In-situ synthesis of ultra-fine ZrB₂-ZrC-SiC nanopowders by sol-gel method

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Abstract

ZrB₂-ZrC-SiC nanopowders with uniform phase distribution were prepared from cost-effective ZrOCl₂·8H₂O by a simple sol-gel method. The synthesis route, ceramization mechanism and morphology evolution of the nanopowders were investigated. ZrB₂-ZrC-SiC ceramic precursor can be successfully obtained through hydrolysis and condensation reactions between the raw materials. Pyrolysis of the precursor was completed at 650 °C, and it produced ZrO₂, SiO₂, B₂O₃ and amorphous carbon with a yield of 39% at 1300 °C. By heat-treated at 1500 °C for 2 h, highly crystallized ZrB₂-ZrC-SiC ceramics with narrow size distribution were obtained. With the holding time of 2 h, both the crystal size and the particle size can be refined. Further prolonging the holding time can lead to serious particles coarsening. Studies

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on the microstructure evolution of the generated carbon during the ceramic conversion demonstrates the negative effect of the ceramic formation on the structure order improvement of the carbon, due to the large amount of defects generated in it by the boro/carbothermal reduction reactions.

Keywords: A: Sol-gel; C: ZrB_2 -ZrC-SiC; Nanopowder

1. Introduction

Carbides and diborides of transition metals with melting temperature higher than 3000 °C, such as HfC, ZrC, TaC, HfB₂, ZrB₂ and TaB₂, are known as ultra-high temperature ceramic materials (UHTCs). They are fueling the development of aerospace materials, refractory materials and protection materials, etc., owing to their excellent thermochemical properties, outstanding oxidation resistance, high physical stability and mechanical properties in ultra-high temperature environments [1-5]. Zirconium boride (ZrB₂) remains the most promising class in the family of UHTCs, due to its light weight, remarkable mechanical strength and low thermal expansion coefficient. However, the applications of monolithic ZrB₂ in ultra-high temperature fields lag well behind the anticipated level, ascribed to its inherent brittleness, weak oxidation resistance and challenging sintering features [6].

To overcome its drawbacks, ZrB₂-based ceramic composites, such as ZrB₂-ZrC and ZrB₂-SiC binary systems have been prepared using various approaches [7-9]. Compared with monolithic ZrB₂, ZrB₂-based ceramic composite possesses broadened antioxidant range by adjusting its microstructures and compositions, thus exhibiting excellent oxidation resistance and high temperature mechanical properties. As reported previously, the adjunction of SiC can improve the sintering properties, mechanical performance and oxidation resistance of ZrB₂, which is also applicable to ZrC acting as a sintering aid and reinforcing agent [10, 11]. Moreover, both ZrC and SiC enrolled in ZrB₂ based ceramics can play the role as inhibitors for the growth of grains [12, 13]. Besides ZrB₂ based binary systems, investigation concerning

ZrB₂-ZrC-SiC ternary system revealed that the composite exhibited further improved performance than the binary systems [14-15]. The research suggests that mechanical performance of the prepared composites are determined by the microstructure and densification of the sintered bodies, which is directly related to the particle size and homogeneity of the ceramic phases. Definitely, to prepare homogeneous and fine powder mixtures of ZrB₂, ZrC and SiC is crucial to obtain high performance ZrB₂-ZrC-SiC composites.

Recently, ZrB₂-ZrC-SiC ternary system has been widely developed by various methods, such as metallothermic reduction of zircon using M/ZrSiO₄/B₂O₃/C (M = Al, Mg) system [16, 17], or Zr/Si/B₄C system [6], liquid precursor methods using polyzirconoxanesal, boric acid and poly(methylsilylene)ethynylene as precursors [18], and sol-gel procedure using zirconium n-butoxide, boric acid, tetraethyl orthosilicate, and acetyl acetone as raw materials [19]. Among various approaches, sol-gel method becomes popular because it is convenient to be operated and controlled, in which high purity and homogeneity of ceramic components can be obtained at relatively low temperature [18, 20]. During the preparation of zirconium-containing precursor, organic zirconium or anhydrous zirconium, such as polyzirconoxanesal, zirconium n-butoxide and zirconium tetrachloride (ZrCl₄), have been frequently used as the zirconium source. The high cost and poor stability of these zirconium sources restrict the large-scale industrial production of the ZrB₂ based ceramics. To overcome this problem, cost-effective zirconium oxychloride octahydrate (ZrOCl₂·8H₂O) was choosed as zirconium source to fabricate aimed powders. As far as we know,

1 synthesis of $\text{ZrB}_2\text{-ZrC-SiC}$ powder mixture with uniform and fine particle size by
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3 sol-gel method using $\text{ZrOCl}_2\cdot 8\text{H}_2\text{O}$ as zirconium source hasn't been reported so far.
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6 In this work, $\text{ZrB}_2\text{-ZrC-SiC}$ nanopowders with uniform phases distribution were
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8 prepared at a heat-treatment temperature of $1500\text{ }^\circ\text{C}$ through a simple sol-gel method
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10 using safe and cost-effective $\text{ZrOCl}_2\cdot 8\text{H}_2\text{O}$, H_3BO_3 , TEOS and glucose as raw
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12 materials. Ceramization process including the pyrolysis of the gel was investigated
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14 thoroughly. Microstructure development of the $\text{ZrB}_2\text{-ZrC-SiC}$ ceramics during the
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16 ceramization process under various holding times was elaborated. Initial studies on
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18 the microstructure evolution of the generated carbon during the ceramic conversion
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20 were also carried out.
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27 **2. Material and methods**

