ARTICLE IN PRESS

Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

A meltable precursor for zirconium carbide ceramics and C/C-ZrC composites

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ARTICLE INFO

Keywords:
Zirconium carbide
Meltable precursor
Condensation
Pyrolysis

ABSTRACT

For process simplification and rapid densification of ceramic composites, a meltable single-source ZrC precursor was prepared by condensing zirconium acetylacetonate ($Zr(acac)_4$) at 190 °C for 40–150 min. The preparation of ZrC precursor and the conversion from precursor to ceramics were investigated by using FTIR and NMR spectroscopies, GPC, DSC-TGA, XRD, SEM, EDS and TEM. The precursor had low viscosity (~ 10 mPa s) and proper processing window (60 min) for precursor infiltration and pyrolysis (PIP). The ceramic yield at 1650 °C was 29.6%, and EDS revealed that the composition was $(ZrC)_{0.337}(HfC)_{0.0025}(ZrO_2)_{0.044}C_{0.1865}$. The ceramics were composed of 0.2–0.5 µm grains which aggregated to form a stacked structure surrounded by amorphous carbon. The preparation processes were designed, and C/C-ZrC composites with the density of 2.45 g/cm^3 were successfully fabricated through 11 cycles of PIP with $Zr(acac)_4$. In conclusion, the synthetic method provides a simple and cheap route for precursors, and allows combined composite preparation with high efficiency.

1. Introduction

Continuous fiber reinforced ultra-high temperature ceramic matrix composites (UHTCMCs) have excellent mechanical properties, oxidation and ablation resistances at high temperatures, as well as high fracture toughness (~ 18 MPa m$^{1/2}$) compared with those of bulk UHTCs (2–4 MPa m$^{1/2}$) [1–3]. UHTCMCs are promising to be used in nose caps, sharp leading edges of supersonic flight vehicles and solid rocket throats [4,5].

UHTCMCs have mainly been prepared by precursor infiltration and pyrolysis (PIP) [1,6–8], reactive melt infiltration [9] and slurry process [10]. The PIP process has the advantages of low temperature and near net shaping for large, thick, and complex shapes, and has been widely used to prepare C/SiC and SiC/SiC composites, but the lack of suitable precursors for UHTCs such as ZrC and ZrB_2 limits its application in UHTCMCs preparations. Schwab [11], Cai [12], and Chen [13] synthesized ZrC and ZrC-SiC precursors through inorganic and organometallic reactions. Nevertheless, the synthetic processes were complicated, and the raw materials were expensive. Meanwhile, these precursors were sensitive to air and moisture, thus being inconvenient for further composite preparation. Zhao [14] proposed a simple blending method to prepare ZrC precursor, but it was unstable in air due to hydrolysis. Yan [15] reported a polyzirconoxane precursor for ZrC ceramics. Though the ceramic yield reached ~ 46%, the precursor content in solution was as low as 30% due to stability, so the effective transformation ratio was rather low if used in composite preparation. The same problem existed in some other literatures [16,17].

In this study, a precursor for ZrC was synthesized in one step from a low-cost raw material. The precursor had satisfactory processing properties for composite preparation, producing near stoichiometric ZrC after pyrolysis without using any other additives such as phenolic resin. Besides, the precursor was successfully used to fabricate C/C-ZrC composites by PIP.

2. Experimental procedure

2.1. Materials

$Zr(acac)_4$ (technical purity: 99.0%; Yangzhou Xingye Assistant Corporation, Jiangsu Province, China) was used as starting material.

Three-dimensional needled integrated felts with T700 carbon fibers (Toray, Tokyo, Japan) were used as the preforms of the composites, and the volume fraction of carbon fiber was 28%.

