Fabrication and microstructure evolution of C_{sf}/ZrB_2 -SiC composites via direct ink writing and reactive melt infiltration

Jun LU^{a,b,c}, Dewei NI^{a,b,*}, Chunjing LIAO^{a,b}, Haijun ZHOU^{a,b}, Youlin JIANG^{a,b,c},
Bowen CHEN^{a,b,c}, Xuegang ZOU^{a,b,c}, Feiyan CAI^{a,b,c},
Yusheng DING^{a,b,d,*}, Shaoming DONG^{a,b,*}

^aState Key Laboratory of High Performance Ceramics & Superfine Microstructure,
Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China

^bStructural Ceramics and Composites Engineering Research Center, Shanghai Institute of
Ceramics, Chinese Academy of Sciences, Shanghai 200050, China

^cUniversity of Chinese Academy of Sciences, Beijing 100049, China

^dHangzhou Institute for Advanced Study, University of Chinese Academy of Sciences, Hangzhou 310000, China

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Abstract: Fiber damage and uniform interphase preparation are the main challenges in conventional short fiber reinforced ceramic matrix composites. In this work, we develop a novel processing route in fabrication of short carbon fiber reinforced ZrB_2 -SiC composites (C_{sf}/ZrB_2 -SiC) overcoming the above two issues. At first, C_{sf} preforms with oriented designation and uniform PyC/SiC interphase are fabricated via direct ink writing (DIW) of short carbon fiber paste followed by chemical vapor infiltration. After that, ZrB_2 and SiC are introduced into the preforms by slurry impregnation and reactive melt infiltration, respectively. Microstructure evolution and optimization of the composites during fabrication are investigated in detail. The as-fabricated C_{sf}/ZrB_2 -SiC composites have a bulk density of 2.47 g/cm^3 , with uniform weak interphase and without serious fiber damage. Consequently, non-brittle fracture occurs in the C_{sf}/ZrB_2 -SiC composites with widespread toughening mechanisms such as crack deflection and bridging, interphase debonding, and fiber pull-out. This work provides a new opportunity to the material design and selection of short fiber reinforced composites.

Keywords: short fiber reinforced composites; ultra-high temperature ceramics (UHTCs); interphase; orientation

1 Introduction

Ultra-high temperature ceramics (UHTCs) are endowed

with extremely high melting point (over 3000°C), good mechanical properties, and excellent chemical stability at elevated temperatures [1]. These unique combinations of properties make them leading candidates for extremely environmental applications, such as nozzles, leading edges, and engine components of hypersonic aircraft. However, the intrinsic brittleness and poor thermal shock resistance of UHTCs limit their wide

* Corresponding authors.

E-mail: D. Ni, deweini@mail.sic.ac.cn;

Y. Ding, ysding@mail.sic.ac.cn;

S. Dong, smdong@mail.sic.ac.cn

applications [2]. With carbon fiber as reinforcements, it can effectively overcome the above issues of UHTCs. In the past few years, extensive research has been carried out on continuous carbon fiber reinforced UHTC matrix composites (C_f /UHTCs), including design, processing, and properties [3–8], etc. Compared with continuous fibers, short carbon fiber reinforced UHTC composites (C_{sf} /UHTCs) show more superior designability, and are easier to get a high UHTCs content in the composites [9,10]. Accordingly, C_{sf} /UHTCs provide great potential for high-performance UHTCs composites.

Generally, C_{sf} /UHTCs are prepared by ceramic processing, such as hot pressing [11–13], spark plasma sintering [14–16], pressureless sintering, and reactive melt infiltration (RMI). For the C_{sf} /UHTCs composites fabricated by these conventional methods, there are two main bottlenecks. On the one hand, it is difficult to prepare uniform interphase on the surface of the fibers in the above-mentioned processing routes [17]. A weakly bonded interphase can not only improve the toughness of the material through residual stress relaxation and interfacial debonding but also protect the fibers [18,19]. On the other hand, short carbon fibers are damaged significantly during ceramic processing, such as ball milling and pressure-assisted sintering [20]. Consequently, the effect of strengthening and toughening is very limited in conventional C_{sf} /UHTCs composites in which the fibers are randomly distributed [21–24]. As a result, only those fibers perpendicular to the direction of cracks can hinder the crack propagation through fiber pull-out and bridging when C_{sf} /UHTCs break [25]. Recently, direct ink writing (DIW) method, a kind of 3D-printing technology, is used to prepare composites with oriented short carbon fibers [12,26,27]. Due to the ceramic powder is mixed in the inks, intact interphase is difficult to deposit on the fiber surface [28].

