

ZrB₂–SiC spiral fibers prepared by combining liquid rope effect with non-solvent-induced phase separation method: A promising toughening material for ultra-high temperature ceramics

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Abstract: Spiral fibers were considered to be an ideal toughening phase of ultra-high torsional release effect. In this work, ZrB₂ (Z)–20 vol% SiC (S) spiral fiber (ZS_{sf}) with controllable structure was prepared by a combination approach of liquid rope effect and non-solvent-induced phase separation. Dominantly depended on the kinematic viscosity (η), dropping height (H), and flow rate (Q), the geometric parameters of ZS_{sf} involving filament diameter (d) and coil diameter (D) were followed the relationship of $d \approx 0.516 \times 10^{-3} Q^{1/2} H^{-1/4}$ and $D \approx 0.25 \times 10^{-3} (Q/H)^{1/3}$, respectively, within the optimized η of 10–15 Pa·s. Three different microstructures of ZS_{sf} were achieved by adjusting the polymer/solvent/ non-solvent system assisted with phase diagram calculation, including dense, hollow, and hierarchical pore structures. The ZrB₂–SiC with 1 wt% ZS_{sf} composites prepared by hot isostatic pressing (HIP) exhibited a ~30% increase in fracture toughness (K_{IC} , 4.41 MPa·m^{1/2}) compared with the ZrB₂–SiC composite, where the microscopic fracture toughness of the ZS_{sf} was ~80% higher than that of the matrix. The fibers with a ~10 nm *in-situ*-synthesized graphite phase amongst grain boundaries of ZrB₂ and SiC changed the fracture mode, and promoted the crack deflection and pull-out adjacent the interface of matrix and the fiber.

Keywords: ultra-high-temperature ceramics (UHTCs); spiral fibers; liquid rope effect; structure control; fracture toughness

1 Introduction

When hypersonic vehicle travels back to the atmosphere,

the aerodynamic heating would cause the temperature of key components to exceed 2000 °C by oxidation and heat flow, which makes serious challenges for the thermal protection system [1–4]. Ultra-high-temperature ceramics (UHTCs) are considered to be the most promising material, while traditional refractory materials, such as C/C composites and C/SiC composites, cannot

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reply the demanding thermal-protection requirements [5–8]. However, due to the crack sensitivity and lower strain tolerance of single-component UHTCs [9,10], toughening phases need to be used to improve the fracture toughness in practical application [11–14]. Among them, carbon fiber (CF) is considered to be a material that is expected to fundamentally solve the brittleness of ceramics by bridging mechanism and crack deflection, so that the energy applied to the composite material can be slowly released to improve the fracture toughness of the composite material [15–19]. However, not only CFs could prone to chemical reactions with impurities due to poor temperature resistance and antioxidant, but also the interface mismatch during high temperatures reduced the toughening efficiency of CF [20,21]. At the same time, poor dispersion of CF limited the improvement of fracture and thermal vibration properties of CF/UHTC composite materials.

Hasselman's classical fracture mechanics equation [22–24] pointed out that increasing the damage tolerance of materials could also shift the brittle fracture to the non-brittle fracture mode. Analogous to bionics, adjusting the microstructures of UHTC materials (such as spiral structure) could greatly increase the crack propagation path and energy dissipation, thus improving the damage tolerance of the material [25–27]. The spiral structure greatly increased the deformation scale of the material by converting the tensile deformation into torsional deformation, reducing the rapid failure under the tensile stress [28]. Gao *et al.* [29] used the crack bridging model to show that the effect on shock absorption and impact resistance with the spiral structure effectively relieves stress concentration. Els [30] prepared boride two-dimensional (2D) spiral-toughened phases by using a co-extrusion process and observed significant crack deflection in and around the spiral phase. The addition of the spiral phase increased the fracture toughness of the material by up to ~200%.

Chemical vapor deposition (CVD) was considered to be a promising technology to fabricate the spiral micro-fibers compared with the pressure injection molding and thermoplastic extrusion method [31–34]. However, the geometry of ceramic coils by CVD was limited by equipment (filament diameter, $d < 5 \mu\text{m}$), while it was difficult to mass application preparation of ceramic spiral fiber by the above methods limited by preparation accuracy, high equipment cost, and time consumption. In Ref. [35], the YSZ spiral fibers

prepared by the non-solvent phase inversion assisted electrostatic micro-spraying method achieved a breaking elongation of 4.36%. In the method, the phase diagram can be used to describe the thermodynamic properties of the ceramic suspension system, guiding adjustment of the pore structure of the as-received ceramic spiral fibers [36–38]. According to the calculation of the phase diagram, systems of non-solvent-induced phase separation could be selected to construct different pore structures. Therefore, the non-solvent phase inversion assisted electrostatic micro-spraying method was used as the basis for the preparation process of ZrB_2 (Z)–20 vol% SiC (S) spiral fibers (ZS_{sf}) in this work. The effects of the parameters of the phase inversion process on the spiral structure and internal microstructure of the fibers were investigated. The phase evolution and structural changes during the preparation of the ZS_{sf} were explored, and the spiral fiber composites of UHTC materials were prepared and characterized.

2 Experimental

2.1 Raw materials and sample preparation

ZrB_2 and SiC nanoparticles (purity = 99.95%, $50 \pm 25 \text{ nm}$; Aladdin, Shanghai, China) were used for fabricating the ZS_{sf} , while polymer precursors were made by polyether sulfone (PES; BD-5; Baishide, Taizhou, China) and N-methyl-2-pyrrolidone (NMP; analytical reagent (AR), Aladdin, Shanghai, China). First, the polymer suspension was prepared by PES, NMP, and nanoparticles, in which the weight ratios of nanoparticles, PES, and NMP were 2:1:3.5. Ceramic nanoparticles were dispersed in the precursor solution of PES and NMP homogeneously [39,40]. Suspension was achieved by stirring for 8 h at 50°C . Next, the slurry was poured into a beaker with a hole with a diameter of 5 mm at the center of the bottom, and then fell freely from the hole into the non-solvent bath (including water, water–50 vol% NMP, and water–50 vol% glycerin (AR, Aladdin, Shanghai, China)). The shape of spiral fibers was formed under the action of the liquid rope effect, and solidified by non-solvent-induced phase separation. The binder/ceramic mixture was pyrolyzed at 1800°C for 2 h under flowing forming gas (99.99% argon; Air Liquide Co., Ltd., Shanghai, China) for the pyrolysis of polymer into carbon.

