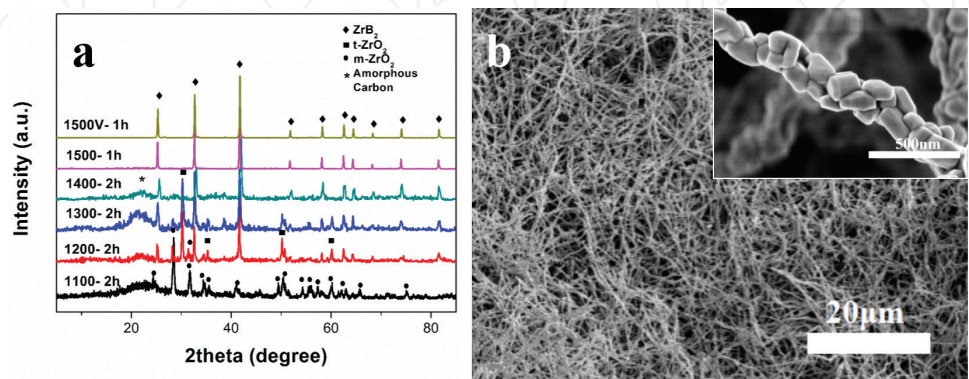
Li et al. [39] used PZO as the zirconia source, PAN as the carbon source and spinning aid to synthesize ZrC nanofibers via electrospinning. In their reaction system, a carbon source played significant role in controlling the microstructure of the pyrolyzed ZrC nanofibers. With sucrose used as the extra carbon source in PZO/PAN spinning solution, fine ZrC nanofibers composed of ZrC nanoparticles were obtained after pyrolysis at 1400°C for 2 h (**Figure 13b**). The as-synthesized ZrC nanofibers were porous. After sintering, bamboo-like structures are formed due to Ostwald ripening.





**Figure 13.** (a) SEM image of ZrC nanofibers heat at 1600°C for 2 h. The spinning solution was prepared from mixing ZTP and phenolic resin with a C/Zr molar ratio of 5.5 [36]. (b) SEM image of ZrC nanofibers after pyrolysis at 1400°C for 2 h under argon flow by using PZO/PAN/sucrose as the spinning solution with a C/Zr molar ratio of 3.3 [39]. (c) and (d) TEM images of ZrC nanofibers after pyrolysis at 1400°C for 2 h electrospun from PZO/PAN spinning solution.

ZrB<sub>2</sub> nanofibers can also be prepared by introducing a boron source into the ZrC spinning solutions [16, 37]. Formation of ZrB<sub>2</sub> was initiated at 1200°C with complete transformation to pure ZrB<sub>2</sub> at 1500°C (**Figure 14**). The as-synthesized ZrB<sub>2</sub> nanofibers were porous and composed of ZrB<sub>2</sub> nanoparticles.