In this work, we develop a novel processing route in fabrication of short carbon fiber reinforced ZrB_2 -SiC composites (C_{sf}/ZrB_2 -SiC) overcoming the above mentioned two issues. At first, C_{sf} preforms with oriented designation and uniform PyC/SiC interphase are fabricated via DIW of short carbon fiber inks followed by chemical vapor infiltration. After that, ZrB_2 and SiC are introduced into the preforms by slurry impregnation and reactive melt infiltration, respectively. Based on the fine structure design and processing control, the fibers and uniform weak interphase are well protected during fabrication. A non-brittle fracture

is achieved in the C_{sf}/ZrB_2 -SiC composites accordingly. Microstructure evolution and optimization of the composites during fabrication are investigated in detail.

2 Experimental

2.1 Material

Commercially available ZrB_2 (purity > 99%, particle size: 1–3 μ m; Shanghai Yaotian New Material Technology, Shanghai, China) and short carbon fibers (M40, average length: 200–500 μ m; Toray Industries, Tokyo, Japan) were used as the raw materials. Polyvinyl pyrrolidone (PVP, $M_w = 1,300,000$, purity: 99%; Sinopharm Chemical Reagent, Adamas, Shanghai, China), polyvinyl butyral (PVB, $M_w = 90,000$ –120,000, purity: 99%; Aladdin, Shanghai, China), and methylcellulose (MC, purity: 0.4 Pa·s; Adamas, Shanghai, China) were used as the binder, dispersant for ZrB_2 , and dispersant for C_{sf} , respectively.

2.2 Preparation of C_{sf} paste and preforms

The preparation of C_{sf} paste included three steps: (I) C_{sf} and MC (1 wt% of short carbon fibers) were first added to deionized water to prepare uniformly dispersed fiber suspension by ultrasonication. (II) PVP (constant weight ratio of PVP: C_{sf} = 1:3) was added into ethanol as binder by magnetic stirring. (III) The above two solutions obtained by (I) and (II) were mixed by magnetic stirring in water bath at $\sim 50^\circ\text{C}$. The C_{sf} paste was obtained after evaporation of ethanol and deionized water until the fiber concentration achieving $\sim 70\%$ and the short carbon fiber suspension became toothpaste-like.

After that, C_{sf} paste was transferred into a print nozzle and installed in a 3D printer (Regenovo 3D bioprinter V2.0, Regenovo Biotechnology Co., Ltd., Shanghai, China). C_{sf} preforms were printed using a nozzle with inner diameter of 0.84 mm driven by nitrogen at a pressure of 0–0.6 MPa. The speed of the nozzle moving in the x -axis and y -axis directions was set to 0–5 mm/s and the distance between filaments was set to 0.5 mm. The dimensions of the preforms were set to 40 mm $\times$ 30 mm $\times$ 5 mm. The C_{sf} preforms were printed layer by layer under the control of computer with a designed route. When the first layer was completed on a glass, the next layer would be printed after rotating 90° in turn. The C_{sf} preforms

were obtained after about 10 layers of printing followed by dryness at 55 °C for 24 h.

2.3 Fabrication of C_{sf}/ZrB_2 -SiC composites

The C_{sf} preforms were firstly heat-treated to remove the organics in a carbon-tube furnace at 1200 °C under Ar atmosphere. PyC/SiC interphase was then deposited on the fiber surface via chemical vapor infiltration (CVI) successively. The obtained $C_{sf}@PyC/SiC$ preforms had a porosity of ~80 vol%.