2.2 Making reinforced composites

The 1 wt% ZS_{sf} and ZrB_2 –20 vol% SiC powders were thoroughly mixed together by shaking mixing. The resulting powders were loaded into boron nitride-coated graphite hot-press dies. The powders were heated at $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ to $1500\text{ }^\circ\text{C}$, and then slowly heated to $1900\text{ }^\circ\text{C}$ at $5\text{ }^\circ\text{C}\cdot\text{min}^{-1}$, and filled the hot-pressing chamber with argon as a protective gas during this process. Upon reaching $1900\text{ }^\circ\text{C}$, a pressure of 32 MPa was applied for 120 min, after which, the load was removed, and the specimen was cooled to room temperature in the furnace at $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$.

2.3 Measurements of phase, microstructure, and mechanical properties

The scanning electron microscope (SEM; FEI Quanta 200, Eindhoven, the Netherlands) and transmission electron microscope (TEM; Talos F200X G2, Thermofisher, USA) were utilized to observe the morphologies of the ZS_{sf} and the reinforced composite. The phase compositions were evaluated and examined by using the X-ray diffractometer (Ultima IV, Rigaku Co., Japan). The porosity of ZS_{sf} was measured by the Archimedes method for three samples.

The micro-mechanical properties were characterized by the micro-indenter (MHT, Anton Paar, Austria). At least 20 points from each group were taken for assuring representative measuring at a loading rate of $0.3\text{ mm}\cdot\text{min}^{-1}$ with a maximum load of 10 N. The Young's modulus (E), hardness (HV), and fracture toughness (K_{IC}) can be measured through Eq. (1) [41]:

$$\begin{cases} H = \frac{P}{A} \\ E_r = \frac{\sqrt{\pi}S}{2\beta\sqrt{A}} \\ K_{IC} = 0.016\left(\frac{E}{H}\right)^{0.5} \frac{P}{c^{1.5}} \end{cases} \quad (1)$$

where P is the maximum load of indentation test; A is the maximum contact area; E_r is the effective elastic modulus defined by $\frac{1}{E_r} = \frac{1 - \nu^2}{E} + \frac{1 - \nu_i^2}{E_i}$, E_i and

ν_i represent the Young's modulus and Poisson's ratio of the indenter, respectively; ν is the Poisson's ratio of the sample; β is the non-dimensional correction factor to account for deviations from the original stiffness equation, and $\beta = 1.034$ for Vickers indenter; S is

defined as the slope of the upper part of the unloading curve during the initial stage of unloading; and c is the average length of radial crack.

The macroscopic fracture toughness of composites ($3\text{ mm} \times 4\text{ mm} \times 30\text{ mm}$) was measured by the single-edge V-notched beam (SEVNB) method following the ISO 23146:2012 standard [42–44]. A 250- μm diamond grinding wheel was used to cut the U-shaped grooves, and then V-shaped notch was cut by the femtosecond laser (TruMicro 5000, TRUMPF, Germany) in the center of the root of the U-shaped grooves of the test rod. The K_{IC} was determined by using the three-point SEVNB method (Model 5567, Instron, USA), and the K_{IC} values were calculated by Eq. (2) [45]:

$$\begin{cases} K_{IC} = \frac{3P_{\max}S_0\alpha^{0.5}Y(\alpha)}{2BW^{1.5}} \\ Y(\alpha) = \frac{1.99 - \alpha(1 - \alpha)(2.15 - 3.93\alpha + 2.7\alpha^2)}{(1 + 2\alpha)(1 - \alpha)^{1.5}} \end{cases} \quad (2)$$

where $P_{\max}$ is the maximum loading of the three-point SEVNB method; S_0 is the span width; B and W are the width and height of the sample, respectively; α ($= a/W$) is the ratio of notch depth (a) to W ; and $Y(\alpha)$ is the dimensionless correction factor based on α .

3 Results and discussion

3.1 Effect of preparation parameters on the geometry of ZS_{sf}

In this section, micrometer scale fibers are designed and prepared to achieve better toughening effect and sintering performance. In Refs. [46–48], the key parameters affect the formation of spiral fibers and their geometric dimensions, such as flow rate (Q), kinematic viscosity of precursor (η), and dropping height (H). According to Habibi *et al.* [49], liquid rope effect was formed depending on the balance of viscous forces, gravity, and inertia, which could be divided into four different modes: viscous mode, gravitational mode, inertial-gravity mode, and inertial mode. Since the H in this paper was large relative to the diameter, the slurry was under the inertial mode (I), where the long tail of the rope was like a distributed pendulum [50]. When the fixed frequency of the coil is close to a natural frequency of the tail, the long tail enters resonance with the coil. Figures 1(b)–1(e) show the morphologies of the ZS_{sf} precursor with different η

when the H was 30 cm, and the Q was $6 \text{ mL} \cdot \text{min}^{-1}$. Spiral would not be maintained stably with the decrease of η when the coil diameter (D) formed by the spiral was smaller than d , as shown in Fig. 1(e). In addition, the slurry appeared to a drip state instead of a stable spiral with the increase of η , which was consistent with the prediction of the rope-wrap effect under the action of gravity, as shown in Fig. 1(b). According to Wilson [51] and Stokes *et al.* [52], whether a free-falling liquid could form a continuous flow depended on critical mass of droplet (Δm) and retention time (t) at the hole of the stream [51,52]. The slurry had a tendency to form droplets instead of in a stable state of liquid flow with the increase of t and Δm .

$$t \approx \frac{\mu l}{\gamma} \quad (3)$$

$$\Delta m = \sqrt{\frac{3\mu A_0 \rho Q}{g} + \frac{2.40\gamma R_0}{g}} \quad (4)$$

where μ is the viscosity, l is the coil pitch, γ is the liquid surface energy, A_0 is the tube cross-sectional area, ρ is the density of the liquid, g is the acceleration of gravity, and R_0 is the radius of droplets. Zhang [53] also proved that the liquid was more inclined to form a stable liquid flow with a longer stretch with η decreased, thus ensuring a well periodicity in the preparation of ZS_{sf} . When $\eta \approx 10 \text{ Pa} \cdot \text{s}$, the state of the slurry is more suitable for forming a spiral, as shown in Fig. 1(d).

