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The influence of additive content on microstructure and mechanical properties on the C_{sf}/SiC composites after annealed treatment

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ABSTRACT

In this paper, micrometers long and 20–100 nm diameter SiC nanowires had been synthesized in the short cut fiber toughened SiC composites (C_{sf}/SiC) by annealing treatment. The present work demonstrated that it was possible to fabricate the in situ SiC nanowires toughened C_{sf}/SiC composites by annealed treatment. The "vapor–liquid–solid" growth mechanism of the SiC nanowires was proposed. The mainly toughened mechanism concluded grain bridging, crack deflection, fiber debonding and SiC nanowires, which can improve fracture toughness.

1. Introduction

Silicon carbide matrix composites were one of the main candidates for applications under severe conditions owing to its outstanding mechanical, thermal and physical properties [1–3]. However, low fracture toughness hindered wider applications of SiC matrix composites. SiC whiskers and/or nanowires have been widely used as an effective reinforced method. SiC whiskers and/or nanowires had received much attention due to their excellent mechanical properties and chemical stability. SiC whiskers were utilized to toughen the ceramics matrix composites such as Al_2O_3, Si_3N_4 TiC and so on. In the last two decades, the manufacture techniques of SiC nanostructures have been widely developed. Some reports were brought forward for the synthesis of SiC nanowires, including the laser ablation [4], arc discharge [5], chemical vapor deposition with a metallic catalyst [6], decomposition of organic silicon compounds [7], carbon thermal reduction of porous silica/carbon composites [8] and chemical vapor infiltration technique [9]. However, above methods were generally either high cost or complicated. In addition, when SiC whisker or nanowires were usually added into substrate materials by physical mixture methods, then it was very difficult to control uniform distribution of SiC whisker or nanowires in the composites, so this drawback may limit wider applications. As a result, the conception of in situ growth was put forward to resolve the above questions in recent years. Verspui and Knippenherg [10] utilized lanthanum as catalyst to vaporize and form α-SiC whiskers on nucleation sites on the bulk SiC by the re-deposition technology, but the fabrication temperature was too high. Salama and Quick [11] fabricated rich-carbon SiC nano ribbons in a 4H-SiC single crystal wafer by a laser direct-write process. Yang et al. [12] synthesized SiC nanowires in the RS-SiC plate by in situ chemical vapor growth process. However, it was less reported that La_2O_3–Al_2O_3 was utilized to fabricate in situ SiC nanowires in the SiC composites.

In order to meet the application in the Tank armor materials, we began to fabricate the SiC matrix composites with higher fracture toughness. In this paper, we reported the fact that in situ SiC nanowires and carbon fiber were served as the reinforcements in the SiC matrix composites. Carbon whisker reinforced SiC matrix composites had been prepared by hot-pressed sintering and Al_2O_3–La_2O_3 were served as additives. Then the hot-pressed materials were annealed at 1750 °C for 1 h. One purpose was to investigate the effect of the Al_2O_3–La_2O_3 additives system on the densification behavior of the C_{sf}/SiC composites. The other purpose of present work was to investigate the effect of additives ratio on the microstructure and mechanical properties of the C_{sf}/SiC composites after annealed treatment. The growth mechanics and toughening role of the SiC nanowires also had been discussed in details.

2. Experiment and characterization

The commercial α-SiC powder (China, d_{50} = 0.5 μm) and carbon fibers were used to fabricate C_{sf}/SiC composites. The volume proportion of SiC and carbon fiber was 7:3. The additives Al_2O_3 and La_2O_3 were utilized as sintered additive system and the ratio of

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the sintered additive to SiC was 10:90 (weight ratio). The ratio of the Al_2O_3/La_2O_3 were 1:3, 1:1, 3:1 and 5:1. SiC ceramic balls and alcoholic were used as mixture media and dissolvent. The attrition time was 4 h and speed was 180 rpm. The mixture was dried in a rotary evaporator, crushed and screened through a 60 mesh sieve, then put into a graphite crucible. The graphite crucible was covered with BN powders to prevent contact reaction between material powder and crucible. Sintering was performed under a flowing nitrogen atmosphere in a graphite-heated uniaxial hot-pressed furnace, with heated rates of 20 °C/min from room temperature to 1500 °C and 10 °C/min from 1500 °C to 1900 °C. The 30 MPa pressure was applied after 1200 °C. Hot-pressed process was kept at 1900 °C for 1 h under 30 MPa pressure in the Argon gas, then it cooled to room temperature. All the specimens were heat-treated at 1750 °C for 60 min. In this paper, hot-pressed specimens and annealed specimens were denominated HS and AS. HS1, HS2, HS3 and HS4 presented hot-pressed specimens with molar proportion of Al_2O_3 and La_2O_3 were 1:3, 1:1, 3:1 and 5:1. AS1, AS2, AS3 and AS4 presented the annealed specimens with molar proportion of Al_2O_3 to La_2O_3 were1:3, 1:1, 3:1 and 5:1. The hot-pressed specimens and annealed treatment specimens were cut and ground into 3 mm × 4 mm × 36 mm bars to test Flexure strength with a support distance of 30 mm and a cross head speed of 0.5 mm/min. The samples were cut and ground into 2 mm × 4 mm × 22 mm bars with 2 mm deep and 0.2 mm wide notch on a 2 mm × 22 mm surface to measure fracture toughness by a three point technique (SENB) with a 16-mm span at a cross-head speed of 0.05 mm/min. The tensile surfaces were polished and the edges were chamfered. Density was measured by water immersion method. At least five bars were tested for each condition. XRD was applied to determine the phase constitution. The direction perpendicular to hot pressing was evaluated by XRD after the analyzed surface was polished. All the specimens were polished with 1 μm diamond suspension. The surface morphology was surveyed by the SEM. TEM characterization of the grain-boundary and interface was tested using a 200 kV microscope (Model JEM 2010, Japan).