28 **2.1 Chemicals**

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30 Zirconium oxychloride octahydrate ($\text{ZrOCl}_2\cdot 8\text{H}_2\text{O}$, AR) and hydrogen peroxide
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32 (H_2O_2 , AR) were obtained from Sinopharm Chemical Reagent Co, Shanghai, China.
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34 Boric acid (H_3BO_3 , AR), Ethyl orthosilicate (TEOS, AR), D-glucose (AR) and ethanol
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36 (EtOH , AR), were derived from Tianjin Komiou Chemical Reagent Co, Ltd. All
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38 starting materials were used without further processed.
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47 **2.2 Preparation of the precursor**

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49 Preparation of the precursor gel was described as follows. Firstly, 3.2 g of
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51 $\text{ZrOCl}_2\cdot 8\text{H}_2\text{O}$ was dissolved in 20 ml ethanol, and then 2 mL H_2O_2 was added,
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53 dropwise, to obtain a clear and transparent zirconium-containing solution (ZS). In
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55 parallel, 4.3 g H_3BO_3 was dissolved in ethanol heated at $50\text{ }^\circ\text{C}$ for 1 h in the water bath
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1 to obtain boron-containing solution (BS) and TEOS was soluble in ethanol to form
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3 TEOS solution (TS). In addition, glucose was dissolved in deionized water to form a
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5 carbon-containing solution (CS). Secondly, TS and BS were added into ZS dropwise
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7 under continuously stirring. And then, CS was further added into the above mixture
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9 solution to form a homogenous hybrid solution. Finally, the obtained solution was
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11 heated at 80 °C in water bath under continuously stirring for 2-4 h and then the aimed
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13 gel was obtained. The gel was dried at 60 °C overnight to obtain a dark brown dry
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15 product, which would be used as the ceramic precursor in the subsequent
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17 heat-treatment. In this work, the molar ratios of B/Zr, Si/Zr and C/(Zr+B+Si) were
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19 controlled at 2, 3 and 5, respectively.
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27 28 2.3 Ceramization of the precursor 29 30

31 The right amount of dry gel was put into the graphite crucible with a lid and
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33 calcined in flowing Ar (200 cm³/min) in a corundum tube furnace. After evacuation
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35 and introducing argon for three times, the calcining procedure began. In the heating
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37 process, the sample was heated at 900 °C for 1 h with a heating rate of 5 °C/min.
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39 Further increasing the temperature to 1200 °C, the heating rate was reduced to 3°C/min.
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41 And then the sample was heated at 1200, 1300, 1400, 1500 and 1600 °C for 2 h,
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43 respectively. Finally, the tube furnace was cooled to room temperature under flowing
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45 argon. In order to clarify the influence of soaking time on the microstructures of the
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47 prepared ceramics, the samples were heated to 1600 °C and kept at this temperature
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49 for 0.5, 1.5, 2 and 2.5 h under the same condition, respectively.
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58 2.4 Characterization 59 60 61 62 63 64 65

Chemical structure of the precursor was investigated by a Fourier infrared spectrum (FT-IR, VECTOR-22, Germany, Bruker). Ceramic composition and crystallinity of the samples were analyzed using an XRD powder diffractometer (D/max-2200PC, Rigaku, Japan), with the scanning range from 15° to 70° (2 θ). Crystalline sizes of the obtained ceramic phases were calculated by the Scherrer equation. Microstructures of the ceramic powders were identified by a field-emission scanning electron microscopy (FE-SEM, FEI Verios 460, US). An X-ray photoelectron spectroscopy (XPS, AXIS SUPRA, England) was applied to further quantify elemental content, valence bond connection and surface chemical state of the samples. Raman spectra were obtained using a Raman spectrometer (Invia, Renishaw, England) at 532 nm excitation wave-length at room temperature. Pyrolysis process of the precursor from room temperature to 1300 °C was analyzed by a TG/DSC simultaneous thermal analyzer (TG-DSC, TGA Q500, US) at a heating rate 10 °C/min using argon as a shielding gas. DTG curve was got by differencing the TG curve. Distribution of the particle size was obtained using a powder particle size analyzer (NAMO-ZS, Malvern, England). The microstructure and elemental distribution were reflected by a high resolution transmission electron microscope (TEM/HRTEM, FEI Tecnai G2 F20 S-TWIN, US) equipped with an energy dispersive spectroscopy (EDS).

3. Results and discussion

3.1 Preparation and characterization of the precursor

Fabrication process of ZrB₂-ZrC-SiC ceramic nonopowders through sol-gel process is shown in Fig.1, which includes the preparation of the precursor gel and high-temperature treatment of the obtained gel. The precursor preparation mainly involves a few steps , i.e. self-hydrolysis condensation of each raw material and cross-linking between the hydrolyzed products to form a stable gel network structure. It is easy to get a stable precursor with well-interspersed elements at atomic level, which is believed to be the main reason contributing to the uniformly distributed ceramic phases and lowered processing temperature.

