ZrC–ZrB₂–SiC ceramic nanocomposites derived from a novel single-source precursor with high ceramic yield

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Abstract: For the first time, ZrC–ZrB₂–SiC ceramic nanocomposites were successfully prepared by a single-source-precursor route, with allylhydridopolycarbosilane (AHPCS), triethylamine borane (TEAB), and bis(cyclopentadienyl) zirconium dichloride (Cp₂ZrCl₂) as starting materials. The polymer-to-ceramic transformation and thermal behavior of obtained single-source precursor were characterized by means of Fourier transform infrared spectroscopy (FT-IR) and thermal gravimetric analysis (TGA). The results show that the precursor possesses a high ceramic yield about 85% at 1000 °C. The phase composition and microstructure of formed ZrC–ZrB₂–SiC ceramics were investigated by means of X-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM). Meanwhile, the weight loss and chemical composition of the resultant ZrC–ZrB₂–SiC nanocomposites were investigated after annealing at high temperature up to 1800 °C. High temperature behavior with respect to decomposition as well as crystallization shows a promising high temperature stability of the formed ZrC–ZrB₂–SiC nanocomposites.

Keywords: polymer derived ceramics; single-source precursor; ceramic nanocomposite

1 Introduction

Zirconium carbide (ZrC) and zirconium boride (ZrB₂) are members of a family of materials well-known as

ultrahigh temperature ceramics (UHTCs) due to their high melting points (3550 and 3245 °C, respectively), low densities (6.7 and 6.1 g/cm³, respectively), and good thermal conductivities [1–4]. However, each of the bulk materials has weak fracture toughness, poor oxidation resistance and sinterability, which limits their applications under harsh environments [5,6]. Recent research suggests that UHTC composites such

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as MB₂/SiC and MC/SiC (M = Zr, Hf) are more suitable for operation in harsh environments and have therefore attracted significant attention in the past few decades [7–13].

Nanocomposites have received increasing interest, showing that by reducing the size of the components within the composite materials towards the nanoscale, an enormous improvement in their properties (e.g., mechanical, electrical, optical, etc.) can be achieved [14–16]. To date, hot pressing and spark plasma sintering are still the main tools to synthesize ceramic composites [17–19]. However, these traditional methods require very high temperatures (usually beyond 2000 °C), which are disadvantageous concerning grain growth and consequently mechanical properties of the ceramic parts. One of the most suitable preparative routes towards ceramic nanocomposites was shown to rely on the pyrolytic conversion of preceramic precursors [20–22]. Therefore, the polymer-derived ceramic (PDC) approach is a promising method for preparing UHTC-based nanocomposites since the chemical composition, phase composition, and even the microstructures of ceramic nanocomposites can be designed and tailored. Polymer-derived MB₂/SiC and MC/SiC (M = Zr, Hf) ceramic nanocomposites have drawn great attention during the past 5 years [23–27]. Moreover, the PDC approach is an additive-free method which can prepare the ceramic nanocomposites at low temperature, thus the resultant PDCs are more stable and green [28].

In our previous work, a preceramic precursor allylhydridopolycarbosilane (AHPCS) with various reactive groups (e.g., SiH, SiH₂, SiH₃, and C=C groups) has been modified by borane or transition metal-based compounds [29–32]. The results showed that incorporation of borane or metals plays an important role in the microstructure, high temperature behavior, and functional properties of final ceramics. However, little attention was paid on the introduction of both boron and transition metal into the SiC by the PDC approach [33,34]. It is worth mentioning that the TiC–TiB₂–SiC nanocomposites were successfully synthesized by a PDC route starting from a single-source precursor obtained by modifying the AHPCS with the TEAB as a source of B and Cp₂TiCl₂ as a source of Ti. This work opens a new synthetic route towards the preparation of SiC–MC–MB₂ (M = Ti, Zr, Hf) ceramic nanocomposites [34].