Both H and Q had significant impacts on the

geometry of the ZS_{sf} . In Fig. 2, as the Q decreases from 25 to $3 \text{ mL} \cdot \text{min}^{-1}$, and the H increases from 10 to 40 cm, the d of the ZS_{sf} decreases from ~ 1500 to $\sim 100 \mu\text{m}$. A higher H and/or a lower Q resulted in a smaller dimension of the spiral fibers due to the smaller cross-sectional area of the slurry as it enters the water. In the steady-state continuous liquid flow, the d was proportional to $Q^{1/2}H^{-1/4}$ under the condition that the initial velocity could be neglected [50]. The variation trends of D and l with the preparation parameters of the spiral fiber are the same as that of d . According to Ref. [50], in the inertial mode (I), the tail is strongly stretched by gravity, which is balanced by the viscous resistance sum. The relationship among d , l , D , and preparation parameters of small-angle spiral fibers is shown in Eq. (5):

$$\begin{cases} d \propto Q^{1/2}H^{-1/4} \\ l \propto \left(\frac{\eta Q}{H}\right)^{1/3} \\ D \propto \left(\frac{\eta Q}{H}\right)^{1/3} \end{cases} \quad (5)$$

Among them, the small-angle helix had a small helix angle ($< 10^\circ$), so it can be approximately considered that there was a proportional relationship between l and d . A linear fitting analysis was performed on the average size of the ZS_{sf} and the

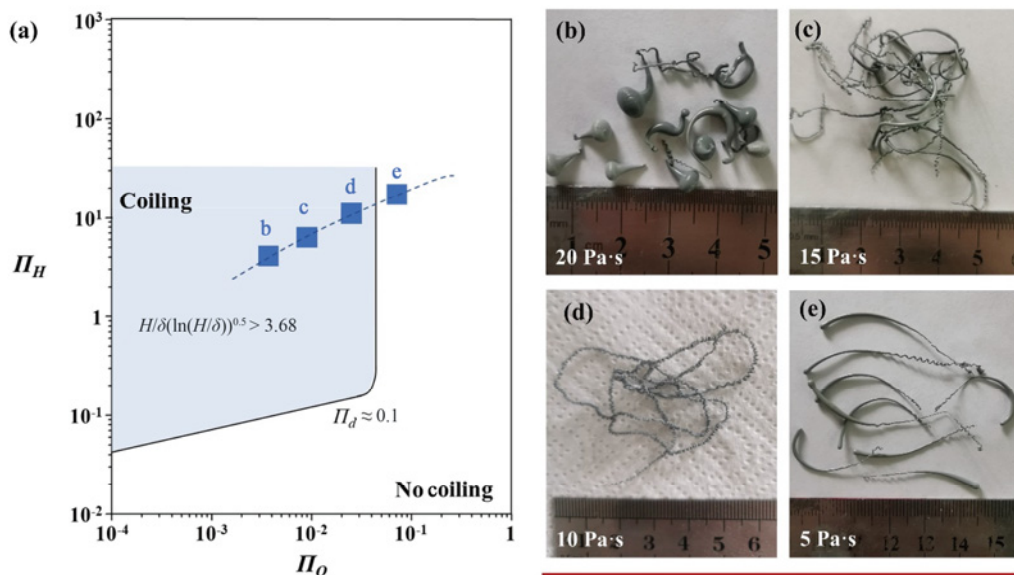


Fig. 1 (a) Formation conditions of ZS_{sf} (Π_H and Π_Q are the factors of independent dimensions in the liquid rope effect, where $\Pi_H = H(g/\eta^2)^{1/3}$ and $\Pi_Q = H(g/\eta^5)^{1/3}$) and fiber morphologies with η equal to (b) $\sim 20 \text{ Pa} \cdot \text{s}$, (c) $\sim 15 \text{ Pa} \cdot \text{s}$, (d) $\sim 10 \text{ Pa} \cdot \text{s}$, and (e) $\sim 5 \text{ Pa} \cdot \text{s}$. Reproduced with permission from Ref. [50] for (a), © Cambridge University Press 2016.

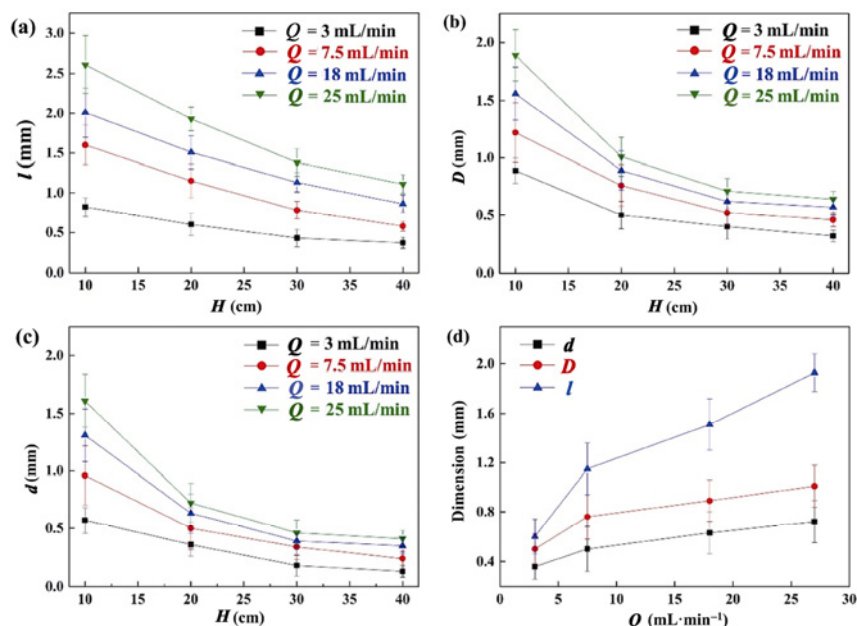


Fig. 2 Effects of Q and H on the preparation parameters of ZS_{sf} : (a) l - H , (b) D - H , (c) d - H , and (d) l - Q , D - Q , and d - Q when $H = 20$ cm.

