J Mater Sci (2010) 45:6401–6405
DOI 10.1007/s10853-010-4722-y

A simple way to prepare precursors for zirconium carbide

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Received: 4 November 2009 / Accepted: 15 June 2010 / Published online: 9 July 2010

Abstract A precursor for zirconium carbide was obtained by just blending zirconium butoxide $Zr(OC_4H_9)_4$ (ZTB) and divinylbenzene (DVB). This precursor satisfied the requirements for use in ceramic matrix composites fabrication via precursor infiltration and pyrolysis (PIP) process, that is, it was a solution, cross-linked at 150 °C for 2 h, and transformed to ZrC matrix upon heat treatment at 1,600 °C with a ceramic yield around 40%. The cross-linking behavior, pyrolysis process, and optimal molar ratio (ZTB and DVB) of the precursor were investigated by IR, DSC–TGA, and XRD analysis. ZTB and DVB decomposed into ZrO_2 and carbon, respectively, at 400–500 °C, and ZrO_2 and carbon reacted with each other via carbo-thermal reaction at higher temperature to form ZrC.

Introduction

Zirconium carbide (ZrC) is a good candidate for ultra-high temperature applications such as nose caps and sharp leading edges for supersonic flight vehicles and rocket nozzles due to its high melting point (3,400 °C), good chemical inertness, low evaporation, high hardness, and good ablation resistance [1]. It also can be used as diffusion barrier in nuclear industry and cutting tools. Therefore, the inherent brittleness, low reliability, and poor shock resistant properties of ZrC bulk ceramic limit its application. Fiber reinforced ceramic matrix composites might overcome these drawbacks, and yet few papers were published about ZrC matrix composites. Dong et al. [2] reported unidirectional carbon fiber reinforced C/ZrC–SiC composites by slurry and hot pressing method. Zhang et al. [3] reported 2D C/ZrC–SiC composites by CVI process. Hu et al. [4] reported carbon cloth reinforced 2D C/SiC–ZrC composites by slurry and precursor infiltration and pyrolysis (PIP) process. These reports, however, are limited to 1D or 2D composites and cannot be extended to preparation of three dimensional (3D) textile reinforced composites because of lacking facile preparation method of ZrC, either by vapor or liquid route.

Usually ZrC can be prepared by carbothermal reduction of carbon and ZrO_2 [5–7], mechanical alloying [8], self-propagating high-temperature synthesis [9, 10], et al. However, most of the methods are only suitable for powder synthesis. Sol–gel is a potential method to prepare precursors for ZrC. Preiss et al. [11] used chelated derivatives of zirconium *n*-propoxide and various soluble carbon-yielding compounds to synthesize ZrC fibers, films, and powders. Dolle et al. [12] synthesized nano-size ZrC powder with zirconium *n*-propoxide and saccharose. The main drawback of sol–gel method is low content of end product (ZrC) in the solution and usually the solution needs to be concentrated.

PIP process is an effective method to prepare continuous fiber reinforced ceramic matrix composites, while the precursor for PIP process is a key raw material. The precursor must be dissolved into a solution, or be melt, to the best can be cross-linked, has a high ceramic yield upon pyrolysis, and furthermore, can be easily stored with a long shell life. The difficulty to prepare ZrC matrix composites by PIP method comes mainly from the lack of proper precursors.

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In this article, a simple way was presented to prepare ZrC precursor, and accordingly cross-linking, pyrolysis behaviors of the precursor were investigated.

Experimental procedure

Zirconium butoxide $Zr(OC_4H_9)_4$ (ZTB, diluted in 14 wt% butanol) was used as ZrO_2 precursor, and divinylbenzene (DVB, diluted ~50 wt% in xylene) was used as carbon source. During heat treatment, ZTB was supposed to transform completely into ZrO_2, and DVB into carbon with yield ~30 wt% according to our experiment results. After simple calculation theoretical molar ratio of Zr and C is 1/3 according to the following reaction (1).

$$ZrO_2 + 3C = ZrC + 2CO\uparrow \quad (1)$$

ZTB and DVB solutions were used as received. First, DVB was added to ZTB at certain molar ratios (Table 1), stirred for 1 h, and a homogeneous solution was obtained. Then the solution was transferred into a tube and cross-linked at 150 °C for 2 h, and a light yellow solid was obtained. All the operations should be isolated from the humidity because ZTB is easy to hydrolyze.