As it is well known, the melting points of ZrC and ZrB₂ are even higher than those of TiC and TiB₂, respectively. Therefore, in the present work, novel

ZrC–ZrB₂–SiC ceramic nanocomposites were prepared by a single-source-precursor route, with AHPCS, TEAB, and Cp₂ZrCl₂ as starting materials. Compared with Ref. [27], the absence of oxygen in the polymeric precursors is an advantage since a carbon reduction process accompanied by decomposition can be avoided [35]. Detailed polymer-to-ceramic transformation of the resultant single-source precursor as well as crystallization, nanoscaled microstructure, and decomposition behavior of final ZrC–ZrB₂–SiC nanocomposites were investigated.

2 Experiment

2.1 Materials

In this work, all synthetic manipulations were performed using high vacuum or inert atmosphere techniques as described by Drezdson [36]. AHPCS with the formal composition [SiH_{1.30}(CH₃)_{0.60}(CH₂CH=CH₂)_{0.10}CH₂]_n was prepared as previously described, by a one-pot synthesis with Cl₂Si(CH₃)CH₂Cl, Cl₃SiCH₂Cl, and CH₂=CHCH₂Cl as the starting materials [37]. Bis(cyclopentadienyl) zirconium dichloride (Cp₂ZrCl₂) and trimethylamine borane (TEAB) were purchased from J & K and stored in fridge under 4 °C until use. Chloroform (CHCl₃) was distilled prior to use. The Ar atmosphere was used in thermal analysis and pyrolysis process with a purity of 99.99%. Other commercially available reagents were used as received.

2.2 Single-source precursor synthesis

One typical synthesis of single-source precursor was achieved with the following procedure. Firstly, 3.000 g AHPCS and 0.479 g TEAB were added to the Schlenk flask equipped with an argon inlet and reflux condenser with an argon outlet. After magnetic stirring for 12 h at room temperature (RT) and subsequent evaporation of the N(C₂H₅)₃ solvent, the resultant boron-modified AHPCS is denoted as AB. After that, 1.216 g Cp₂ZrCl₂ was introduced into another Schlenk flask, and then CHCl₃ was added to dissolve Cp₂ZrCl₂. And then, the obtained Cp₂ZrCl₂ solution was added to AB. The obtained solution was then stirring for 12 h at RT. Finally, the CHCl₃ solvent was stripped off under vacuum to form a yellow rubbery solid. The resultant AHPCS modified with Zr and B is denoted as ABZ. A series of single-source precursors ABZs with different B and Zr contents in the feed were prepared (Table 1).

Table 1 Content of Zr and B in the feed for the synthesis of single-source precursors

Precursor	Zr (wt%) ^a	B (wt%) ^b	Molar ratio Zr/B
ABZ-1	12.62	1.50	1:1
ABZ-2	12.62	3.00	1:2
ABZ-3	12.62	4.50	1:3

^aWeight ratio of Zr to AHPCS.^bWeight ratio of B to AHPCS.

2.3 Ceramic nanocomposite synthesis

Three steps including cross-linking, pyrolysis, and annealing were involved to synthesize ceramic nanocomposites. Firstly, the resultant single-source precursor was cross-linked in a 170 °C oil bath for 6 h. After the heat treatment, a compact and grey-yellow solid was obtained. Secondly, to investigate structural evolution during the polymer-to-ceramic transformation, the cross-linked samples were pyrolyzed as follows: heating up to the targeted temperature (300, 600, or 900 °C) with a rate of 5 °C/min, hold for 2 h, followed by cooling down to room temperature. Finally, the amorphous ceramic (pre-pyrolyzed at 900 °C) was annealed at different temperatures in the range of 1200–1800 °C. The pre-pyrolyzed sample was transferred to a graphite crucible in a tube furnace and then heated rapidly in argon to a targeted temperature at a rate of 40 °C/min and kept at this temperature for 2 h. After annealing, the resulting ceramic was furnace-cooled to RT.