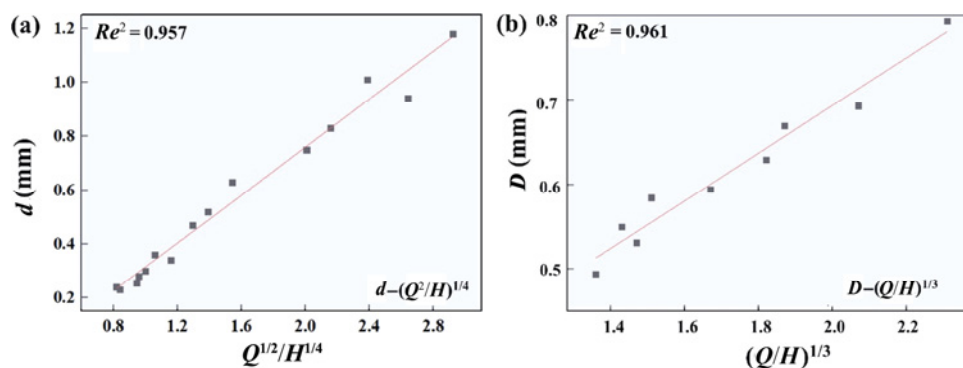


Fig. 3 Linear fitting of ZS_{sf} geometry parameters to preparation parameters: (a) $d \approx 0.516 \times 10^{-3} Q^{1/2}/H^{1/4}$ and (b) $D \approx 0.25 \times 10^{-3} (Q/H)^{1/3}$.

preparation parameters, and the obtained results are shown in Fig. 3. The linear regression between the d and D of the ZS_{sf} (reliability factor ($Re^2 > 0.95$)) showed an obvious positive correlation. From the derivation of the first paragraph in Section 3.1, we speculated that the ZS_{sf} prepared was in inertial mode, and was confirmed by the good fitting parameters. When $Q = 3 \text{ mL} \cdot \text{min}^{-1}$, $\eta = 10 \text{ Pa} \cdot \text{s}$, and $H = 40 \text{ cm}$, the D value is between 300 and 350 μm , and the d is between 80 and 120 μm . The geometry dimension was basically controlled within the scale of 100 μm , which was more valuable as a toughening phase.

3.2 Effect of non-solvent systems on the microstructure of ZS_{sf}

The mechanical properties of ZrB_{2sf} depend largely on their surface density and internal pore structure, which

was jointly determined by the thermodynamic properties of the precursor and the non-solvent bath [28]. The phase diagram is a powerful tool to describe the thermodynamic properties of the polymer/solvent/non-solvent system. Therefore, the effect of the phase inversion process on the microscopic morphology of ZS_{sf} was explored by the phase diagram simulation by MATLAB (MathWorks, USA), and the ZS_{sf} with different pore structures and higher densities were obtained.

The ternary phase diagram obtained by calculation is shown in Fig. 4 (for detailed calculation methods of the phase diagram, please refer to the Electronic Supplementary Material (ESM) in which the left side and right side of the double nodal line were the homogeneous phase and phase separation area, respectively. In Refs. [54–56], the non-equilibrium phase transformation process was easy to form an

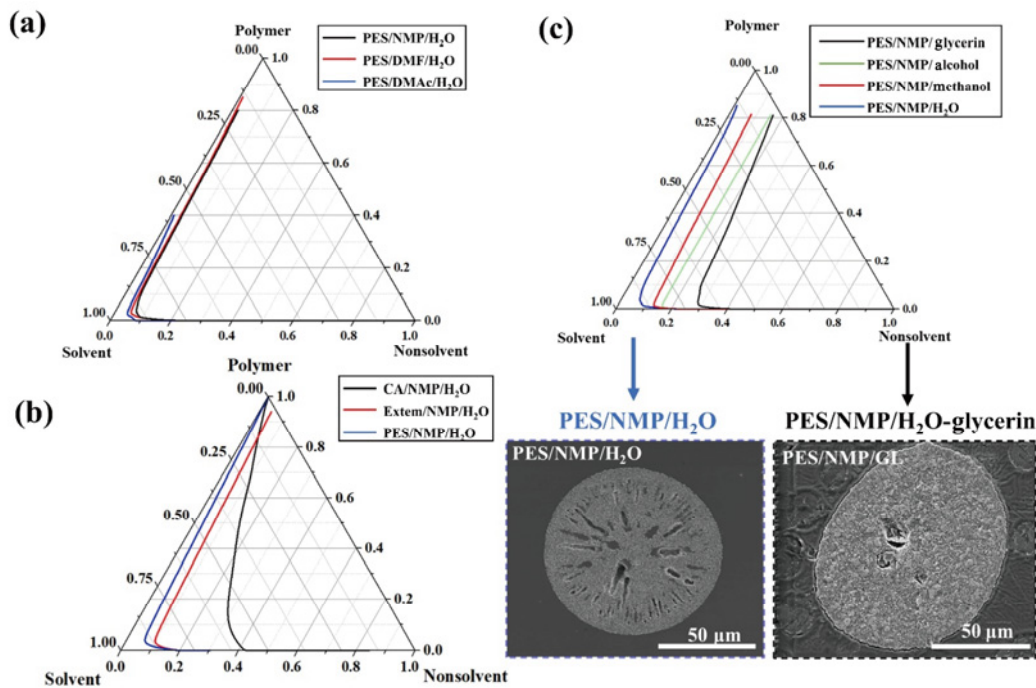


Fig. 4 Phase diagram calculation of polymer/solvent/non-solvent system and internal pore structure control: (a) different solvents, (b) different polymers, and (c) different non-solvent and typical morphologies of the PES/NMP/non-solvent system.

asymmetric finger-like pore structure, while the delayed phase transformation tended to form a sponge-like pore structure with uniform scale. This was also confirmed by the cross-sectional morphologies of the ZS_{sf} prepared by the two systems (Fig. 4). As the area of the homogeneous phase of the PES/NMP/H₂O and PES/NMP/H₂O–50 vol% glycerin (GL) systems gradually increases, the path of the phase separation process during the phase inversion process gradually increases, which made the balance phase inversion process gradually dominate. The morphology of the formed microspheres also changed from hierarchy structure to the sponge-like structure.

The PES/NMP/H₂O, PES/NMP/H₂O–50 vol% NMP, and PES/NMP/H₂O–50 vol% GL systems were selected and sintered at 1800 °C with a heating rate of 5 °C·min^{−1} for 2 h (marked as H₂O–1800 °C, H₂O/NMP–1800 °C, and H₂O/GL–1800 °C, respectively). The ZS_{sf} retains the characteristic original structure after sintering, as shown in Fig. 5. According to the specific pore morphology produced by different phase inversion systems, the ZS_{sf} prepared in this paper can be divided into three types, which were defined as hierarchy structure, core-shell structure, and dense structure. The proposed mechanism of ceramic hollow fiber membranes could explain the relationship between the particle size of the ZS_{sf} product and its internal structure [57]. ZS_{sf} prepared with slow interdiffusion

rates of solvent and non-solvent tended to delay non-solvent-induced phase separation, which was the case with the formation of dense pore structure. On the other hand, the film produced by rapid precipitation rapidly solidifies in the surface layer and produces volume shrinkage to form surface folds, which would entrain the non-solvent into the interior to form a finger-like pore structure. Since the coagulation bath contains NMP, the coagulation bath inside would dissolve a part of the organic matter in the H₂O/NMP–1800 °C, which formed central macropores under the action of surface energy reduction. In addition, Fig. 5 shows that the fibers of the H₂O–1800 °C and H₂O/GL–1800 °C system maintain a good spiral structure, but the fibers of the core-shell structure were prone to collapsing due to the lack of internal support during the sintering process.