Finally, pyrolysis was carried out with a graphite furnace in flowing argon (purity 99.999%) at a heating rate of 10 °C/min, and held at the highest temperature for 1 h.

The apparent volume shrinkages during cross-linking treatment were measured as follows. The mixture was transferred into a test tube with an inner diameter of 20 mm. The height of the liquid was measured by vernier caliper. After cross-linking, the solid was taken out from the test tube, and its diameter and length were tested to calculate the volume shrinkage.

Infrared spectroscopy (IR, Niolet-360) was performed on the precursor and pyrolysis products with KBr pellets. Liquid samples were pasted on the KBr pellets. Solid samples were mixed with KBr powder and pressed into thin pellets. The thermodynamic change of the precursor was measured by differential scanning calorimetry–thermogravimetric analysis (DSC–TGA, STD Q600 V8.2 Build 100) in argon atmosphere with a heating rate of 5 °C/min. The phase compositions were examined using X-ray diffractometry (XRD, Siemens D-500) with Cu Kα radiation.

Results and discussion

Compatibility investigation of ZTB and DVB

When DVB was added into ZTB, two separate layers appeared. The mixture changed into a homogeneous light yellow solution right after stirring, and the solution remained stable for over 1 week. The solution was easy to flow and the viscosity was near that of water, though the real viscosity was not measured. When the solution was exposed to air (humidity), it would hydrolyze in several hours (depending on humidity) and a white powder appeared because of ZTB hydrolyzation, so the solution must be stored in protection of inert gas (nitrogen).

Cross-linking treatment

After cross-linking treatment, there were almost 30% volume shrinkage (by simple calculation of diameter and length), and over 50% weight loss for the samples (Table 1).

The IR spectra of ZTB, DVB, and the mixed precursor ZC13 (before and after cross-linking treatment) were shown in Fig. 1. The spectra of the precursor showed all the characteristic peaks of ZTB and DVB, much like stacking of two separate spectra, indicating that the preparation of precursor was a process of mixing without any chemical reactions. The stirring of the solution was carried out in order to promote the molecular mixing of ZTB and DVB.

After cross-linking treatment, the spectra of the precursor (Fig. 1) changed mainly in two aspects: one was the disappearance of peaks from C=C bond at 1640 cm^{-1}, which means cross-linking of DVB; the other was that most narrow, sharp peaks reflecting fine structures were replaced by broad, stunt peaks. During this process, the peaks from Zr–O bonds (700–400 cm^{-1}) remained unchanged.

Pyrolysis process

The pryolysis process of the above cross-linked precursors was investigated from 300 to 1,600 °C. First, the colors of the precursors changed after heat treatment, from light yellow at 300–400 °C, to brown at 500 °C, and gradually

Table 1 Characteristics of the precursors

Samples	Zr/C (molar ratio)	Shrinkage (vol%)	Solid yield after cross-linking (wt%)	Ceramic yield (wt%)	
				1,200 °C	1,600 °C
ZC13	1/3	29.4	46.42	60.15	48.98
ZC15	1/4.5	29.9	42.52	60.77	46.20
ZC16	1/6	30.1	47.53	49.97	42.09

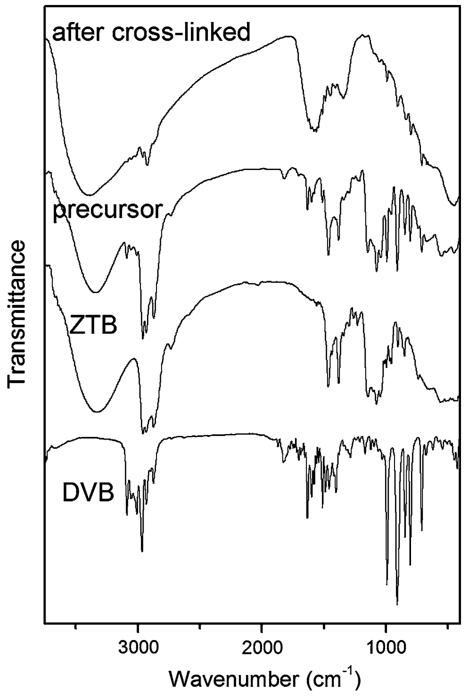

Fig. 1 IR spectra of sample ZC13 (before and after cross-linking treatment), ZTB, and DVB