The possible reactions occurred during the preparation of the gel are proposed via series of chemical equations 1~8. Hydrolysis and condensation of ZrOCl₂·8H₂O happened to form Zr-O-Zr bonds (reactions 1 and 2). During this process, since the ZrOCl₂·8H₂O hydrolysis solution is acidic, the hydrolysis reaction is inhibited. Therefore, the addition of a small amount of H₂O₂ reduces the acidity of the solution, and promotes the hydrolysis of ZrOCl₂·8H₂O and the formation of a zirconium complex. Hydrolysis and condensation of TEOS generate Si-O-Si (reactions 3 and 4), and [B(OH)₄]⁻ is formed from H₃BO₃ (reaction 5). By mixing above solution, the molecular chain will be further crosslinked through reactions 6~8, as well as the connection with glucose through dehydration reactions between hydroxyl groups. The crosslinked network may be further hybridized to form a highly branched structure, in which all the elements are uniformly distributed.

FT-IR spectrum of as-prepared precursor is exhibited in Fig. 2. The peaks positioned at 461 and 680 cm^{-1} are identified as Zr-O-Zr [21] and Zr-O [22] stretching vibration, respectively. The hydrolysis and condensation reactions of TEOS motivated the peaks appeared at 820 cm^{-1} and 1090 cm^{-1} , assigning to stretching vibration of Si-O-Si bond [23, 24]. The band at 1237 cm^{-1} is caused by B-O bond [25]. The peak

located at 1424 cm^{-1} is ascribed to B-O-C bond [26, 27]. The peak at 939 cm^{-1} is related to Zr-O-C bond [26]. The appearance of these two peaks demonstrates the connection between glucose and hydrolysates of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and H_3BO_3 . The band observed at 1690 cm^{-1} is attributed to C=O stretching and bending vibrations, and the bands positioned at 2920 cm^{-1} and 3730 cm^{-1} are assigned to the stretching vibration of C-H and -OH bonds [28], respectively, all of which are corresponding to glucose bonds. Additionally, the band at 3210 cm^{-1} corresponds to Si-OH functional groups [29]. According to the above analysis, it can be deduced that Zr, Si, B elements have been successfully incorporated into the precursor network, and exist in the form of Zr-O, Zr-O-C, Zr-O-Zr, B-O-C and Si-O-Si bonds, indicating a highly branched structure.

TG-DTG-DSC curves of the obtained precursor gel are shown in Fig. 3. As observed, four main mass loss stages are responsible for the TG profile: (a) Below 200°C , an initial weight loss of about 25 % with the peak weight loss rate at 110°C was resulted from solvent evaporation and loss of bond water [30, 31], showing two exothermic peaks at about 110°C and 160°C , respectively. (b) From 200°C to 500°C , mass loss of 20 % was observed, which was due to the escape of small molecules, i.e. the by-products of cross-linking process, showing an endothermic peak at 330°C . In addition, $\text{B}_2\text{O}_3(\text{s})$ transformed into liquid in this event [32]. (c) From 500°C to 630°C , weight loss was 10 %, the endothermic peak at 560°C , which was also the temperature of maximum weight loss rate, was created by the pyrolysis of the precursor network, accompanied by the formation of oxide ceramic products [31]. (d)

Above 630 °C, the TG curve performs a flat with no obvious mass loss, indicating that the ceramic process of the precursor was basically completed and the ceramic yield was 39 % at 1300 °C. In addition, there was a huge endothermic range at around 900 °C, inferring the crystallizing process of the ceramic products [28]. Moreover, a slight weight loss can be observed at temperatures higher than 1200 °C, indicating that carbonization reactions may be stimulated at higher temperatures.

3.2 Characterization of the ceramic products

Compositions, morphologies and particle size distributions of the ceramic products pyrolyzed at 1600 °C for 2 h are given in Fig.4. From the XRD pattern in Fig. 4a, all the peaks could be assigned to ZrB₂, ZrC or SiC phases, demonstrating that compositions of the ceramics were ZrB₂, ZrC, and SiC and the formation of ZrB₂-ZrC-SiC ceramics without impurity. Furthermore, the sharp diffraction peaks and high intensities indicate that the phases are in high crystalline form. From the SEM images shown in Fig. 4(b), the ceramic product is in granular shape, and the particle size is relatively uniform. The average size and size distribution of the ceramics are presented in Fig. 4(c), it shows that the average size was about 220 nm and the D₅₀ is 255 nm, and the large size at around 5 μm may be caused by agglomeration.

Fig. 5 shows TEM, HRTEM and EDS analysis of the ceramics products. The TEM images in Fig. 5a and c further confirm that the ceramic powders are irregular particles, and the average particle size is about 220 nm. The lattice spacing distances of 0.238 nm, 0.217 nm and 0.155 nm are depicted in Fig. 5b, which are in good