2.4 Characterization

Fourier transform infrared spectra (FT-IR) were recorded on a Nicolet Avator 360 apparatus (Nicolet, Madison, WI, USA) in the range of 4000–400 cm⁻¹ with KBr plates for liquid samples and KBr disks for solid samples. Thermal behavior of the single-source precursor was performed on a thermal gravimetric analysis (TGA) (SHIMADZU, DTG-60H, Japan) in argon gas with a heating rate of 10 °C/min ranging from room temperature to 1000 °C. X-ray diffraction (XRD) studies were carried out on a PAN-alytical X'Pert PRO diffractometer (PANalytical, Netherlands), using graphite-monochromated Cu K α radiation. The specimens were continuously scanned from 10° to 90° (2 θ) at a speed of 0.0167 (°)/s. The Zr and Si contents were measured by IRIS Intrepid Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Thermo Electron Corporation, America). The boron fraction was calculated

as the difference between 100% and the values of the other elements. Transmission electron microscopy (TEM; JEM-2100, JEOL, Tokyo, Japan) was used to observe the microstructure of the samples annealed at different temperatures and the TEM specimens were prepared by mechanical grinding.

3 Results and discussion

3.1 Single-source precursor synthesis

To investigate structural evolution of preceramic precursor during the single-source precursor synthesis, the FT-IR spectra of the starting materials (AHPCS and Cp₂ZrCl₂), intermediate polymer AB, and resultant ABZ-1 were performed and the results are shown in Fig. 1. In our previous work, AHPCS can react with TEAB without using catalyst via the hydroboration reaction (B–H/C=C) at RT [34], which is confirmed by that the C–H stretch in C=C–H groups (3077 cm⁻¹) and C=C stretch (1630 cm⁻¹) peaks significantly decreased after the reaction comparing the FT-IR spectra of AHPCS and AB. After the successful introduction of boron into the AHPCS, the obtained intermediate polymer AB was chemically modified by the Cp₂ZrCl₂. It is observed that the absorption bands of C=C and B–H groups disappear in the ABZ-1 in comparison with AB, indicating that the hydroboration (C=C/B–H) is completed. Based on the findings that hydrosilylation (Si–H/C=C) can be effectively catalyzed by bis (cyclopentadienyl)-metal complexes [35], we assume that the hydroboration may be improved by the introduction of Cp₂ZrCl₂. It is worth mentioning that the intensities of Si–H band at 2140 cm⁻¹ and SiH₂ band at 940 cm⁻¹ significantly decrease in the ABZ-1, due to the occurrence of HCl elimination namely dehydrochlorination (Si–H/Cp₂ZrCl₂) [31,35]. It is obvious that the obtained ABZ-1 contains characteristic peaks of AHPCS and Cp₂ZrCl₂. Several appearances of absorption peak at 3101 cm⁻¹ (C=C–H stretch in Cp rings), 1438 cm⁻¹ (C–C stretch in Cp rings), 1016 cm⁻¹ (C–H in plane deformation in Cp rings), 813 cm⁻¹ (C–H out of plane deformation in Cp rings) are observed [38]. It indicates that Cp₂ZrCl₂ was successfully introduced into the AHPCS, which is consistent with our previous work [31]. In conclusion, the introduction of both boron and the Cp₂ZrCl₂ into the AHPCS is confirmed by the FT-IR results.

Fig. 1 FT-IR spectra of (a) original AHPCS, (b) AB, (c) ABZ-1, and (d) Cp_2ZrCl_2 .

3.2 Polymer-to-ceramic transformation

Generally, the cross-linking of the polymeric precursors is a prevalent method for increasing the ceramic yield because it reduces the amount of volatile decomposition products [16]. The obtained ABZ precursors were cross-linked at 170 °C for 6 h and the cross-linking of ABZ-1, ABZ-2, and ABZ-3 precursors was investigated by means of FT-IR as shown in Fig. 2. It is observed that the intensities of Si–H band at 2140 cm^{-1} decrease significantly and the SiH_2 band at 940 cm^{-1} even disappears in the ABZ precursors in comparison with cross-linked AHPCS due to the occurrence of dehydrochlorination ($\text{Si-H/Cp}_2\text{ZrCl}_2$), self-hydrosilylation (Si-H/C=C), and dehydrocoupling (Si-H/Si-H) of the AHPCS. Besides, it was reported that the bis(cyclopentadienyl)–metal complexes can serve as catalysts for both Si–Si dehydrocoupling and hydrosilylation reactions [39–42], which may contribute to the consumption of Si–H groups.