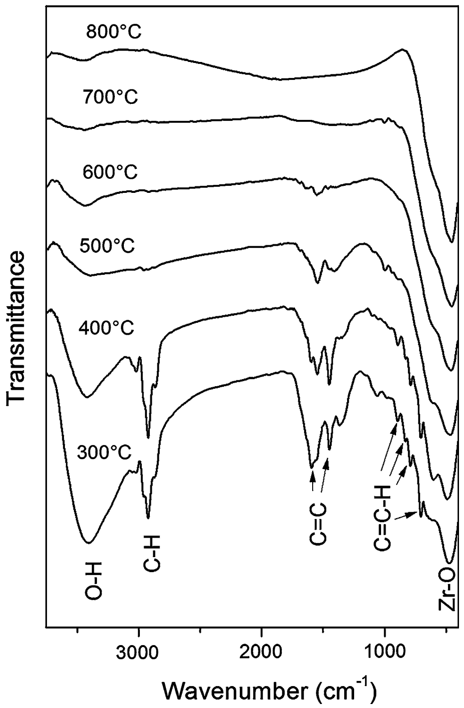

Fig. 2 IR spectra of sample ZC13 after heat treatment at 300–800 °C

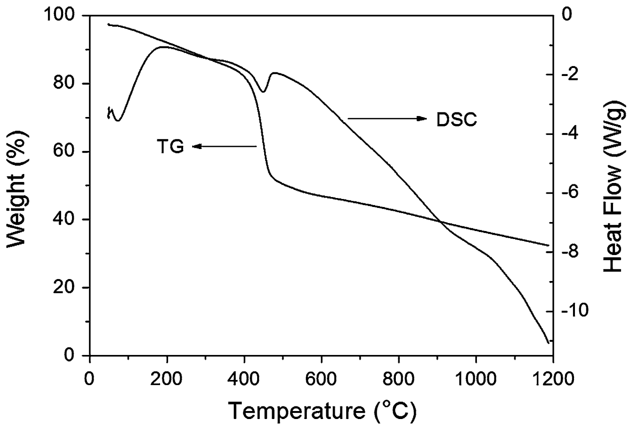

Fig. 3 DSC–TGA analysis of the cross-linked sample ZC13

to gray and black when over 500 °C. This phenomenon indicated the carburization process of the precursors. When heat treatment at 300–400 °C, the cross-linked precursor was still organic and the yellow color came from zirconium complexes. When the temperature was 500 °C and higher, the decomposition of the precursors began, leading to organic groups missing and carbon formation, thus color change (brown, gray, and finally black).

Figure 2 shows the IR spectra of the sample ZC13 after heat treatment at 300–800 °C. The single peak between 700 and 400 cm^{-1} was characteristic of Zr–O bonds, which existed through 300 and 800 °C. The remain of solvent component of *n*-butanol was indicated by the large, broad peak for the OH stretching vibration over the range of 2700–3700 cm^{-1} at 300 and 400 °C. The stretching vibrations from C–H bonds of alkyl and phenyl (2960–2850 cm^{-1} and 3100–3000 cm^{-1}, respectively) were still visible at 400 °C. The strong stretching vibrations from C=C bonds of phenyl was an intense peak in the spectra. After heat treatment at 500 °C, the intensities of O–H, C–H, and C=C peaks were much weaker, which indicated that most of the organic components were decomposed in the range of 400–500 °C. There was only Zr–O bond exist in the spectra above 600 °C.

Figure 3 depicted the DSC–TGA curves of the precursor after cross-linking treatment at 150 °C. TGA analysis showed that there was ~20% mass loss till 400 °C, which was attributed to the volatilization of the residual solvent butanol and some impurities from DVB. The large weight loss (30%) occurred during 400–500 °C due to the decomposition of organic components, and accordingly DSC results showed an endothermic peak at 447 °C.