1 agreement with the (200) plane of ZrC, the (101) plane of ZrB₂ and the (200) plane of
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3 SiC, respectively. Besides, a thin layer of amorphous carbon adjacent to the ceramic
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5 phases can be easily noted (as indicated by the circle in Fig. 5b), indicating the
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8 obtained SiC-ZrB₂-ZrC ceramics are rich in carbon. Compositions of the sample were
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10 identified by EDS shown in Fig. 5(d-g). Considering the light element boron cannot
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12 be detected due to the limitation of the instrument, Zr, Si, and C were identified by
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14 EDS. EDS mapping result confirms the uniform distribution of all the ceramic
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16 elements, reflecting the uniform distribution of ZrC, ZrB₂ and SiC ceramic phases. It
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18 is generally established that the sol-gel method contributes to the uniformly mixing of
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20 ceramic elements at atom level, which enables the homogeneous distribution of
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23 ceramic phases.
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31 To further identify the chemical state and bond structure of the as-prepared
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33 ceramics, XPS analysis was carried out (Fig. 6). In the XPS survey spectrum (Fig. 6a),
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35 peaks ascribed to Si_{2p} (98 eV), Zr_{3d} (181 eV), C_{1s} (282 eV), and O_{1s} (529 eV) were
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37 observed, among which the expected B element was not found either. The relative
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39 content of these elements are 11.5 at%, 1.9 at%, 69.1 at%, 17.5 at%, respectively. The
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41 presence of the oxygen element indicates the potential existence of residue oxides in
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43 the ceramic products. From the XPS fitting spectra of Zr_{3d} in Fig. 6(b), the peaks
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45 centered at around 177, 180 and 182 eV correspond to Zr-C, Zr-B and Zr-O bonds
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47 [33-35], respectively, confirming the small amount of ZrO₂ residue. In the Si_{2p} XPS
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49 spectra (Fig. 6c), the single peak positioned at 98 eV fits Si-C bond, which holds the
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51 evidence for the generation of SiC. In Fig. 6(d), deconvolution of C_{1s} can be fitted
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into four components at 279.9 eV (C-O) [36], 282.4 eV (C-Zr), 283.6 eV (C-Si) [33, 37] and 286.6 eV (C-Si-O) [37], respectively. This result confirms the existence of carbon residue as observed in the HRTEM image. Therefore, as an important component of the ceramics, the microstructure of the carbon is another factor we should pay attention to, and the evolution of carbon during the synthesis will be discussed in detail in the following section.

3.3 The mechanism of ceramization

XRD results of the ceramic powders prepared at various temperatures are shown in Fig. 7 and the corresponding compositions are provided in Table 1. At 1200 °C, only broad peaks assigned to ZrO_2 and SiO_2 can be observed. In addition, diffraction peaks for pyrolysis carbon were not observed due to its low crystallinity. And also, B_2O_3 was not detected resulting from the low atomic number and easy vaporization at high temperatures [7]. By increasing the temperature to 1300 °C, the crystallinity of the sample was improved to a certain extent, whereas ZrO_2 and SiO_2 still remained as the main components. At 1400 °C, while the ZrO_2 phase was dominant, ZrO_2 got to crystallize, and the diffraction peaks of ZrB_2 and SiC appeared, demonstrating that initiation of carbonization was activated at this temperature with the generation of ZrB_2 and SiC . At 1500 °C, the target phases, ZrC , ZrB_2 and SiC without impurities were picked out, and the crystallinity of all the phases increased, indicating that the residual ZrO_2 could be transformed into ZrC at this stage. Further increasing the temperature to 1600 °C, the crystallinity of the ceramics were further strengthened. Therefore, it can be concluded that carbonization reaction accomplished completely,

and highly crystallized ZrC, ZrB₂ and SiC phases were synthesized in a single step heat treatment at 1500 °C.

In general, SiC phase is obtained from the reaction between SiO₂ and carbon, based on the following reactions:

The above reactions can be considered as a solid-solid reaction:

$$\Delta G^\theta = -339.70T + 606540.2 \text{ J} \cdot \text{mol}^{-1}$$

Reaction 11 is extremely endothermic and it will proceed slowly through reaction 9 and reaction 10.

Furthermore, the generated CO from the above reactions can also participate in the reaction of consuming SiO₂ as shown in reaction 12. And CO may react with SiO to form SiC through reaction 13.

ZrB₂ ceramics can be synthesized through the borothermal reduction of ZrO₂, and the process of which has been reported by other literatures [27]. Single ZrB₂ phase can be obtained if the quantity of B₂O₃ was sufficient.

$$\Delta G^\theta = -845.35T + 1458474.8 \text{ J} \cdot \text{mol}^{-1}$$

$$\Delta G^{\theta} = -505.72T + 414.08 \text{ J} \cdot \text{mol}^{-1}$$

The formation of ZrC is mainly resulted from the reaction between ZrO₂ and carbon shown in reaction 16:

$$\Delta G^{\theta} = -349.70T + 670443.5 \text{ J} \cdot \text{mol}^{-1}$$

Reaction (16) is highly endothermic. At elevated temperatures, reaction (16) will take place to form ZrC. While it seems that ZrC will be transformed into ZrB₂ through reaction 15 if B₂O₃ is available. However, due to the inevitable loss and lack of B₂O₃ which is easily evaporated, the formed ZrC did not have the chance to transform into ZrB₂ through reaction 15 in our work. Furthermore, it is possible that unreacted ZrO₂ remained in the final ZrB₂-ZrC-SiC ceramics as impurity, which confirms the result of XPS analysis.

Based on the thermodynamic calculation, the estimated ΔG^{θ} changes of reactions 11, 14 and 16 to form SiC, ZrB₂ and ZrC are negative above 1500, 1500 and 1650 °C, while the corresponding phases were formed at 1400, 1400 and 1500 °C, respectively. The reason for the decreased reaction temperature could be explained as the uniformly distributed ceramic elements and the excess amount of carbon. In addition, the feasibility of reaction 11 and 14 (Fig. 8a), as well as the higher stability of ZrB₂ compared with SiC and ZrC (Fig. 8b) further confirms the result of XRD.