Fig. 2 FT-IR spectra of cross-linked (a) AHPCS, (b) ABZ-1, (c) ABZ-2, and (d) ABZ-3 at 170 °C.

In order to understand the structural evolution of polymer-to-ceramic conversion, taking ABZ-1 as an example, the FT-IR spectra of samples treated at different temperatures were performed and the results are shown in Fig. 3. It is obvious that the intensity of absorption bands of Si–H at 2140 cm^{-1} decreases a lot from RT to 600 °C, due to the dehydrochlorination ($\text{Si-H/Cp}_2\text{ZrCl}_2$) and self-hydrosilylation (Si-H/C=C) of the AHPCS. The absorption bands of C–H in Cp rings at 3105 and 814 cm^{-1} become much weaker from 170 to 300 °C and finally disappear at 600 °C, which should be attributed to the decomposition of Cp rings. The organic groups such as Si–H, Si– CH_3 , and Si– CH_2 –Si almost decomposed at 900 °C since their characteristic bands vanished, indicating that the polymer-to-ceramic transformation is almost complete. At 900 °C, it is observed that one broad peak at around 780 cm^{-1} attributed to the amorphous SiC frame work structure retained. After pyrolysis at 900 °C, the resulting ceramics were annealed at 1200, 1400, 1600, and 1800 °C, further heating leads to the sharpening of the SiC band and a shift in its position from 780 to 860 cm^{-1} , consistent with the formation of crystalline SiC [29].

The FT-IR spectroscopic results were further supported by the results of TG analysis. As shown in Fig. 4, the TGA and DTG curves (the first time derivative of the TG) reveal that there are 3 main steps during the pyrolysis of the ABZ-1. The first step started from ambient temperature to approximately 150 °C with the DTG peak at 64 °C. During this step, a small weight loss of ca. 2.5% can be seen, due to the decomposition of Cp rings from the precursor. The

Fig. 3 FT-IR spectra of ABZ-1 treated at different temperatures in argon.

Fig. 4 TG and DTG (the first derivative of the TG) curves of the ceramization process of ABZ-1.

second step is in the range of 150–250 °C with the DTG peak at 208 °C. As shown in Fig. 3, the further decomposition of Cp rings took place with the annealing temperature increasing from 170 to 300 °C, which accounts for a weight loss of 5.0% within the second step. The third step of weight loss occurred in the range of 400–600 °C, a weight loss of 5.0% is detected, due to the complete decomposition of Cp rings at 600 °C which is confirmed by the FT-IR results that the absorption bands of C–H in Cp rings at 3105 and 814 cm^{-1} disappear at 600 °C. Between 600 and 900 °C, there is a slight weight loss around 2.5%, attributed to the decomposition of organic side groups –CH₃ as discussed in Fig. 3. From 900 to 1000 °C, there is no obvious weight loss, indicating the completion of polymer-to-ceramic transformation, which agrees well with the FT-IR results. In general, the results show that the precursor possesses a high ceramic yield about 85% at 1000 °C.

3.3 Composition and microstructure of ceramics

In order to investigate the crystallization behavior of ABZ-derived ceramics, XRD patterns of the samples were measured with increasing the annealing temperature and the results are shown in Fig. 5. It can be seen that ABZ-derived ceramics remain amorphous up to 1200 °C. Further heating at 1400 °C, the obtained ceramic shows a crystalline feature. Among these diffraction peaks, the three major peaks at $2\theta = 35.8^\circ$ (111), 60.7° (220), 72.2° (311), are attributed to β -SiC. The peaks at 33.0° (111), 38.3° (200), 55.3° (220), 65.9° (311) are the characteristic diffraction of ZrC and it means that cubic ZrC was formed. At 1600 °C, it is observed that the new diffraction peaks appear at 25.2° (001), 2.6° (100), 41.7° (101) and these peaks are attributed to

Fig. 5 XRD patterns of the ABZ-1 derived ceramics annealed at different temperatures.

characteristic diffraction peak of ZrB₂. According to the above-mentioned XRD results, ZrC–ZrB₂–SiC nanocomposites were successfully prepared after annealing amorphous ceramic at 1600 °C. Further heating at 1800 °C led to the sharpening of characteristic peaks of β -SiC, ZrC, and ZrB₂, indicating the improved crystallization degree.