After that, ZrB_2 and SiC were introduced into the $C_{sf}@PyC/SiC$ preforms by slurry impregnation (SI) and RMI, respectively. ZrB_2 slurry (60 wt%) with phenolic resin, PVB, and pore former were obtained by ball-milling in a polyethylene bottle using SiC balls and ethanol as the media. Then the ZrB_2 slurry was introduced into the $C_{sf}@PyC/SiC$ preforms by vacuum impregnation and then heat-treated at 900 °C in Ar atmosphere so that C_{sf}/ZrB_2 -C porous preforms were obtained. Finally, Si melt was infiltrated into the C_{sf}/ZrB_2 -C porous preforms under vacuum at 1490 °C and C_{sf}/ZrB_2 -SiC composites were formed. The schematic of the fabrication process is shown in Fig. 1.

2.4 Characterizations

The rheological behavior of the ink was determined by a stress-controlled rheometer (Universal Stress Rheometer SR5, Rheometric Scientific, USA). Microstructure of the C_{sf} preforms and composites were observed using a field emission scanning electron microscope (FESEM; Hitachi SU8220, Tokyo, Japan) along with energy-dispersive spectrometry (EDS; Inca energy, Oxford, UK) for elemental analysis. Phase composition was

analyzed by an X-ray diffractometer (XRD; D8 Discover Davanci, Bruker Vorporation, Germany). Pore size distribution of the porous preforms was determined by mercury porosimeter (AutoPoreIV9510, Micromeritics Instrument Corporation, Shanghai, China). Density and open porosity of the composites were determined by the Archimedes method using distilled water as media. Calculation process is as follows:

$$\rho = M_1 \times \rho_0 / (M_3 - M_2) \quad (1)$$

$$P = (M_3 - M_1) / (M_3 - M_2) \times 100\% \quad (2)$$

where ρ and P are the bulk density and open porosity of the composites, respectively. ρ_0 is the density of deionized water at room temperature, M_1 is the dry weight of the sample, M_2 is the floating weight of the sample saturated with water, and M_3 is the weight of the sample saturated with water in the air.

Orientation parameter (f_p) similar to “Hermans’ orientation parameter” [29] of the fibers in the composites was determined by the equations below [30]:

$$\langle \cos^2 \phi \rangle = \left[\sum_j N(\phi_j) \cos^2 \phi_j \right] / N_{\text{total}} \quad (3)$$

$$f_p = 2 \langle \cos^2 \phi \rangle - 1 \quad (4)$$

where ϕ is the angle between the fibers and x -axis identified by image analysis. The short carbon fibers are perfectly oriented in the composite when f_p tends to 1, and randomly distributed when f_p tends to 0. Fracture behavior of the composites was measured by a single-edge-notched beam (SENB) method with a specimen size of 30 mm × 6 mm × 3 mm, notch length of 3 mm, notch depth of 1.5 mm, crosshead speed of 0.5 mm/min, and support span of 24 mm.

Fig. 1 Schematic diagram of the procedure for C_{sf}/ZrB_2 -SiC composite fabrication.

3 Results and discussion

3.1 Preparation and optimization of C_{sf} paste & preforms

The good rheology of the paste is critical for successive 3D-printing. And uniform dispersion of C_{sf} is the premise for good rheology. MC is a nonionic surfactant with excellent wettability, dispersibility, and adhesion properties [31], which can be absorbed on the surface of carbon fibers and get a good colloidal stability in an aqueous solution as shown in Fig. 2(a) [32]. Without the addition of MC, the short carbon fibers will get

together and agglomerate under the surface tension, as shown in Fig. 2(c). The introduction of MC can form a colloid layer surrounding the fibers and separate them from each other (Fig. 2(d)), improving the stability of C_{sf} in the suspension effectively. On the other hand, PVP has the same π - π bond like graphene, and it can be physically absorbed on the surface of C_{sf} in polar solution, i.e., aqueous or ethanol [33,34]. Therefore, PVP addition can further improve the dispersion and stability of C_{sf} suspension. The slurry becomes a pseudoplastic fluid with shear thinning. As a pseudoplastic fluid, when the slurry flows in the cylindrical nozzle, the shear force decreases nonlinearly along the radial