Combined with the above analysis and the morphology development of the ceramic products, the ceramization process can be proposed, as illustrated in Fig. 9. When the heat-treatment temperature was 1200 °C, the pyrolysis of the precursor had

1 already completed. At this stage, the main compositions of the product were
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3 amorphous oxides and pyrolytic carbon. At 1300 °C, the reactions between the formed
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6 oxides and carbon began, while the bulk structure was destroyed, showing a tendency
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9 to form granular morphology with pores. When the temperature reached 1400 °C, the
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12 pyrolytic carbon was excessively consumed due to the boro/carbonization reactions,
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15 thus forming granular ceramic products with particle size about 200 nm. At this stage,
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18 ZrB₂ and SiC were preferentially formed. With the temperature increasing to 1500 °C,
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21 the ceramic products remained granular, and the particles were uniform with size less
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24 than 200 nm, but agglomeration tended to occur. Since the carbonization reaction to
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27 form ZrC had completed, ZrC, ZrB₂ and SiC phases all appeared at this temperature.
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30 When the treatment temperature was 1600 °C, the phase compositions were similar to
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33 that of 1500 °C, and the morphology of the ceramic product did not fluctuate too much
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36 compared with that of 1500 °C, the granular morphology became more distinct and the
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39 particle got some certain coarsening features, while more agglomeration can be
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42 observed.

43 3.4 Effect of holding time on the microstructure of the ceramics

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45 Fig. 10 displays the XRD patterns of the ceramic powders prepared at 1600 °C
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48 with various holding times and the calculated crystalline sizes of the ZrB₂, ZrC and
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51 SiC phases. From the XRD patterns in Fig. 10(a), only ZrC, ZrB₂ and SiC diffraction
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54 peaks can be observed, indicating that compositions of all the samples were ZrC, ZrB₂
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57 and SiC. However, it is easily noted that crystallinity of the ceramics was quite low
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60 with 1 h holding time, although the desired phases ZrC, ZrB₂ and SiC can be formed
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under this condition. Sharper diffraction peak and higher intensities of the diffraction peaks can be obtained as expected by extending the holding time, confirming the improvement in crystallinity. As seen from Fig. 10(b), significant growth of the ZrC, ZrB₂ and SiC crystals can be observed when prolonging the holding time from 1 h to 1.5 h. As the holding time is further extended, the grain sizes for all these ceramics tend to gradually decrease, indicating that the prolonged holding time contributed to the grain refinement.

Combined with the above analysis and the morphology development of the ceramic products, influence of holding time on microstructure evolution of the ceramic powders are described in Fig. 11. When the holding time was set to 1 h, the ceramic particles were irregular, and part of which was enclosed together. There was a large amount of pyrolyzed carbon and the crystallinity of the ceramics was extremely low, which justified the observed morphology. By increasing the holding time from 1 to 1.5 h, the as-prepared ceramic particles were even and uniformly distributed (about 250 nm). As the holding time prolonged to 2 h, the size of the ceramic particles decreased (about 220 nm) and the size distribution was kept uniform; however, serious agglomeration can be observed, which may be resulted from the relatively high specific surface area. Further extending the holding time to 2.5 h, the grains grew abnormally and the grains were coarsened into a large block.

3.5 Microstructures of the carbon in the obtained ceramics

As discussed, there was residue carbon phase existed in the as-prepared ZrB₂-ZrC-SiC ceramic powders. Since the physical and chemical characteristics of

the carbon phase, such as thermal conductivity, thermal shock resistance, electrical resistivity and so on are greatly affected by its microstructure [38, 39]. As an important component in the ceramics, microstructures of the carbon phase have a significant effect on the performance of the materials [40, 41]. However, there are no reports concerning the structure changes of the carbon phase in the precursor conversion process, especially in the presence of ZrB₂-ZrC-SiC ceramics. Therefore, microstructures of the precursor derived carbon in ZrB₂-ZrC-SiC ceramics was investigated in this work using Raman spectra. The Raman spectra specializes in featuring the fine structure of carbon materials. Usually, two specific absorption peaks can be detected for carbonaceous materials. One located at 1340-1360 cm⁻¹ (D-band) represents turbostratic structure, and the other peak located at 1580-1600 cm⁻¹ (G-band) corresponds to normal graphite structure [42]. For higher structure-ordered materials, 2D peaks around 2700 cm⁻¹ appear. The full width at half maximum of the bands, the microcrystalline planar size L_a ($4.35R^{-1}$), relative intensity of D band and G band (I_D/I_G ratio, R) are commonly utilized to characterize the structure of carbon materials.

Raman spectra of the pyrolyzed carbon obtained at various temperatures and holding times are presented in Fig. 11(a) and (c), and the calculated I_D/I_G and L_a values are exhibited in Fig. 11(b) and (d). Distinctly, all the samples show broad D peaks and G peaks, which indicates the presence of amorphous carbon in the materials [43]. Effect of heat-treatment temperatures on the microstructures of the carbon was analyzed, as shown in Fig. 11(a) and (b). From 1200 °C to 1300 °C, I_D/I_G value