In addition, the phase inversion pore morphology was also affected by the kinetic factors during the phase separation process. However, for the ZS_{sf} prepared in this Study, due to the small diffusion path (~50 μm), it is less affected by the kinetics. According to Guo *et al.* [58], it is speculated that when the diameter of the ZS_{sf} reaches the millimeter level, other structures, such as inner dense-shell porous, may appear.

3.3 Sinter behavior and phase composition of ZS_{sf}

Figure 6 shows the X-ray diffraction (XRD) pattern

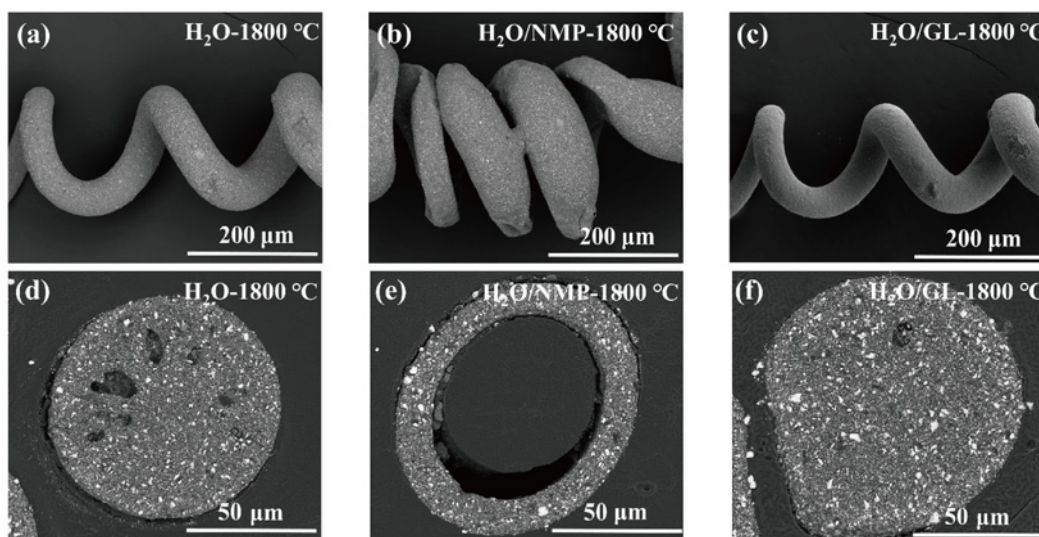


Fig. 5 Surface and cross-sectional morphologies of ZS_{sf} prepared by different polymer/solvent/non-solvent systems: (a, d) H_2O -1800 °C, (b, e) H_2O/NMP -1800 °C, and (c, f) H_2O/GL -1800 °C.

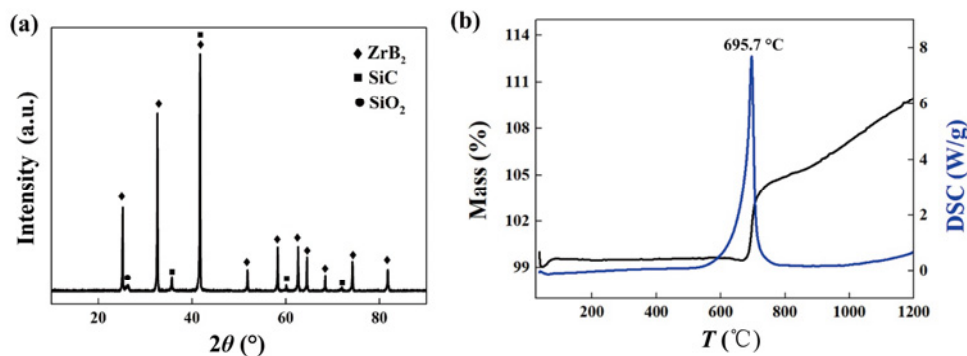


Fig. 6 (a) XRD diffraction pattern and (b) TG/DSC curves of original ZS_{sf} sintered at 1800 °C.

and thermogravimetric (TG)/differential scanning calorimetry (DSC) curves of original ZS_{sf} of H_2O/GL -1800 °C. The sintered product retained the original phase composition well except a small amount of surface oxidation. Due to the pyrolysis of the organic precursor, a certain amount of carbon element would remain in the matrix. According to the analysis of the carbon sulfur analyzer (G4 ICARUS HF, Bruker, Germany), the proportion of carbon generated by the cracking of the organic matter was about 15 wt%. The TG/DSC curves in the air atmosphere were used to characterize the antioxidant properties of the ZS_{sf} ; it could be seen from Fig. 6(b) that the obvious exothermic peak at 695.7 °C (began at ~510 °C) would be caused by the oxidation of ZrB_2 and SiC (the oxidation temperatures of SiC, ZrB_2 , and C in air were at 500, 700, and 420 °C, respectively). The slow oxidation over 800 °C may be due to the inhibition effect of the oxide film formed by the oxidation of SiC,

which achieves the retention of well antioxidant properties of pyrolytic carbon in ZS_{sf} .

In order to study the carbon phase and distributions inside the ZS_{sf} , the SEM and energy dispersive spectroscopy (EDS) characterizations were used for microscopic element analysis. In Fig. S1 in the ESM, the sample can be divided into three phase regions, which are composed of ZrB_2 , SiC, and carbon phase due to different contrasts. A homogeneous wrapping of carbon is identified, and details can be found in Fig. S1 in the ESM. To prove the existence and distribution of carbon element, the phase compositions of the ZS_{sf} were further studied by the high-resolution TEM (HRTEM). In Fig. 7(a), the grain sizes of ZrB_2 and SiC are about 1 μm and 200 nm, respectively, in which there is a good connection between the grains. The pyrolytic carbon exists in the form of a graphitic phase around the grains of SiC and ZrB_2 , and its lattice structure exhibits a discontinuous morphology, as