When the temperature was over 500 °C, the weight appeared a steady though slow decrease (total 25%) till 1,200 °C, indicating residual groups losing.

Carbo-thermal reduction between ZrO_2 and carbon did not happen below 800 °C, and this was approved by XRD patterns (Fig. 4). There was no diffraction peak observed in the curve of 300 °C, which meaned the cross-linked precursor did not decompose or the products did not crystallize. The onset of tetragonal ZrO_2 (*t*-ZrO_2) crystallization

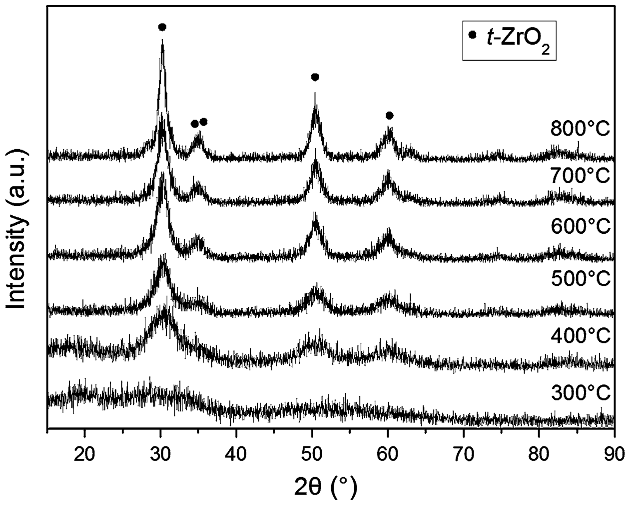

Fig. 4 XRD patterns of sample ZC13 after heat treatment at 300–800 °C

Table 2 Crystallite sizes of *t*-ZrO$_2$ after heat treatment at 300–800 °C

Temperature (°C)	300	400	500	600	700	800
Crystallite size (nm)	–	3.0	3.7	5.7	6.4	9.0

was apparent by XRD in the 400 °C products, but the peaks were weak and broad. With temperature increase, the significant change was the intensity increase of *t*-ZrO$_2$ peaks, thus the crystallization degree increase of *t*-ZrO$_2$. There was no diffraction peak of carbon in the curves because carbon remained amorphous. According to Scherrer equation, the crystallite sizes of *t*-ZrO$_2$ in the products were at nanometer level (Table 2).

When sample ZC13 was treated at higher temperatures, the phase composition and crystal structure changed (Fig. 5). The XRD patterns of this sample showed that some *t*-ZrO$_2$ had transformed to monoclinic ZrO$_2$ (*m*-ZrO$_2$) below 1,200 °C, and formation of ZrC was observed at 1,400 °C, which is lower than the temperature 1,653 °C by thermodynamics calculation [13]. This was because carbon and zirconium oxide had been mixed at the molecular level, and also pyro-carbon was more fresh and active. ZrC became the dominant phase at 1,600 °C, although a substantial amount of *m*-ZrO$_2$ was still present, while *t*-ZrO$_2$ phase almost disappeared. Again there were no peaks from carbon, because carbon was amorphous. The ceramic yield of sample ZC13 after cross-link was about 48.98 wt% at 1,600 °C.

The stoichiometric molar ratio of ZTB and DVB was basically 1:3 according to reaction (1), but pure ZrC was not obtained at 1,600 °C. In order to synthesize ZrC without oxide, several molar ratios of ZTB and DVB were used (see Table 1). The XRD patterns (Fig. 6) showed that there was still little *t*-ZrO$_2$ phase in all samples at 1,600 °C, and the relative amount of *m*-ZrO$_2$ in the sample decreased with the increase of DVB (ZC15 and ZC16). For the sample of ZC16 after heat treatment at 1,600 °C, ZrC was the major crystalline phase, again little ZrO$_2$ existed, showing that even if carbon was in excess, the complete transformation of ZrO$_2$ was difficult. Although excess carbon and oxygen existed, the XRD pattern of ZC16 after 1,600 °C matched the PDF card of #73-0477 perfectly, indicating that the crystal has a Zr/C molar ratio of 1:1.