Fig. 2 (a) Schematic diagram for MC absorbed on the carbon fiber surface and dispersing the carbon fibers; (b) shear force distribution and fiber orientation process in the nozzle structure; (c) optical image of C_{sf} agglomeration; (d) optical image of C_{sf} with good dispersion; (e) apparent viscosity of C_{sf} paste as a function of shear rate; (f) storage modulus and loss modulus of C_{sf} paste as a function of shear stress.

direction [35]. The slurry and the superficial fibers will be subjected to shear force from the nozzle wall while the inner slurry and fibers will only suffer a limited shear force from the superficial slurry. As a result, the superficial slurry flows faster than the inside, forming the shearing force which makes the superficial fibers quickly rotate to the flowing direction. Because the nozzle is long enough, the internal fibers gradually turn to the flowing direction as shown in Fig. 2(b). As a result, most carbon fibers are well oriented.

With the evaporation of deionized water and ethanol, the viscosity of the suspension rose rapidly. The final C_{sf} paste exhibited obvious shear-thinning effect and suitable viscoelasticity for DIW. Under shearing force, the short carbon fibers in the suspension aligned along the flow direction, which reduced the resistance of suspension flowing. Figure 2(e) presents the viscosity of the C_{sf} paste, which shows an obvious shear-thinning phenomenon as discussed above. Figure 2(f) suggests that when shear stress is higher than yield stress (6.27 Pa), the storage modulus of the C_{sf} paste is lower than the loss modulus, indicating a viscous fluid, which is good for the C_{sf} paste flowing through the nozzle. As the C_{sf} paste is extruded from the nozzle, shear stress reduces dramatically. When the shear stress is lower than the yield stress, the storage modulus (10^4 – 10^5 Pa) becomes higher than the loss modulus in

turn, indicating an elastic fluid, which is beneficial to maintain the shape of the filaments and C_{sf} preforms after printing.

Figure 3(a) shows the DIW fabrication of C_{sf} preforms. When the obtained C_{sf} preforms were dried, MC molecules formed a gel based on hydrogen bonds, preventing the shrinkage of PVP molecules. As a result, the volume shrinkage of C_{sf} preforms is as low as 5.6 vol%. Figure 3(b) shows that the shape of the filaments is stable and the fibers are closely connected by organics and oriented obviously. After organics were removed by heat-treatment, the oriented C_{sf} were exposed completely and ready for interphase deposition (Fig. 3(c)). The content of C_{sf} in the as-fabricated preforms is ~21 vol%.

To characterize the shear stress-induced orientation of the C_{sf} , the angles between C_{sf} and main axis at different districts were measured, as shown in Fig. 3(c). Figure 3(d) gives the statistic angle distribution of C_{sf} along x-axis after more than 400 C_{sf} were counted, which shows that the angles are mainly distributed between -30° and 30° , especially between -10° and 10° , indicating the C_{sf} are well aligned. The orientation parameter is calculated according to Eqs. (3) and (4). The calculated orientation parameter f_p is 0.84, which further confirms the good orientation of C_{sf} in this work.

Fig. 3 (a) Optical image of C_{sf} preform fabrication by DIW, (b) SEM images of C_{sf} preform before heat-treatment, (c) SEM images of C_{sf} preform after heat-treatment, and (d) statistic angle distribution of C_{sf} .

3.2 Fabrication and microstructure evolution of C_{sf}/ZrB_2-SiC composites

As described above, PyC/SiC interphase was deposited on the surface of C_{sf} by CVI after organics removal. As shown in Fig. 4, a uniform and intact interphase is obtained, where the PyC is around 300 nm in thickness and the SiC layer is around 3 μm . The deposition of PyC/SiC interphase also makes the C_{sf} connect to each other and endows the $C_{sf}@PyC/SiC$ preforms rigidity. The thin PyC interface does not close the pores in the filaments and the subsequent SiC deposition is not affected (Fig. 4(a)). However, after deposition of the thick SiC layer (Figs. 4(b) and 4(c)), most of the pores in the C_{sf} filaments are closed, which adversely affects the subsequent densification process of the composites.