1 increases and L_a value decreases, indicating the increasing in defect amount [44]
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3 Between 1300 and 1500 °C, the fluctuation of the ID/IG and L_a curves are not obvious,
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5 while the ID/IG value shows the tendency to decrease and L_a value tends to increase.
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7 During this stage, the boro/carbothermal reduction reactions occurred intensively, and
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9 the pyrolytic carbon was consumed. During this process, the carbon cluster domains
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11 were destroyed, introducing defects into the local carbon phases. However, from the
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13 perspective of the long-range in the carbon phase, the structure order was improved
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15 gradually on the whole, which was manifested in the obvious appearance of the 2D
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17 peak. Further increasing the temperature from 1500 to 1600 °C, boro/carbothermal
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19 reduction reactions had accomplished, and the carbon structure was rapidly optimized
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21 in this temperature range, as demonstrated by the obviously decreased ID/IG value
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23 and increased L_a value.
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34 Regarding the effects of holding times, it can be noted that ID/IG value increases
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36 and L_a value decreases as the holding time increases from 1 h to 1.5 h, implying that
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38 boro/carbothermal reduction reactions were in progress, thus breaking the carbon
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40 domain and causing the increase in defect amount. Further increasing the soaking
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42 time from 1.5 to 2.5 h, ID/IG value decreases and L_a value increases significantly,
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44 demonstrating that the generation process of the ceramics had accomplished, and the
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46 structure order of the residue carbon was improved during this stage. Therefore, it can
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48 be deduced that generation process of the ceramics, i.e. the boro/carbothermal
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50 reduction reactions to form the aimed ceramic phases, could introduce a large amount
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52 of defects into the carbon phase, and the structure order of which was rapidly
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optimized once the ceramization process was accomplished.

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4. Conclusions

This work reported in-situ synthesis mechanism and microstructure evolution of ZrB₂-ZrC-SiC nanopowders through sol-gel process using ZrOCl₂·8H₂O, H₃BO₃, TEOS and glucose as raw materials. Zr, Si and B elements were successfully incorporated into the hybrid structured precursor, and the yield of which was 39% at 1300 °C. ZrB₂ and SiC were easily formed by pyrolyzing the precursor at 1400 °C. Highly crystallized ZrB₂-ZrC-SiC ceramic powders with uniform size distribution were obtained by calcining the precursor at 1500 °C for 2 h. Crystal size of the ceramic phases can be refined by extending the holding time. Whereas, the particle size experienced a process of decrease first and then increase. With the increase of temperature or holding time, microstructure of the carbon phase showed no obvious improvement. The reason may be due to the large amount of defects generated by the boro/carbothermal reduction reactions to form ZrB₂-ZrC-SiC ceramics.

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References

- [1] K. Gürcan, E. Ayas, H. Gaşan, Formation of TaB₂ powders from high energy ball milling and borothermal reduction process, *Mater. Chem. Phys.* 235 (2019) 121732.
- [2] W.Z. Sun, J.G. Cheng, Z.K. Huang, Y. Jiang, L.E. Wu, L.M. Liu, ZrC formation and the phase relations in the SiC-SiO₂-ZrC-ZrO₂-CaO system, *Ceram. Int.* 42 (2016) 10165-10170.
- [3] W. Wang, Q. Fu, B. Tan, Effect of in-situ grown SiC nanowires on the mechanical properties of HfC-ZrB₂-SiC modified C/C composites, *J. Alloys Compd.* 726 (2017) 866-874.
- [4] H. Wu, W. Zhang, J. Zhang, Pyrolysis synthesis and microstructure of zirconium carbide from new preceramic polymers, *Ceram. Int.* 40 (2014) 5967-5972.
- [5] Z. Zhao, P. Hui, F. Liu, X. Wang, B. Li, Y. Xu, L. Zhong, M. Zhao, Fabrication of TaC coating on tantalum by interstitial carburization, *J. Alloys Compd.* 790 (2019) 189-196.
- [6] Q. Qu, J. Han, W. Han, X. Zhang, C. Hong, In situ synthesis mechanism and characterization of ZrB₂-ZrC-SiC ultra high-temperature ceramics, *Mater. Chem. Phys.* 110 (2008) 216-221.
- [7] B. Xie, L. Ma, X. Lin, Y. Liu, Y. Zhang, H. Gong, W. Zhang, Synthesis of ZrB₂-SiC powders in one-step reduction process, *Ceram. Int.* 44 (2018) 19522-19525.
- [8] F. Li, Z. Xu, K. Zhao, Y. Tang, Fabrication of ZrB₂-ZrC composite nanofibers with eutectic composition by electrospinning and carbothermal reduction, *Mater. Lett.* 230 (2018) 249-252.

- [9] B. Zhao, Y. Zhang, J. Li, B. Yang, T. Wang, Y. Hu, D. Sun, R. Li, S. Yin, Z. Feng, T. Sato, Morphology and mechanism study for the synthesis of $\text{ZrB}_2\text{-SiC}$ powders by different methods, *J. Solid State Chem.* 207 (2013) 1-5.
- [10] F. Li, Y. Cao, J. Liu, H. Zhang, S. Zhang, Oxidation resistance of ZrB_2 and $\text{ZrB}_2\text{-SiC}$ ultrafine powders synthesized by a combined sol-gel and boro/carbothermal reduction method, *Ceram. Int.* 43 (2017) 7743-7750.
- [11] B. Xie, L. Ma, D. Gao, X. Lin, Y. Liu, Y. Zhang, H. Gong, Influence of SiC on phase and microstructure of ZrB_2 powders synthesized via carbothermal reduction at different temperatures, *Ceram. Int.* 44 (2018) 8795-8799.
- [12] H.-L. Liu, G.-J. Zhang, J.-X. Liu, H. Wu, Synergetic roles of ZrC and SiC in ternary $\text{ZrB}_2\text{-SiC-ZrC}$ ceramics, *J. Eur. Ceram. Soc.* 35 (2015) 4389-4397.
- [13] H.-L. Liu, J.-X. Liu, H.-T. Liu, G.-J. Zhang, Changed oxidation behavior of $\text{ZrB}_2\text{-SiC}$ ceramics with the addition of ZrC, *Ceram. Int.* 41 (2015) 8247-8251.
- [14] S.-Q. Guo, Y. Kagawa, T. Nishimura, D. Chung, J.-M. Yang, Mechanical and physical behavior of spark plasma sintered $\text{ZrC-ZrB}_2\text{-SiC}$ composites, *J. Eur. Ceram. Soc.* 28 (2008) 1279-1285.
- [15] X. Lv, S. Yu, M. Ge, Y. Tian, W. Zhang, Synthesis and microstructure of continuous composite ceramic fibres of $\text{ZrC/ZrB}_2\text{-SiC}$ derived from polymeric precursors, *Ceram. Int.* 42 (2016) 9299-9303.
- [16] S.M. Emami, E. Salahi, M. Zakeri, S.A. Tayebifard, Synthesis of $\text{ZrB}_2\text{-SiC-ZrC}$ nanocomposite by spark plasma in $\text{ZrSiO}_4/\text{B}_2\text{O}_3/\text{C/Mg}$ system, *Ceram. Int.* 42 (2016) 6581-6586.