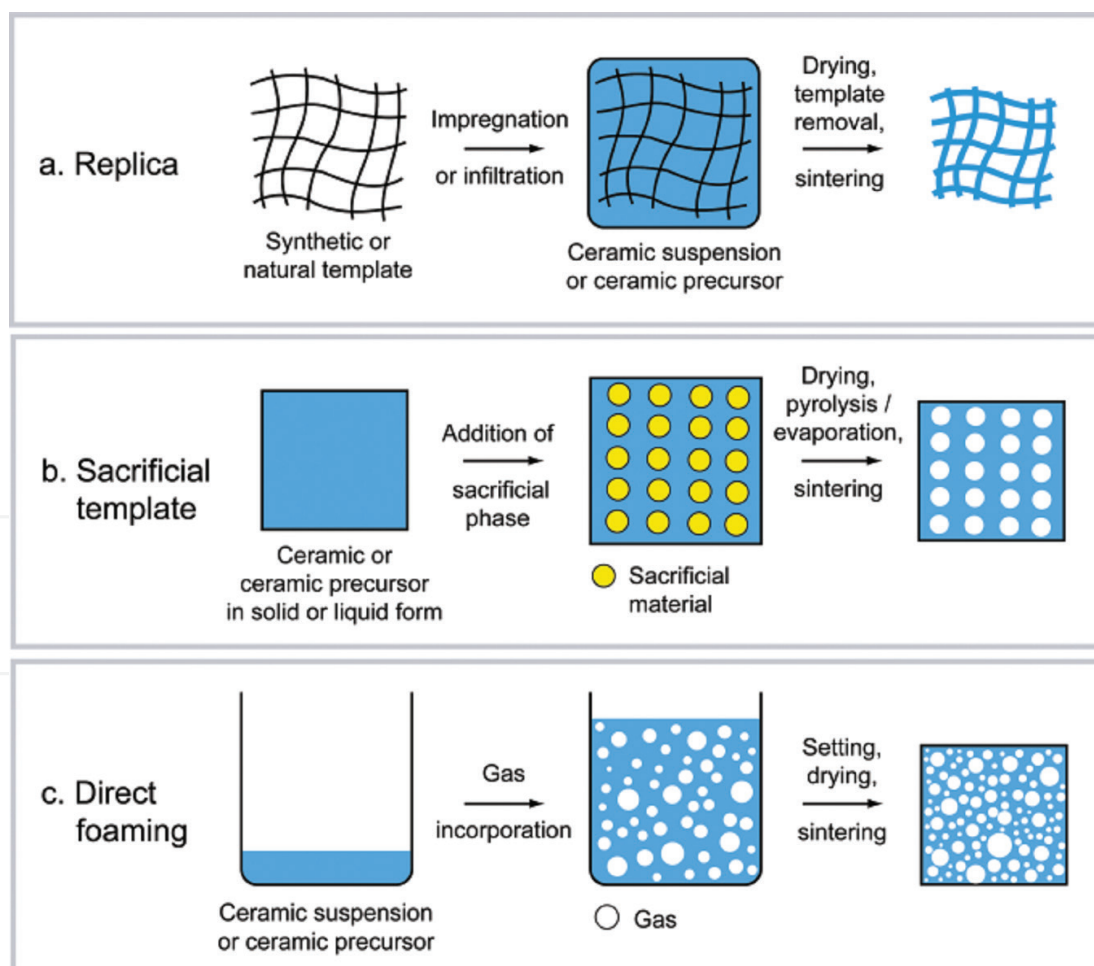


**Figure 14.** (a) XRD patterns of the nanofibers after pyrolysis. From bottom to top: 2 h at 1100°C, 2 h at 1200°C, 2 h at 1300°C, 2 h at 1400°C, and 1 h at 1500°C in an argon atmosphere; 1 h at 1500°C in vacuum. (b) SEM image of ZrB<sub>2</sub> nanofibers after pyrolysis at 1500°C for 1 h in argon. The scale bar in the inset is 500 nm [16].

## 5. UHTC-based porous ceramics via sol-gel routes

Materials containing tailored porosity exhibit special properties and features that usually cannot be achieved by their conventional dense counterparts [42, 43]. Nowadays, therefore, porous materials find many applications as end products in several technological processes. Due to the intrinsic properties of porous ceramics, such as lightweight, low thermal conductivity, high specific strength, and excellent thermal insulation, UHTC-based porous ceramics could be applied as the promising candidate materials in thermal protection systems of hypersonic vehicles.

The processing routes used for the production of porous ceramics can be classified into replica, sacrificial template, and direct-foaming methods, as schematically shown in **Figure 15** [42]. It is important to get a well-dispersed ceramic slurry or liquid precursor for the fabrication of porous ceramics with tailored microstructure and chemical composition. Sol-gel techniques have been widely used as ceramic precursors to prepare porous ceramics, such as zirconia, alumina, and silicon carbide–based porous ceramics.



**Figure 15.** Scheme of possible processing routes used for the production of macroporous ceramics [42]. (a) Replica method; (b) Sacrificial template method; (c) Direct foaming method.