Densification of the $C_{sf}@PyC/SiC$ preforms includes two steps. At first, porous ZrB_2-C is introduced into the preforms by slurry impregnation, and then the preforms are further densified by Si infiltration (Fig. 1). After PyC/SiC deposition, the main pores in the preforms are mainly located among C_{sf} filaments with a size of hundreds of microns. Therefore, ZrB_2-C can be effectively introduced into the preforms by slurry impregnation. Figure 5 shows the SEM images and pore size distribution of the porous $C_{sf}@ZrB_2-C$. After slurry impregnation, the introduced ZrB_2-C is mainly located among the C_{sf} filaments, but also enters the fiber bundles as shown in Fig. 5(a). The C_{sf} and PyC/SiC interphase remain intact without obvious damage occurred (Fig. 5(b)). The microstructure shows that the

introduced ZrB_2-C is uniformly distributed with micro-nano pores embedded, which can provide a channel for Si infiltration (Fig. 5(c)).

The obtained $C_{sf}@ZrB_2-C$ has an open porosity of ~20 vol%. Based on pore size distribution, they can be divided into three types, which are mainly caused by two different reasons (Fig. 5(d)). The nano-pores with a diameter of less than 0.1 μm and micro-pores with a diameter between 0.1 and 100 μm are mainly caused by pore former removal during heat-treatment. The volume of these two types of pores is accounted for 24 and 51 vol%. A few large pores (> 100 μm , ~25 vol%) are also presented, which are mainly located on the surface of preforms and caused by slurry outlet flowing during solidification after slurry impregnation. It is expected that such micro-nano multi-level pores can promote the kinetics of Si infiltration to get a dense matrix [36]. Besides open pores, some closed pores also exist in the $C_{sf}@ZrB_2-C$. The closed pores mainly originate from the DIW process, during which air enters into the paste and is difficult to remove completely. As a result, pores are left inside the filaments, which are partly closed after PyC/SiC deposition.

The C_{sf}/ZrB_2-SiC composites are finally obtained after Si infiltration, where the Si melt reacted with carbon to form SiC based on the chemical reaction as Eq. (5)

Thermodynamic calculation by HSC chemistry version 6.0 (Outokumpu Research Oy, Pori, Finland)

Fig. 4 SEM images and EDS analysis of C_{sf} preform after PyC/SiC interphase deposition: (a) surface after PyC interface, (b) surface after SiC interphase, (c) section after SiC interphase deposition, (d) EDS spectrum of Spot 1, (e) EDS spectrum of Spot 2, and (f) line scan spectrum in (c).

Fig. 5 SEM images and pore size distribution of porous $C_{sf}@ZrB_2-C$: (a) low magnification of the $C_{sf}@ZrB_2-C$, (b) SEM image of the fiber bundle location, (c) SEM image of the matrix, and (d) cumulative volume percentage and incremental intrusion vs pore size diameter of the $C_{sf}@ZrB_2-C$.

indicates that Gibbs free energy change (ΔG) of Eq. (5) is about -55.19 kJ/mol at $1490^\circ C$. The as-fabricated C_{sf}/ZrB_2-SiC composites have a density of ~ 2.47 g/cm³ with a porosity of around 18.8%. The volume fractions of the ZrB_2 and SiC are ~ 29.4 and ~ 30.7 vol%, respectively. The high porosity of the composite is partially due to the large pores which are

mainly located on the surface of the $C_{sf}@ZrB_2-C$ preforms and caused by slurry outlet flowing during solidification after slurry impregnation. Some of these large pores were filled with molten Si (Fig. 6(a)) while still many were not and remained in the final composite between the filaments. In addition, some pores closed by thick silicon carbide cannot be infiltrated by Si and stay as

Fig. 6 SEM images and EDS analysis of C_{sf}/ZrB_2-SiC composites: (a) polished surface, (b) section of fiber bundle, (c) high magnification image in (a), and (d) EDS spectrum of Spot 1.