- [17] M. Jalaly, M. Tamizifar, M.S. Bafghi, F.J. Gotor, Mechanochemical synthesis of $\text{ZrB}_2\text{-SiC-ZrC}$ nanocomposite powder by metallothermic reduction of zircon, *J. Alloys Compd.* 581 (2013) 782-787.
- [18] Y. Li, W. Han, H. Li, J. Zhao, T. Zhao, Synthesis of nano-crystalline $\text{ZrB}_2/\text{ZrC/SiC}$ ceramics by liquid precursors, *Mater. Lett.* 68 (2012) 101-103.
- [19] F. Li, X. Huang, Preparation of highly porous $\text{ZrB}_2/\text{ZrC/SiC}$ composite monoliths using liquid precursors via direct drying process, *J. Eur. Ceram. Soc.* 38 (2018) 1103-1111.
- [20] Y.-N. Cao, S. Du, J.-K. Wang, H. Zhang, F.-L. Li, L.-L. Lu, S.-W. Zhang, X.-G. Deng, Preparation of zirconium diboride ultrafine hollow spheres by a combined sol-gel and boro/carbothermal reduction technique, *J. Sol-Gel Sci. Techn.* 72 (2014) 130-136.
- [21] J. He, Y. Gao, Y. Wang, J. Fang, L. An, Synthesis of $\text{ZrB}_2\text{-SiC}$ nanocomposite powder via polymeric precursor route, *Ceram. Int.* 43 (2017) 1602-1607.
- [22] K. Li, X. Zhou, Z. Zhao, C. Chen, C. Wang, B. Ren, L. Zhang, Synthesis of zirconium carbide whiskers by a combination of microwave hydrothermal and carbothermal reduction, *J. Solid State Chem.* 258 (2018) 383-390.
- [23] A. Najafi, F. Golestani-Fard, H.R. Rezaie, N. Ehsani, Effect of APC addition on stability of nanosize precursors in sol-gel processing of SiC nanopowder, *J. Alloys Compd.* 505 (2010) 692-697.
- [24] A. Najafi, F.G. Fard, H.R. Rezaie, N. Ehsani, Synthesis and characterization of SiC nano powder with low residual carbon processed by sol-gel method, *Powder*

Technol. 219 (2012) 202-210.

[25] C. Liu, L. Zhang, X. Li, X. Chang, Y. Wu, X. Wang, Synthesis, characterization, and ceramization of a carbon-rich SiCw-ZrC-ZrB₂ preceramic polymer precursor, Ceram. Int. 45 (2019) 16097-16104.

[26] H. Moayyeri, R. Mehdiavaz Aghdam, R. Ghelich, F. Golestani-fard, In situ synthesis of ZrB₂-ZrC-SiC ultra-high-temperature nanocomposites by a sol-gel process, Adv. Appl. Ceram. 117 (2018) 189-195.

[27] H. Ji, M. Yang, M. Li, G. Ji, H. Fan, X. Sun, Low-temperature synthesis of ZrB₂ nano-powders using a sorbitol modified sol-gel processing route, Adv. Powder Technol. 25 (2014) 910-915.

[28] Y. Liu, R. Geng, Y. Cui, S. Peng, X. Chang, K. Han, M. Yu, A novel liquid hybrid precursor method via sol-gel for the preparation of ZrB₂ films, Mater. Design. 128 (2017) 80-85.

[29] A. Najafi, F. Golestani-Fard, H.R. Rezaie, N. Ehsani, A study on sol-gel synthesis and characterization of SiC nano powder, J. Sol-Gel Sci. Techn. 59 (2011) 205-214.

[30] B. Yang, J. Li, B. Zhao, Y. Hu, T. Wang, D. Sun, R. Li, S. Yin, Z. Feng, Q. Tang, T. Sato, Synthesis of hexagonal-prism-like ZrB₂ by a sol-gel route, Powder Technol. 256 (2014) 522-528.

[31] Y. Zhang, R. Li, Y. Jiang, B. Zhao, H. Duan, J. Li, Z. Feng, Morphology evolution of ZrB₂ nanoparticles synthesized by sol-gel method, J. Solid State Chem. 184 (2011) 2047-2052.

[32] Y. Cao, H. Zhang, F. Li, L. Lu, S. Zhang, Preparation and characterization of

ultrafine $\text{ZrB}_2\text{-SiC}$ composite powders by a combined sol-gel and microwave boro/carbothermal reduction method, *Ceram. Int.* 41 (2015) 7823-7829.