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https://doi.org/10.1016/j.ceramint.2018.03.007
Received 1 January 2018; Received in revised form 24 February 2018; Accepted 1 March 2018
0272-8842/

Please cite this article as: Li, Y., Ceramics International (2018), https://doi.org/10.1016/j.ceramint.2018.03.007

2.2. Precursor preparation

Zr(acac)$_4$ (1 mol) was added to a 1000 mL three-necked flask (equipped with a mechanical stirrer, N_2 inlet/outlet, and a condenser). The flask was heated to 190 °C in an oil bath and held for different times: 40 min, 60 min, 80 min, 100 min, 120 min and 150 min. The obtained ZrC precursors were labeled as ZC40, ZC60, ZC80, ZC100, ZC120 and ZC150, respectively.

2.3. Ceramic preparation

Pyrolysis was carried out in a graphite furnace using flowing argon (purity: 99.999%) at 1200–1700 °C for 1 h.

2.4. C/C-ZrC composites fabrication

For comparison with composite preparation in Ref. [17], the felts were coated with PyC interphase (~ 1.34 μm) by chemical vapor infiltration using propylene as the precursor gas. The PyC-coated preforms were covered by Zr(acac)$_4$ powders and placed in an autoclave which was evacuated and then heated to 190 °C for 150 min. During heating, Zr(acac)$_4$ melted, infiltrated into the preform by capillary forces, and condensed *in situ*. After impregnation, the samples were treated at 1650 °C for 1 h in flowing argon (purity: 99.999%). The infiltration, condensation and treatment were repeated for 11 cycles and C/C-ZrC composites were obtained.

2.5. Characterizations

The viscosities of ZrC precursor at 190 °C were measured by NDJ-1 rotation viscometer. The timer was started when Zr(acac)$_4$ was put into a 250 mL beaker. After the precursor melted, its viscosity was measured every 1–5 min.

The molar ratio of C/ZrO_2 in pyrolysis product at 1200 °C was calculated from the data through an oxidation test. The pyrolysis product was ground to powders, put into a corundum crucible, and oxidized at 1000 °C for 1 h in air in a muffle furnace. Carbon was oxidized to CO/CO_2 and lost, leaving ZrO_2. The samples before and after oxidation were weighted. Considering some carbon may be left, the calculated values had certain errors.

The structures were characterized by FTIR spectrometer (Avaar 360, Nicolet, Madison, WI), GPC (Wyatt Instrument with a Dawn Heleos-II detector, THF as solvent), NMR spectrometer (Agilent 400/54, Palo Alto, USA; ^{13}C NMR and ^{1}H NMR, methanol-*d$_4$* as solvent), XRD diffractometer (Siemens D-500, Germany; Cu K_α radiation), SEM (S4800, Hitachi, Japan), EDS (S4800, Hitachi, Japan) and TEM (Tecnai G2 F20, USA). Contents of oxygen and carbon were measured by oxygen-nitrogen analyzer (EMGA-820, Horiba, Japan) and carbon-sulfur analyzer (EMIA-320V2, Horiba, Japan), respectively. DSC-TGA (NetzschSTA449C, Selb, Germany) was used to trace the pyrolysis process in an argon atmosphere at a heating rate of 10 °C/min.

The apparent density and open porosity of C/C-ZrC composites were measured by the Archimede's method. The microstructure was examined by environmental electron microscope (Quanta 200, Eindhoven, Holland).

3. Results

3.1. Condensation process

3.1.1. Polycondensation reaction

The appearances of the precursors are shown in Fig. 1. Zr(acac)$_4$ existed as white powders. After heating and melting, the product colors changed from light yellow (ZC40) to brown (ZC80) and dark brown (ZC120 and ZC150) as the holding time increased.

ZC80, ZC100, ZC120 and ZC150 were soluble in ethanol, but parts of ZC40 (26.6%) and ZC60 (7.9%) were insoluble. FTIR spectra show that these insoluble parts (the soluble parts are labeled as ZC40* and ZC60*, respectively) are Zr(acac)$_4$ (Supplementary material), so Zr(acac)$_4$ completely reacted within a minimum of 80 min.