closed pores in the filaments (Fig. 6(b)). As a result, the final composite has a high porosity. XRD pattern shows the phase composition of the obtained C_{sf}/ZrB_2-SiC (Fig. 7). In addition to C, ZrB_2 , and SiC, Si residuals are also detected, which is very common in Si infiltrated composites. The Si residuals are mainly located among the C_{sf} filaments (Fig. 6(a)) and generally have a large size ($> 100 \mu m$). During RMI, Si cannot fully fill in the large pores and completely react with the carbon in the

Fig. 7 XRD patterns of C_{sf}/ZrB_2-C after SI and C_{sf}/ZrB_2-SiC composites after RMI.

preform, leaving pores or Si residuals in the final composite. Therefore, Si residuals might be reduced by decreasing the large pores in the C_{sf}/ZrB_2-C preforms. From the section of the fiber bundle, it can be found that the carbon fibers and PyC/SiC interphase are well protected without obvious erosion (Fig. 6(b)). It can be found that ZrB_2 grains surrounded with Si residuals grow up remarkably due to the effect of liquid-phase assisted mass transfer (Fig. 6(c)).

3.3 Fracture behavior of C_{sf}/ZrB_2-SiC composites

The fracture behavior of the C_{sf}/ZrB_2-SiC composites was analyzed by bending test. Figure 8(a) shows the crack propagation and fracture surface of the C_{sf}/ZrB_2-SiC composites after bending test. The composites perform obvious non-brittle fracture characteristics. The sample were tilted during machining, resulting in more fibers at the upper fiber bundle regions and less fibers at the lower fiber bundle regions in Fig. 8(a). As the crack passes through the composite, the more fibers there are, the more crack deflects. As a result, the crack deflection is less at the lower fiber bundle regions in Fig. 8(a). As discussed above, the carbon fibers and

Fig. 8 Typical crack propagation behavior and fracture surface of the C_{sf}/ZrB_2-SiC composite after bending test: (a) crack propagation path, (b) magnification of crack propagation path, (c) fracture surface, and (d) magnification of fracture surface.

PyC/SiC interphase are well protected without obvious erosion in the as-fabricated C_{sf}/ZrB_2 -SiC composites. C_{sf} are debonded from the weak PyC interphase when cracks propagate to the carbon fibers, and no direct broken fibers are observed. Some C_{sf} slip from the composites and form crack bridging or fiber pull-out, which promote the cracks deflecting along the C_{sf} oriented direction, as shown in Fig. 8(b). On the fracture surface of the composites (Figs. 8(c) and 8(d)), widespread toughening mechanisms such as crack deflection and bridging, interphase debonding, and fiber pull-out can also be observed clearly. The toughening mechanisms in the as-fabricated C_{sf}/ZrB_2 -SiC composites mainly resulted from the well-protected C_{sf} and weak interphase, which consumes the crack propagation energy remarkably. This work provides a new opportunity to the material design and selection of short fiber reinforced UHTC composites.

4 Conclusions

In this work, a novel processing route that combined with DIW and RMI was developed to fabricate C_{sf}/ZrB_2 -SiC composites. The rheology of the C_{sf} paste, microstructure evolution, and toughening mechanisms of the composites were analyzed and discussed. At first, C_{sf} paste suitable for DIW was obtained with the help of the binder and dispersant, showing an obvious shear-thinning behavior. The C_{sf} were well oriented by the shearing force from the nozzle during DIW, with an orientation parameter $f_p \approx 0.84$. Based on the fine structure design and processing control, the fibers and uniform PyC/SiC interphase are well protected during fabrication. The as-fabricated C_{sf}/ZrB_2 -SiC composites have a density of $\sim 2.47 \text{ g/cm}^3$. Beneficial to the weak bonding between fibers and matrix, non-brittle fracture is achieved in the C_{sf}/ZrB_2 -SiC composites accordingly, with widespread toughening mechanisms such as crack deflection and bridging, interphase debonding, and fiber pull-out. Although further optimization of the fabrication processing is still required, this work provides a new opportunity to the material design and selection of short fiber reinforced composites.

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