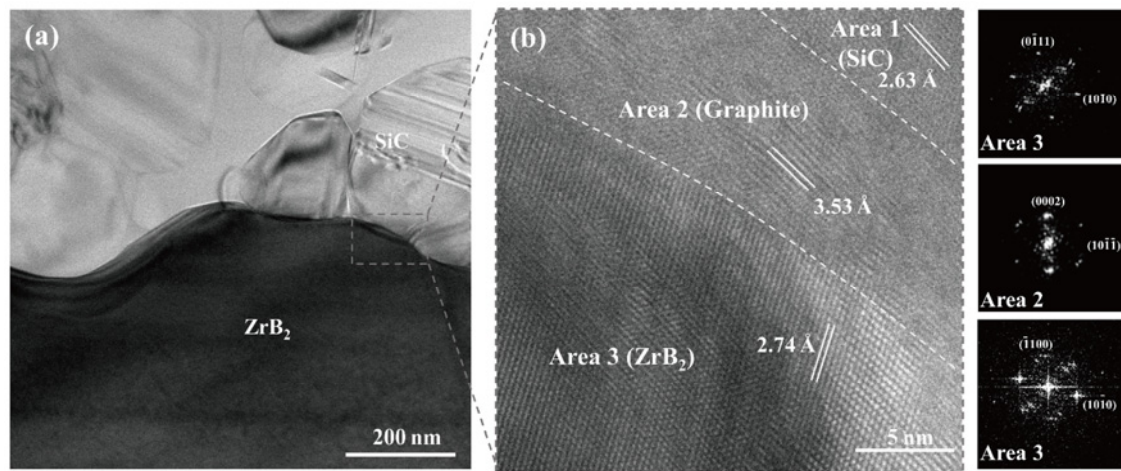


Fig. 7 (a) Cross-sectional morphologies by the TEM image of ZrB_2/SiC and (b) HRTEM image of ZrB_2/SiC with the selected area electron diffraction patterns.

shown in Fig. 7(b). The thickness of the graphite layer was about 20 interplanar crystal spacings. According to Shahedi Asl *et al.* [59], graphite as a uniform-distribution phase between SiC and ZrB_2 grains could improve the fracture toughness and strain tolerance of ZrB_2 -SiC material with graphite nano-flakes pulling out, crack deflection, as well as crack bridging. At the same time, graphite as a sintering aid also promotes densification during the condition of pressureless sintering to improve the strength of ZrB_2/SiC .

3.4 Microstructures and mechanical properties of ZrB_2 -SiC composites with ZrB_2/SiC

The ZrB_2/SiC with a dense and hierarchy structure in Section 3.2 was used as the toughening phase (1 wt%) to prepare composites. The composites prepared by the H_2O/GL -

1600 °C ZrB_2/SiC , H_2O/GL -1800 °C ZrB_2/SiC , and H_2O -1800 °C ZrB_2/SiC were denoted as Composite a, Composite b, and Composite c, respectively, while the control sample was denoted as Composite blank. Figure 8 shows the cross-sectional morphologies of the composites. The symmetrical distribution of multiple sets of cross-sections along the same axis shows that the arrangement of the spiral lines is preserved in the matrix. The porosity of H_2O -1800 °C ZrB_2/SiC was 30%, while the density of H_2O/GL -1800 °C ZrB_2/SiC could reach 93%. In addition, due to the possible volume shrinkage of the hierarchical pore structure during the sintering process, a clear boundary was formed between the fibers of the hierarchical pore structure and the matrix.

To elucidate the bonding between matrix and fibers, the TEM and EDS were used for analyzing the elements

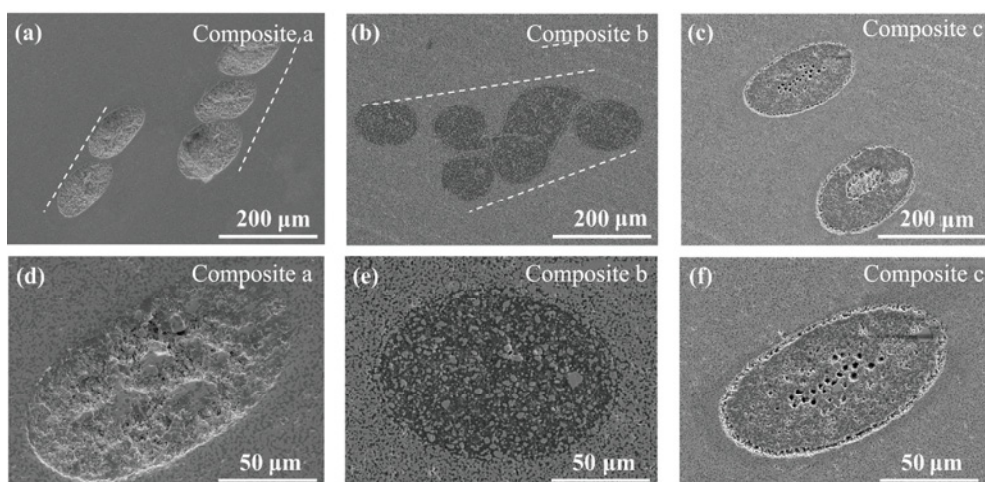


Fig. 8 Cross-sectional morphologies of ZrB_2 -SiC composites toughened by ZrB_2/SiC : (a, d) H_2O/GL -1600 °C, (b, e) H_2O/GL -1800 °C, and (c, f) H_2O -1800 °C.

and morphologies at the interface. In Composite b, dense sintering occurred between the fiber and the matrix with no obvious boundary phenomenon (Fig. 9(b)). From the EDS analysis, ZS_{sf} surface was oxidized at a thickness of about 4 μm , while the original composition was better preserved in the matrix. In Fig. 9 and Fig. S2 in the ESM, the grain size of ZS_{sf} with secondary sintering is slightly smaller than that in the matrix. The existence of graphite had two effects. First, it hindered the gaseous phase diffusion through boundary, which was a major mechanism that led to abnormal grain growth [60,61]. Second, graphite as a sintering aid could promote the solid phase diffusion, which would improve the densification behavior and pore elimination of ZrB_2 -SiC ceramics [62,63]. Both effects would lead to smaller and more uniform grain sizes after sintering.

The micro-mechanical properties of the matrices and the fibers of Composites b, c, and blank were tested by the indentation method representatively. As shown in Fig. 10, the composite with ZS_{sf} achieved

lower E and HV than that with dense ZS_{sf} . The ZS_{sf} with a dense structure showed better K_{IC} than the matrix and the ZS_{sf} with a hierarchy structure. The fracture toughness of ZS_{sf} was improved by 80% compared with those of the matrix and contrast group, which reached to $6.63 \text{ MPa}\cdot\text{m}^{1/2}$.