The FTIR spectra of Zr(acac)$_4$, ZC40*, ZC60*, ZC80, ZC100, ZC120 and ZC150 are shown in Fig. 2. The absorption peaks are assigned as follows: ν(=CH), 2993; ν(CH$_3$), 2958; ν(C=O), 1592; ν(C=C), 1524; δ(CH$_3$), 1457 and 1364; δ(C-H), 1404; ν(C-O), 1280; ν(=CH), 1135; ρ(CH$_3$), 1007; ν(C-C), 927; γ(=CH), 771; δ(C-C(O)-C), 647; δ(C-C=O), 533; ν(Zr-O), 424. The ν(C=O) and ν(C=C) peaks of acetylacetone (Hacac) are located at 1705, 1727 and 1620 cm^{-1} (Supplementary material), which shift to lower wavenumbers in Zr(acac)$_4$ due to the aromatic cyclic structure of acac ligand [15] (Fig. 3). The spectra of ZrC precursors contain nearly all peaks of Zr(acac)$_4$, indicating the existence of aromatic cyclic structure. The corresponding peaks are weakened after the polycondensation reaction, indicating that Zr(acac)$_4$ lost part of acac ligands at 190 °C. The possible structural formula of ZrC precursors is shown in Fig. 3. The molecular chain consisted of Zr centers connected with each other by –OC(CH$_3$)CHH(CH$_2$)O- formed by acac ligand losing one H atom. As a result, there are some new absorption peaks in the spectra of ZrC precursors: ν(C=C), 1631; δ(=CH$_2$), 1480; ν(C-O), 1212; τ(=CH$_2$), 994; ω(=CH), 845.

ZC150 was prepared only by heating Zr(acac)$_4$ at 190 °C, so there must be some by-products of the polycondensation reaction (Hacac) in the ZrC precursor and the ^{1}H NMR spectra of ZC150 are complex (Fig. 4). The peaks at 8.441 ppm and 8.278 ppm can be attributed to H-2, which split into two peaks due to the aromatic cyclic structure and inductive effect of π electron cloud in C=C. Meanwhile, there are peaks corresponding to all H atoms, verifying the structural formula of this ZrC precursor.

As evidenced by FTIR and ^{13}C NMR spectra, the condensed liquid parts were Hacac (Supplementary material). The possible polycondensation reaction is shown in Fig. 3.

3.1.2. Viscosity of ZrC precursor

Viscosity is a vital factor for precursor to fabricate composites by PIP, and the viscosity of polymer is influenced by its molecular weight. Fig. 5 presents GPC traces of the ZrC precursors. There are a few divided peaks (a, b, c, d and e), indicating that the precursors had wide molecular weight distributions. The number-average molecular weights (*Mn*) of ZrC precursors relative to polystyrene standards were determined by the GPC traces in Fig. 5 (Table 1). Based on *Mn* and the structural formula of ZrC precursor (Fig. 3), the degree of polymerization (*n*) was ~2 during 40–100 min and increased to ~ 3 during 120–150 min.

In short, Zr(acac)$_4$ melted at 190 °C and then reacted to produce polyzirconoxane (ZrC precursor). The polycondensation reaction proceeded as the holding time increased. *Mn* of the precursors rose, which affected their viscosities. If the viscosities were measured after the precursors melted at 190 °C, the values were inaccurate due to further reaction during melting. Thus, the viscosity was measured during precursor preparation and many values were recorded to study the curve (Fig. 6). The viscosity could not be measured until Zr(acac)$_4$ was kept at 190 °C for 35 min, suggesting it almost melted. At 40 min, 73.4% of Zr(acac)$_4$ reacted and the viscosity decreased to ~ 10 mPa s. During 40–100 min, *n* of ZrC precursor remained at ~ 2, so the viscosity changed a little, which was as low as 10–148 mPa s, markedly benefiting infiltration in the PIP process. The processing window was also enough (around 60 min) for complete infiltration. After 100 min, *n* of ZrC precursor gradually increased to 3, and the viscosity rose dramatically.

3.2. Pyrolysis process

The major constituent of ZrC precursor was polyzirconoxane which was usually obtained by chelation of Hacac to zirconium [15,16,18,19]