[33] E. Beche, M. Balat-Pichelin, V. Flaud, J. Esvan, T. Duguet, D. Sciti, D. Alfano, XPS and AES studies of UHTC $\text{ZrB}_2\text{-SiC-Si}_3\text{N}_4$ treated with solar energy, *Surf. Interface Anal.* 46 (2014) 817-822.

[34] Z. Zhang, Y. Sheng, X. Xu, W. Li, Microstructural Features and Mechanical Properties of In Situ Formed $\text{ZrB}_2\text{/Cu}$ Composites, *Adv. Eng. Mater.* 17 (2015) 1338-1343.

[35] Y.S. Won, Y.S. Kim, V.G. Varanasi, O. Kryliouk, T.J. Anderson, C.T. Sirimanne, L. McElwee-White, Growth of ZrC thin films by aerosol-assisted MOCVD, *J. Cryst. Growth.* 304 (2007) 324-332.

[36] K. Seevakan, A. Manikandan, P. Devendran, Y. Slimani, A. Baykal, T. Alagesan, Structural, morphological and magneto-optical properties of CuMoO_4 electrochemical nanocatalyst as supercapacitor electrode, *Ceram. Int.* 44 (2018) 20075-20083.

[37] D. Gao, Y. Zhang, C. Xu, Y. Song, X. Shi, Atomic oxygen adsorption and its effect on the oxidation behaviour of $\text{ZrB}_2\text{-ZrC-SiC}$ in air, *Mater. Chem. Phys.* 126 (2011) 156-161.

[38] H. Qiu, L. Han, L. Liu, Properties and microstructure of graphitised ZrC/C or SiC/C composites, *Carbon* 43 (2005) 1021-1025.

[39] H. Qiu, Y. Song, L. Liu, G. Zhai, J. Shi, Thermal conductivity and microstructure of Ti-doped graphite, *Carbon* 41 (2003) 973-978.

[40] Q. Tong, J. Shi, Y. Song, Q. Guo, L. Liu, Resistance to ablation of pitch-derived

ZrC/C composites, Carbon 42 (2004) 2495-2500.

[41] M. Yan, W. Song, C. Zhao-hui, Raman spectroscopy studies of the high-temperature evolution of the free carbon phase in polycarbosilane derived SiC ceramics, Ceram. Int. 36 (2010) 2455-2459.

[42] B. Kwiecinska, I. Suárez-Ruiz, C. Paluszkievicz, S. Rodriques, Raman spectroscopy of selected carbonaceous samples, Int. J. Coal Geol. 84 (2010) 206-212.

[43] X. Ma, L. Li, R. Chen, C. Wang, K. Zhou, H. Li, Porous carbon materials based on biomass for acetone adsorption: Effect of surface chemistry and porous structure, Appl. Surf. Sci. 459 (2018) 657-664.

[44] A.C. Ferrari, Raman spectroscopy of graphene and graphite: Disorder, electron-phonon coupling, doping and nonadiabatic effects, Solid State Commun. 143 (2007) 47-57.

Table and Figure Captions:

Table 1. Compositions of the ceramics prepared at different temperatures

Fig. 1. Schematic of the sol-gel method for fabricating ZrB₂-ZrC-SiC ceramics

Fig. 2. FT-IR spectrum of the precursor

Fig. 3. TG-DTG-DSC curves of the precursor

Fig. 4. (a) XRD pattern, (b) SEM morphology, and (c) particle size distributions of the obtained ceramics calcined at 1600 °C for 2 h

Fig. 5. (a, c) TEM image, (b) HRTEM image, (d, e, f) elemental distribution, (g) EDS spectrum of the obtained ceramics calcined at 1600 °C for 2 h

Fig. 6. XPS spectra of the obtained ceramics calcined at 1600 °C for 2 h, (a) an overview, (b) deconvolution of Zr_{3d}, (c) deconvolution of Si_{2p}, and (d) deconvolution of C_{1s}

Fig. 7. XRD patterns of the ceramic powders prepared at different temperatures

Fig. 8. (a) Gibbs free energy of reactions 11, 14 and 16 as a function of temperature, (b) Temperature dependence of Gibbs energy of ZrC, ZrB₂ and SiC

Fig. 9. (a) SEM images of the ceramic powders prepared at different temperatures, (b) Schematic of phase evolution in the ceramic powders prepared at different temperatures

Fig. 10. (a) XRD patterns of the ceramic powders prepared at 1600 °C with various holding times, (b) Crystalline sizes of the ZrB₂, ZrC and SiC phases

Fig. 11. Morphology development of the ceramic powders prepared at 1600 °C with various holding times, (a) 1 h, (b) 1.5 h, (c) 2 h, (d) 2.5h

Fig. 12. Raman spectra and the parameters of the pyrolyzed carbon prepared at different temperatures (a, b), and at different holding times (c, d)

Table 1. Compositions of the ceramics prepared at different temperatures

Heat treatment temperature (°C)	Composition
1200	ZrO ₂ , SiO ₂ , B ₂ O ₃ , C
1300	ZrO ₂ , SiO ₂ , B ₂ O ₃ , C
1400	ZrO ₂ , ZrB ₂ , SiC, C
1500	ZrB ₂ , ZrC, SiC, C
1600	ZrB ₂ , ZrC, SiC, C

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Fig. 9. (a) SEM images of the ceramic powders prepared at different temperatures, (b)

Schematic of phase evolution in the ceramic powders prepared at different temperatures

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