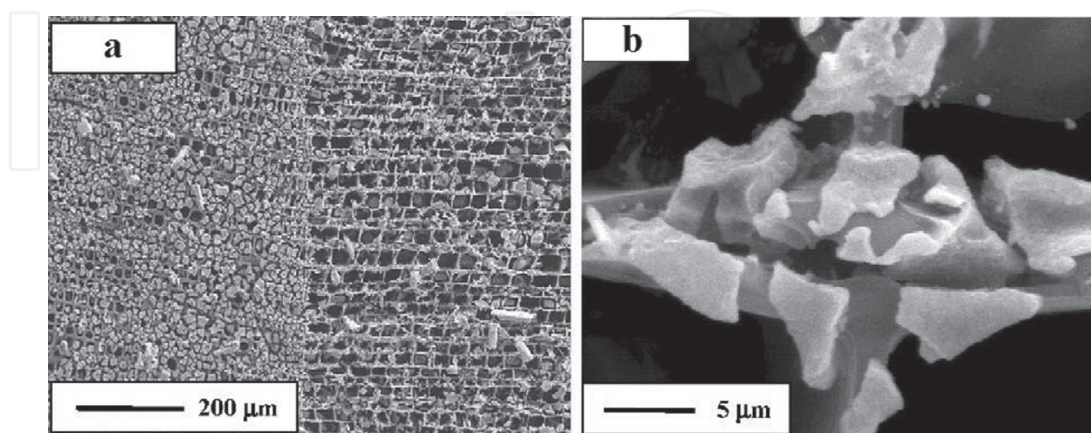


### 5.1. Porous ZrC ceramics prepared from replica routes

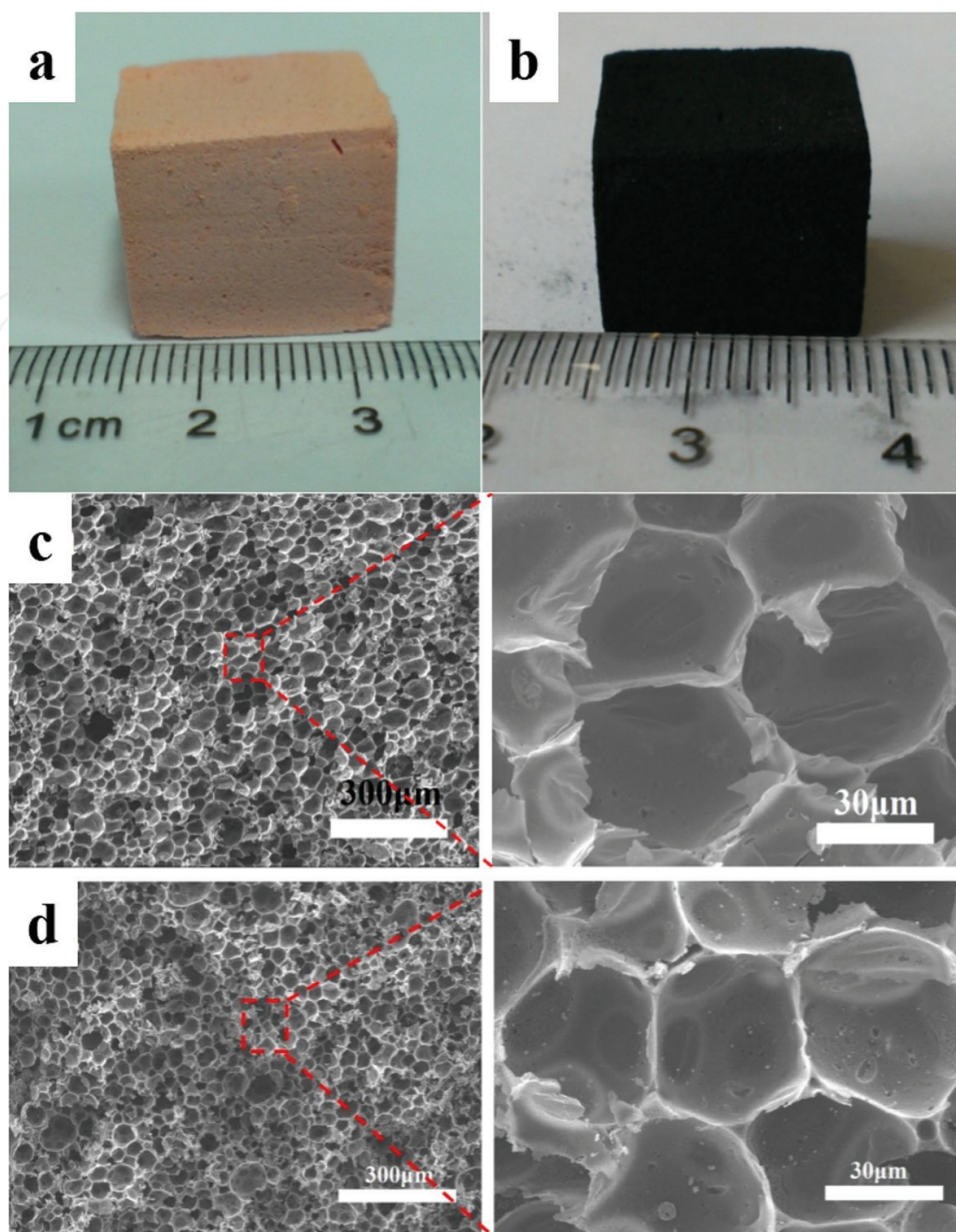
Though sol-gel routes have been established to synthesize UHTC nanopowders and nanofibers, focus on the preparation of UHTC-based porous ceramics is rare. The replica process was applied to prepare porous ZrC/C ceramic by Rambo et al. [44] where pine wood was used as the biological template for manufacturing of highly porous, biomorphic ZrC/C ceramics with zirconium n-propoxide as the zirconia source. Pine wood was first pyrolyzed at 800°C for 1 h under N<sub>2</sub> to obtain a biocarbon template. The biocarbon template was then infiltrated with zirconia sol and dried at 110°C for 1 h to obtain the ZrC/C preceramic. ZrC/C-ceramic was prepared by heating the infiltrated biocarbon template at 1600°C for 1 h under argon flow. The original pine char microstructure was reproduced in the ZrC/C-ceramic. Island-like ZrC particles were observed on the cell walls and in the channels, as shown in **Figure 16**. The porosity of the ZrC/C-ceramic was ~78%.