The effect of boron content in feed on the 1600 °C ceramics was also investigated (Fig. 6). In general, the obtained ceramics with different boron content show the same phase composition. As the TEAB content increases, the intensity of ZrB₂ peaks significantly increases, indicating that the phase composition of the ZrC–ZrB₂–SiC nanocomposites can be tailored by the content of boron in the feed during synthesis of the single-source precursors.

According to the Scherer equation [43], the apparent mean grain size (AMGS) of the β -SiC, ZrC, and ZrB₂ crystalline phase was calculated and the results are shown in Fig. 7. In general, the AMGS of β -SiC is

Fig. 6 XRD patterns of single-source-precursor-derived ceramics annealed at 1600 °C.

Fig. 7 Apparent mean grain size of 1600 °C ceramics derived from single-source precursor and from AHPCS.

15–17 nm for ABZ-derived samples annealed at 1600 °C while that is 29 nm for the AHPCS-derived sample. With respect to ZrC and ZrB₂ crystallites, the AMGS is 33–38 and 27–35 nm for the ABZ-derived samples annealed at 1600 °C, respectively. Moreover, Fig. 7 clearly shows that the introduction of B and Zr into the final ceramic significantly retards the crystal growth of β -SiC even at high annealing temperatures of 1600 °C in comparison with AHPCS-derived ceramic sample. Based on the literature that the resistance to crystal growth was found to be advantageous with respect to the thermal stability of the PDC at high temperatures

[44], the crystallization behavior of the formed ZrC–ZrB₂–SiC nanocomposites shows a promising high temperature stability due to their nanoscaled grain size.

TEM is a powerful method in order to investigate the micro/nanostructure evolution of PDCs. Therefore, the ABZ-1-derived ceramic annealed at 1800 °C was studied by means of TEM with respect to its phase composition and microstructure (Fig. 8). Bright field image (Fig. 8(a)) demonstrates the nanocrystallites with grain sizes in the range of 10–50 nm. As found by the selected area electron diffraction (SAED), the crystalline phases consist of β -SiC, ZrC, and ZrB₂ (Fig. 8(b)). As shown in Figs. 8(c) and 8(d), high-resolution TEM (HRTEM) images exhibit the characteristic nanostructure of the ceramic where crystallites of β -SiC (ca. 50 nm) and ZrC (ca. 25 nm), and poorly organized turbostratic carbon are dispersed in an amorphous ceramic matrix. In general, the ZrC–ZrB₂–SiC nanocomposites were successfully synthesized by the single-source-precursor approach. Besides, the grain sizes are all under 100 nm, indicating that the ZrC–ZrB₂–SiC nanocomposites are promising high-temperature resistant materials.

Fig. 8 (a) Bright field image, (b) selected-area electron diffraction, and (c, d) HRTEM images of ABZ-1-driven ceramic annealed at 1800 °C (insets: diffraction patterns obtained by Fourier filtered transformation).

3.4 Ceramic decomposition

The amorphous ceramics obtained at 900 °C were further annealed at 1400, 1600, and 1800 °C under an argon atmosphere with a holding time for 2 h, and the obtained mass residue of the samples was plotted to study the high temperature stability of the materials (Fig. 9). Based on the XRD results that the ceramic nanocomposites were successfully synthesized after annealing amorphous ceramic at 1400 °C, the mass residue at 1400 °C is considered as a reference defined as 100 wt%. The mass loss of ceramic nanocomposites is 6.9 wt% at 1600 °C, and 7.7 wt% at 1800 °C, attributed to the decomposition of the Si–C–O phase and the evaporation of boron oxides. Between 1600 and 1800 °C, slight mass loss (0.8 wt%) is observed. Moreover, the present ZrC–ZrB₂–SiC ceramic nanocomposites show an even higher temperature stability than our previously reported TiC–TiB₂–SiC ceramic nanocomposites [34]. This result suggests a promising high temperature stability of the synthesized ZrC–ZrB₂–SiC ceramic nanocomposites with a mass residue about 92.3 wt% even upon annealing at 1800 °C for 2 h.