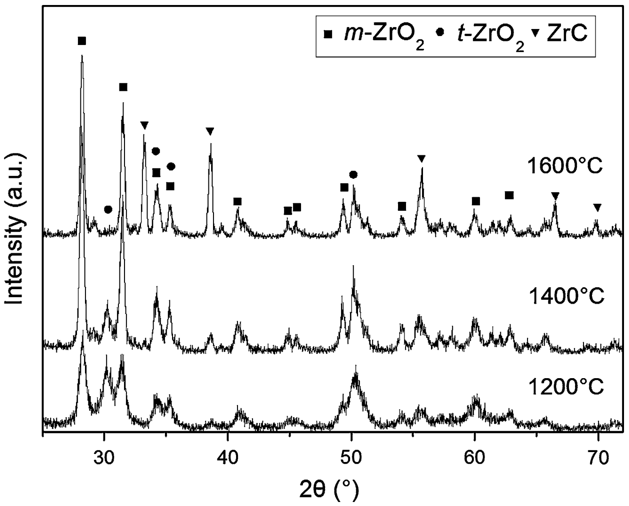

Fig. 5 X-ray diffraction patterns of sample ZC13 after heat treatment from 1,200 to 1,600 °C

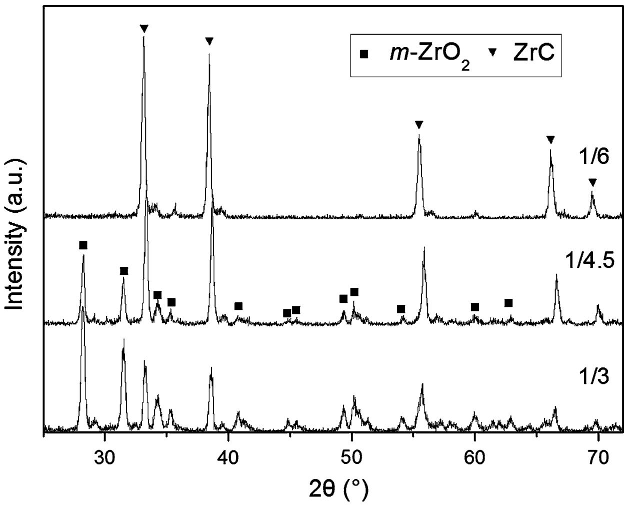

Fig. 6 XRD patterns of the samples with different Zr/C ratios after heat treatment at 1,600 °C

After heat treatment at 1,200–1,600 °C, the crystallite sizes and weight percentages of different phases of ZrC precursor were determined from Figs. 5 and 6 (Table 3). The phase innovation may be deduced according to the weight percentages of different phases at 300–1,600 °C. The

Table 3 Crystallite sizes and phase mass of ZrC precursor after heat treatment at 1,200–1,600 °C

Samples	Heat treatment temperature (°C)	Crystallite size (nm) and wt%		
		m-ZrO_2	*t*-ZrO_2	ZrC
ZC13	1,200	17.5 (68.28)	10.7 (31.72)	None
	1,400	40.5 (85.20)	14.0 (14.80)	Tiny
	1,600	57.0 (79.29)	Tiny	81.1 (20.71)
ZC15	1,600	67.7 (50.41)	Tiny	93.1 (49.59)
ZC16	1,600	Tiny	Tiny	106.4 ($\sim$100)

ZrC precursor decomposed into ZrO_2 and carbon, and then crystallized into *t*-ZrO_2. During 400–800 °C, the crystallite size of *t*-ZrO_2 increased. Then phrase transformation (*t*-ZrO_2 → *m*-ZrO_2) happened during 800–1,600 °C. At temperature higher than 1,400 °C, *m*-ZrO_2 reacted with carbon to form ZrC.

Conclusions

A precursor of ZrC has been prepared by using $Zr(OC_4H_9)_4$ and DVB as zirconia and carbon precursors. The ZrC precursor was stable, cross-linked at 150 °C, decomposed at 400–500 °C, changed into ZrC at over 1,400 °C, and ZrC was the major component at 1,600 °C with optimal Zr/C molar ratio. The ceramic yields of the precursors after cross-linking treatment were about 40% at 1,600 °C. The precursor is being used to prepare ZrC matrix composites.

Acknowledgement This work was financially supported by the National Natural Science Foundation of China.

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