### 5.2. ZrC foams prepared from direct-foaming routes

In direct-foaming methods, porous materials are produced by incorporating air into a suspension or liquid media, which is subsequently set in order to keep the structure of air bubbles created [42]. The consolidated foams are afterwards heated at high temperatures to obtain porous ceramics. Li et al. [15] prepared ZrC foams by employing a commercial direct-foaming technique for phenolic resins. Zirconia sol was used as the zirconia precursor, while commercial foamable phenolic resin was used as the carbon source and foaming aid. By thermal-setting the wet foam and pyrolyzing the foamed green body at 1600°C, highly porous ZrC foam was prepared. The density and porosity of as-prepared ZrC foam were 0.16–0.19 g/cm<sup>3</sup> and 83–90%, respectively. The as-prepared ZrC foam showed closed cell structures with average cell sizes about 40 μm, as shown in **Figure 17**. The as-synthesized ZrC foam displayed excellent thermal stability up to 2400°C. However, it is not possible to precisely control the residue carbon in the ZrC foam in their reaction system. Foamability of the mixtures originated due to phenolic resin decreased as the Zr content increased. About 47 wt% amorphous carbon was observed in the final ZrC foam.



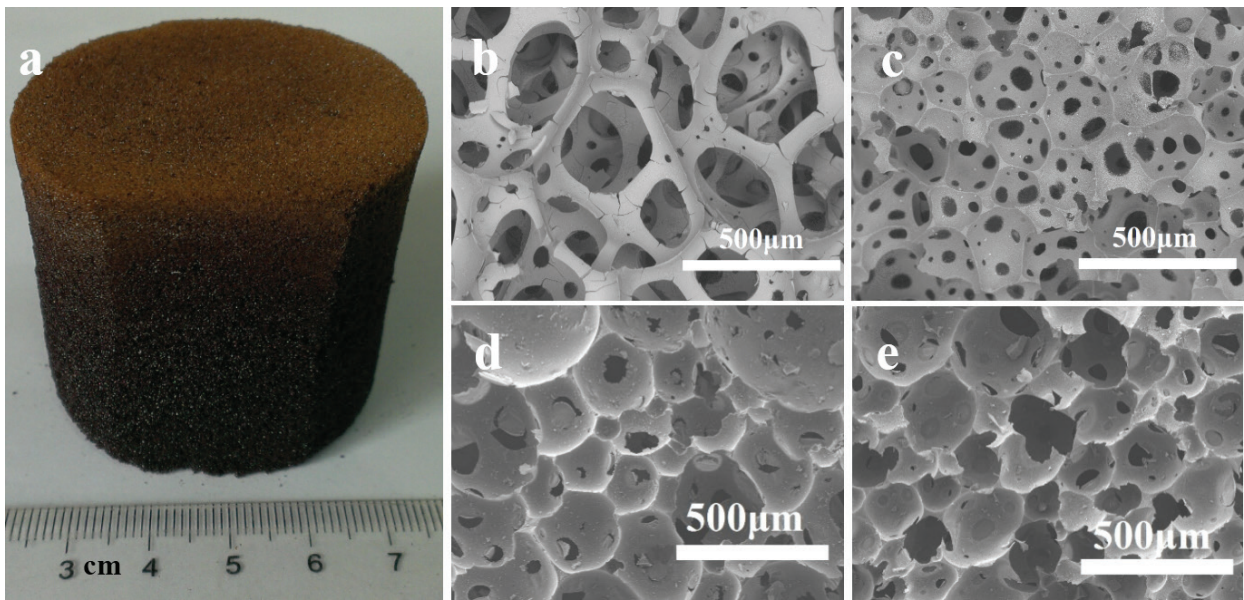
**Figure 16.** SEM images of the biomorphic ZrC/C-ceramic at different magnifications [44]. (a) Low magnification SEM image. (b) Higher magnification SEM image of a typical strut from (a).



**Figure 17.** (a) Photographs of the foamed green body and (b) ZrC ceramic foam obtained from pyrolysis at 1600°C for 1 h. SEM images of (c) the preceramic foam and (d) ZrC foam after pyrolysis at 1600°C for 1 h in Ar [15].