A penalty for the porous materials is a severe reduction in their stiffness and strength through power law scaling: $E \propto (1 - \rho_t)^\varphi$ and $HV \propto (1 - \rho_t)^\psi$, where ρ_t is the total porosity, and φ and ψ are the fitting exponents generally greater than 1 [64]. In Fig. 11, the ZS_{sf} plays a significant role in hindering the propagation of cracks. The cracks on the fibers showed obvious crack deflection and the initiation of secondary cracks (Figs. 12(e) and 12(f)). According to Shahedi Asl *et al.* [65–67], graphite and graphene in ZrB_2 -SiC material could form an effective weak interface, which changed the fracture mode from mixed fracture to tectonic fracture, as shown in Figs. 12(a)–12(d). The multiple deflections and occurrence of secondary cracks also increase the work required for crack propagation,

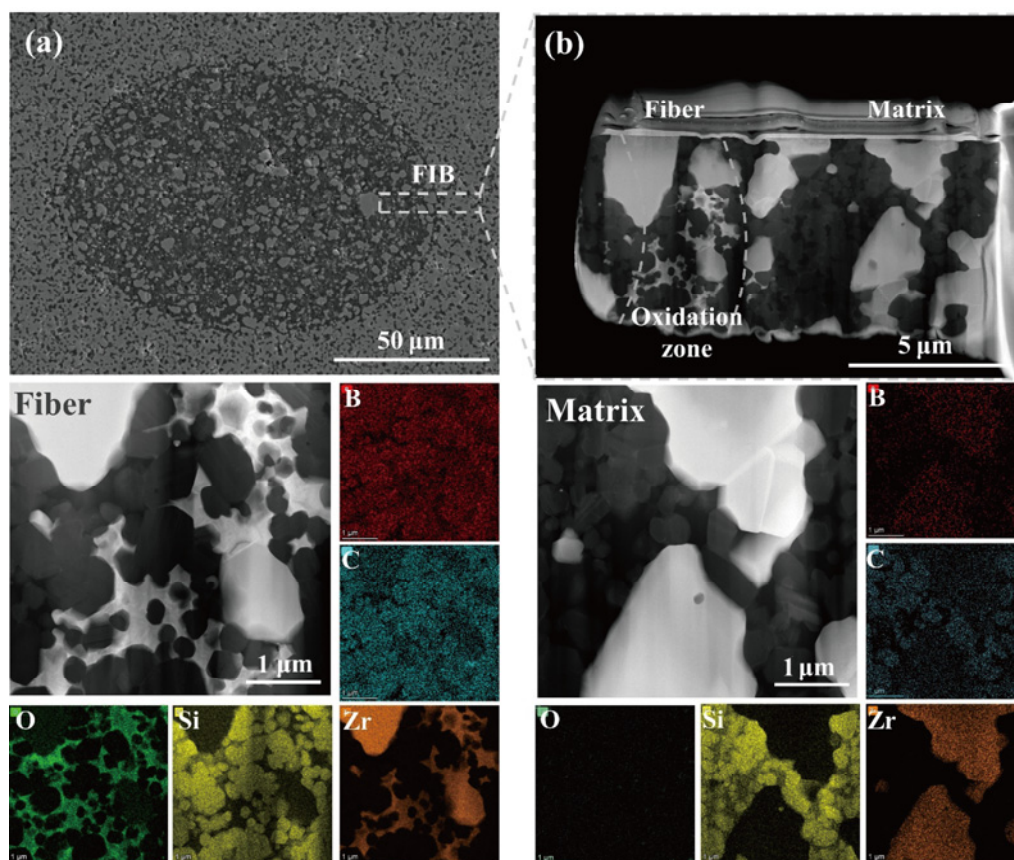


Fig. 9 (a) Cross-sectional morphologies and EDS analysis of composite material toughened by $\text{H}_2\text{O}/\text{GL-1800}^\circ\text{C}$ ZS_{sf} and (b) cross-sectional morphologies and EDS analysis by the TEM images of interface between fibers and matrix by the focused ion beam (FIB) and TEM-EDS elemental analysis.

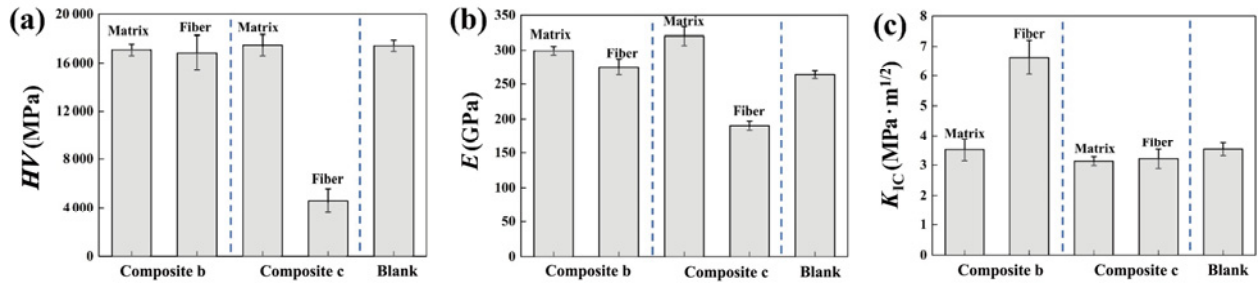


Fig. 10 (a) HV , (b) E , and (c) K_{IC} of the composites of ZrB_2 -SiC nano-powders with ZS_{sf} .

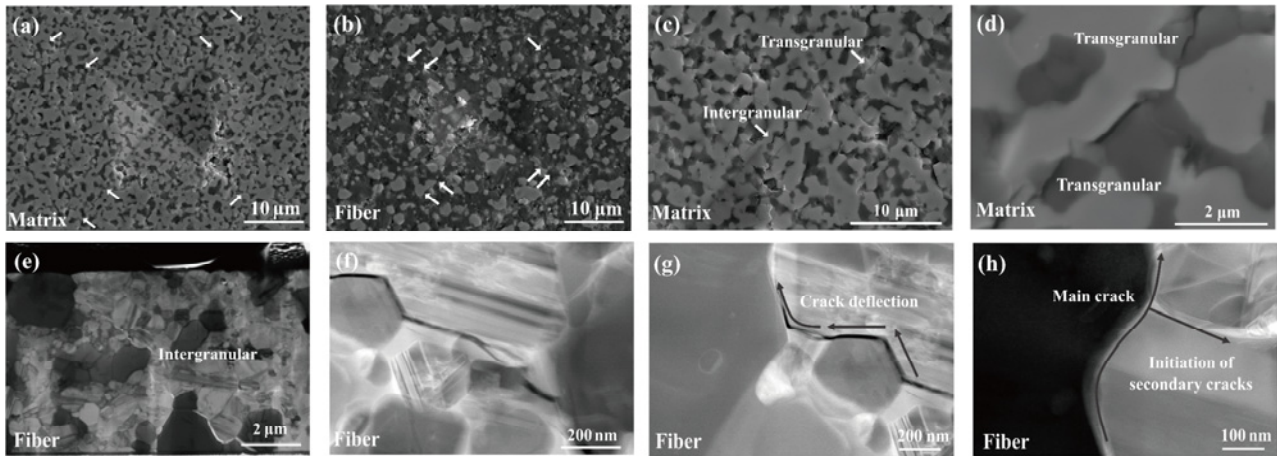


Fig. 11 Indentation morphologies of Composite b: (a) matrix and (b) fiber; SEM/TEM micro-morphologies of fiber crack propagation of (c, d) matrix and (e, f) fiber; and (g) crack deflection and (h) generation of secondary cracks in ZS_{sf} .