To investigate the composition evolution of the ceramics annealed at different temperatures, the chemical compositions of selected ceramics were thus determined by combination of bulk chemical analysis and atomic spectroscopic method, and the results are shown in Table 2. The amorphous ceramic obtained at 900 °C has a small amount of hydrogen due to the relatively low annealing temperature. After annealing at 1200 °C, hydrogen was removed completely and the decomposition of the Si–C–O phase (formed by the reactions of oxygen and moisture adsorbed on the surface of the polymers during the ceramization processes) started, leading to slight decrease of oxygen content. At 1400 °C,

Fig. 9 Mass residue of ABZ-1 derived ZrC–ZrB₂–SiC ceramic nanocomposites after annealing at high temperatures.

Table 2 Chemical composition of ABZ-1 derived ceramics annealed at different temperatures

Annealing temperature	Chemical composition (wt%)						Empirical formula
	Si ^a	Zr ^a	C ^b	O ^c	B ^d	H ^e	
900 °C	55.01	3.64	31.60	8.73	0.36	0.66	SiB _{0.017} C _{1.340} Zr _{0.020} O _{0.278} H _{0.336}
1200 °C	53.02	4.06	34.54	7.96	0.42	—	SiB _{0.020} C _{1.520} Zr _{0.024} O _{0.263}
1400 °C	52.58	4.21	34.87	7.83	0.51	—	SiB _{0.025} C _{1.547} Zr _{0.025} O _{0.261}
1600 °C	57.97	5.13	35.15	1.18	0.57	—	SiB _{0.025} C _{1.415} Zr _{0.027} O _{0.036}
1800 °C	58.55	4.87	35.42	0.70	0.46	—	SiB _{0.020} C _{1.412} Zr _{0.026} O _{0.021}

^aMeasured by ICP-MS.

^bMeasured by carbon/sulfur analyzer.

^cMeasured by oxygen/nitrogen analyzer.

^dDetermined by the difference.

^eMeasured by elemental analyzer EA/MA1110.

the gradual decomposition of the Si–C–O phase accounts for the slight decrease of oxygen content. Meanwhile, the phase separation occurred to form ZrC–SiC ceramic composites (Fig. 6). After annealing at 1600 °C, the oxygen content significantly decreases due to the further decomposition of the Si–C–O phase, which is consistent with the 6.9 wt% weight loss between 1400 and 1600 °C shown in Fig. 9. At 1800 °C, the chemical composition of the ceramic shows no obvious changes besides the slight decreasing of oxygen content. Therefore, the weight loss between 1600 and 1800 °C is negligible (0.8 wt%).

4 Conclusions

In summary, the ZrC–ZrB₂–SiC nanocomposites were successfully synthesized by a single-source-precursor route starting from the AHPCS as a SiC precursor and the TEAB as a source of B and Cp₂ZrCl₂ as a source of Zr. The obtained single-source precursor was characterized and its structural evolution during the polymer-to-ceramic transformation was investigated by FT-IR. It is worth mentioning that the precursor possesses a high ceramic yield about 85% at 1000 °C. The phase composition and microstructure of resultant ZrC–ZrB₂–SiC ceramics were investigated by means of XRD and HRTEM. The XRD results show that the phase separation occurred at 1400 °C, and ZrC–ZrB₂–SiC nanocomposites were successfully prepared after annealing amorphous ceramic at 1600 °C due to the formation of β-SiC, ZrC, and ZrB₂ nanocrystallite phases. The HRTEM images again confirm that the crystalline phases consist of nanoscaled β-SiC, ZrC, and ZrB₂ after annealing at high temperature of 1800 °C.

Meanwhile, the weight loss of the formed ZrC–ZrB₂–SiC nanocomposites is quite low (7.7 wt%) after annealing at 1800 °C for 2 h, indicating a promising high temperature stability. Moreover, further studies devoted to the functional properties of the single-source-precursor-derived ZrC–ZrB₂–SiC nanocomposites will be of great fundamental interest and are now in progress.

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