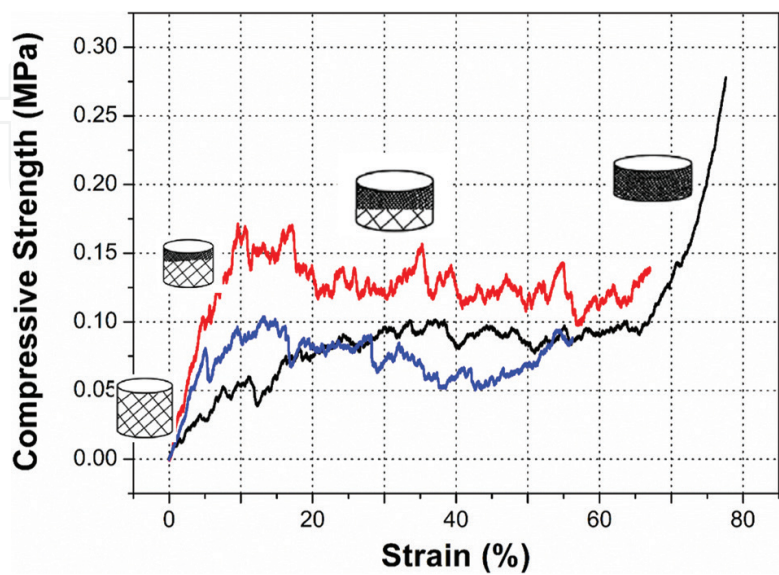
Li et al. [45] developed another method for the preparation of stoichiometric ZrC foams by direct foaming of zirconia sols. Sucrose used as a carbon source was dissolved into zirconia sol to get a foamable sol. The stabilization of the wet foam was based on the gelation of the zirconia sol under thermal aging. The microstructure of the ZrC foams can be tailored by controlling the foaming parameters, such as the viscosities of the sols, the concentration of the blowing and curing agents. The ZrC foams prepared with open- or closed-cell structures are shown in **Figure 18**. The densities of the stoichiometric ZrC foams were in the range of 0.12–0.53 g/cm<sup>3</sup>.





**Figure 18.** (a) Photograph of the preceramic foam prepared from direct foaming of zirconia sol. SEM images of the preceramic foams after being pyrolyzed at 1500°C foaming by precursor sol with various viscosities. (b), 1552 cP; (c), 2025 cP; (d), 2699 cP; (e), 2954 cP [45].

**Figure 19** shows compressive stress-strain curves for ZrC foams prepared from direct foaming of zirconia sols [45]. In compression, all show a linear-elastic regime followed by a plateau of roughly constant stress, leading into a final regime of steeply rising stress. Upon compression, the foam undergoes a progressive collapse of the cells, with the lower part of the foam remains completely undamaged. In the plateau region, the stress is assumed to be independent of the strain as part of the structure collapses, while other parts of the structure remain elastic. Beyond the plateau, densification takes place and the stress rises sharply as complete densification begins.



**Figure 19.** Typical compressive stress-strain response of ZrC foams prepared from direct foaming of zirconia sols [45].

## 6. Conclusions

A sol-gel technique has been applied to prepare UHTC-based materials using metal alkoxide and oxychloride as a metal precursor. First, sols of metal oxide are prepared by hydrolysis of a metal precursor with the modification of bidentate ligands (e.g.,  $\beta$ -diketones, acetic acid, and cellulose acetate) to slow down the system's reactivity. Then soluble carbon- and boron-containing compounds, such as sucrose, phenolic resin, PAN, boric acid, and triethyl borate, are introduced to metal oxide sols. The hybrid sols are dried, cured, and heated at high temperatures to complete the conversion of metal oxides to nonoxides. UHTC nanopowders can be synthesized at 1300–1600°C under a protective atmosphere. The average size of the crystallites is controlled in the range of 60–200 nm by controlling the synthesis parameters. UHTC nanofibers can be synthesized by combining a sol-gel technique with spinning techniques, such as dry spinning and electrospinning. The as-synthesized UHTC nanofibers are porous and composed of nanoparticles. Porous UHTC materials with controllable cell structures can be prepared by the replica technique and direct-foaming methods. The as-prepared porous UHTC materials possess high porosities and can withstand 2400°C high temperature aging.

Although sol-gel routes provide great possibilities to produce UHTC-based materials with desired shapes, the high temperature thermal reduction process is still an indispensable procedure during which large mass loss occurs. It is still highly welcomed to synthesize UHTC precursors with high ceramic yield by directly converting into UHTC materials without the reduction process.

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