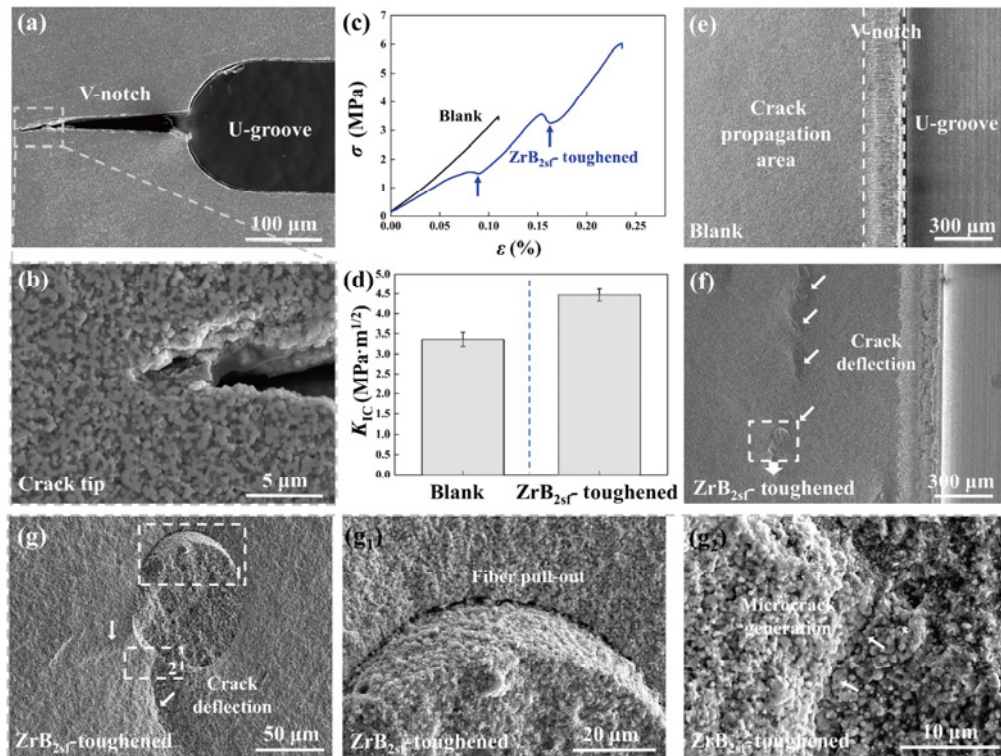


Fig. 12 Micro-morphologies of SEVNB samples: (a) macroscopic morphology and (b) crack tip; (c) σ - ϵ loading curves (where σ is the bending stress, and ϵ is the bending strain) and (d) K_{IC} of blank and ZS_{sf} -toughened composite; (e) and (f) show the fracture morphologies of blank and ZS_{sf} -toughened composites, respectively; and (g) detail morphologies of ZS_{sf} -toughened composite.

thereby inhibiting the propagation of the crack. Meanwhile, the addition of graphite refined the grains of $\text{ZrB}_2\text{-SiC}$ by impeding effects on diffusion of the grain boundary, thereby improving the fracture toughness of the material. Combined with the above two effects, the fracture toughness of ZS_{sf} was increased by more than 80% compared with that of the matrix.

To further illustrate the toughening mechanism of ZS_{sf} on $\text{ZrB}_2\text{-SiC}$, the SEVNB method was used to characterize the macroscopic fracture toughness of the composites. Figures 12(d)–12(f) show that the ZS_{sf} -toughened Composite b achieved a $\sim 30\%$ increase in fracture toughness compared with the $\text{ZrB}_2\text{-SiC}$ composites, while the fracture surface presented significant crack deflection between the ZS_{sf} and matrix. He *et al.* [68,69] indicated that the crack propagation direction would be deflected on the interface due to the difference energy release rate of brittle and toughened phase, which well agreed with the cracking propagation (Fig. 12(g)). The spiral fibers fractured in halfway instead of being pulled out completely because of the physical engagement of the ZS_{sf} and the matrix. Multiple pull-out and breakage of the ZS_{sf} would cause the loading curve to show fluctuations, as shown by the arrows in Fig. 12(c). In addition, the crack deflection and secondary microcracks, as shown in Fig. 12(g₂), also favored the increase of fracture toughness of composites. Further research on the mechanism of crack deflection would be reported in the coming work.

4 Conclusions

For the preparation of toughening phase of UHTCs, micron-scale $\text{ZrB}_2\text{-20 vol\% SiC}$ spiral fiber precursors were prepared by a combination of rope winding effect and non-solvent-induced phase separation, and then sintered by vacuum sintering to obtain different spiral structures and microstructures. By adjusting the preparation parameters H , Q , and η , the geometric size of the spiral fiber could be quantitatively controlled. Through phase diagram calculation and system selection, the pore structure of ZS_{sf} could be effectively controlled to three different structures, including dense, hollow, and hierarchy structures. The fracture toughness of the ZS_{sf} reinforced composite reaches $4.41 \text{ MPa}\cdot\text{m}^{1/2}$, which was $\sim 30\%$ higher than that of the $\text{ZrB}_2\text{-20 vol\% SiC}$ composite. The microscopic fracture toughness of the ZS_{sf} was $\sim 80\%$ higher than that of the matrix due to

the beneficial effect of graphite on improving mechanical properties and refining grains. Meanwhile, the improvement of macroscopic fracture toughness was mainly attributed to the crack deflection and fiber pull-out on interface between matrix and fibers. The novel ZS_{sf} ceramic spiral fiber provides a new way to the toughening of UHTCs.

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Electronic Supplementary Material

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