3. Results and discussions

3.1. The phase constitution

X-ray diffraction patterns of hot-pressed and annealed materials were showed in Fig. 1. From the data, α-SiC was present as a major phase, and it can be noted that the wider peak of the amorphous carbon peak existed near 26° in all materials. The weaker peak of $LaAlO_3$ phase was found as minor phase, but it was difficult to detect the existence of low eutectic phase $LaAl_{11}O_{18}$. There was no significant change in the phase constitution for the C_{sf}/SiC composites after annealed treatment at 1750 °C for 1 h. However, there was stronger diffraction peak of SiC after annealed treatment than that in the hot-pressed materials. Perhaps, this phenomenon would have had more relevant with the volatilization of grain boundary phase would have more important effect on the intensity of the diffraction peak of the SIC.

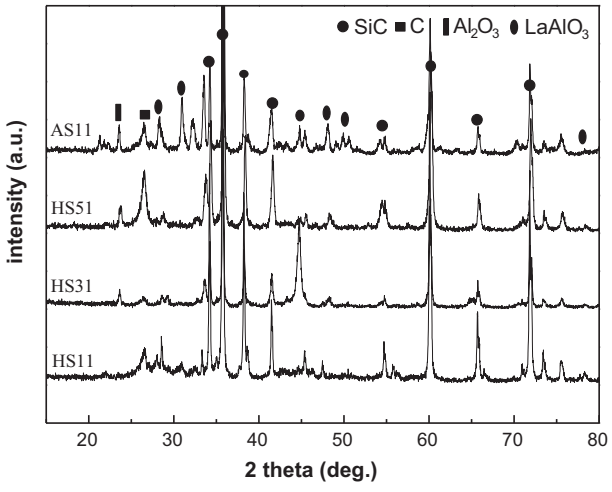

Fig. 1. X-ray diffraction patterns of hot-pressed and annealed specimens.

3.2. The analysis of mechanical properties

The mechanical properties of hot-pressed specimens (HS) and annealed specimens (AS) were illustrated in Table 1. The final relative density of all samples was higher than 97% theory density. During the hot-pressed sintered process, the sintered additives had transformed into crystals grain boundaries phase $LaAlO_3$. It was proved that the sintered additive system (La_2O_3–Al_2O_3) was effective for the densification of the C_{sf}/SiC composites. According to Table 1, for all the hot-pressed specimens, flexural strength was above 230 MPa and fractural toughness was above 4.8 MPa $m^{1/2}$. The HS3 had the highest fractural toughness (about 5.28 MPa $m^{1/2}$) and the highest flexural strength (about 261 MPa). In addition, the AS3 specimen had excess La_2O_3, residual La_2O_3 distributed between the interface of SiC grains and carbon whiskers and it would improve fractural toughness.

Annealing treatment has an important influence on the mechanical properties of SiC composites. The AS3 specimen had more excellent mechanical properties, which flexural strength and fracture toughness were about 294 MPa and 6.44 MPa $m^{1/2}$, respectively. Compared with the HS3 specimen, the mechanical properties of AS3 specimen were improved obviously because of the existence of SiC nanowires after annealed treatment, while mechanical properties of deficient-lanthanum C_{sf}/SiC composites decreased. At the same time, the densities of the annealed specimens were lower than the hot-pressed specimen. Fig. 2 showed the matrix surface morphology of the HS3 and A3 specimen. During the annealed process, the volatilization of second phase resulted in reduced relative densities and mechanical properties.

The typical fracture surface of annealed specimens with different La_2O_3 content was illustrated in Fig. 3. The in situ SiC nanowires were found in the annealed specimen. The number of SiC nanowire was influenced by the molar ratio of Al_2O_3/La_2O_3 and La_2O_3 content. It was difficult for low content La_2O_3 to detect the trace of SiC nanowire (Fig. 3(a) and (b)). SiC nanowires dispersed uniformly in the AS3 specimen (Fig. 3(c)), with the diameter from 20 nm to 100 nm and micrometers length. For the annealed specimens, the carbon fibers were damaged so that the reinforced role of carbon fiber became lower. At the same time, the more poles were found on the surface of the SiC matrix. The damaged carbon fibers and the more poles would decrease the mechanical properties, while the SiC nanowire would improve the mechanical properties. So the

Table 1
The mechanical properties of hot-pressed and annealed materials.

Material denomination	Flexure strength (MPa)	Fracture toughness (MPa $m^{1/2}$)	Relative density (%)
HS1	239 ± 5.2	4.88 ± 0.26	96.8
HS2	245 ± 4.5	5.12 ± 0.19	98.7
HS3	261 ± 6.7	5.28 ± 0.32	99.1
HS4	231 ± 5.2	5.07 ± 0.26	98.4
AS1	226 ± 3.3	5.05 ± 0.32	94.9
AS2	238 ± 3.9	5.13 ± 0.32	95.9
AS3	294 ± 4.6	6.44 ± 0.21	96.2
AS4	218 ± 3.7	4.96 ± 0.24	94.3

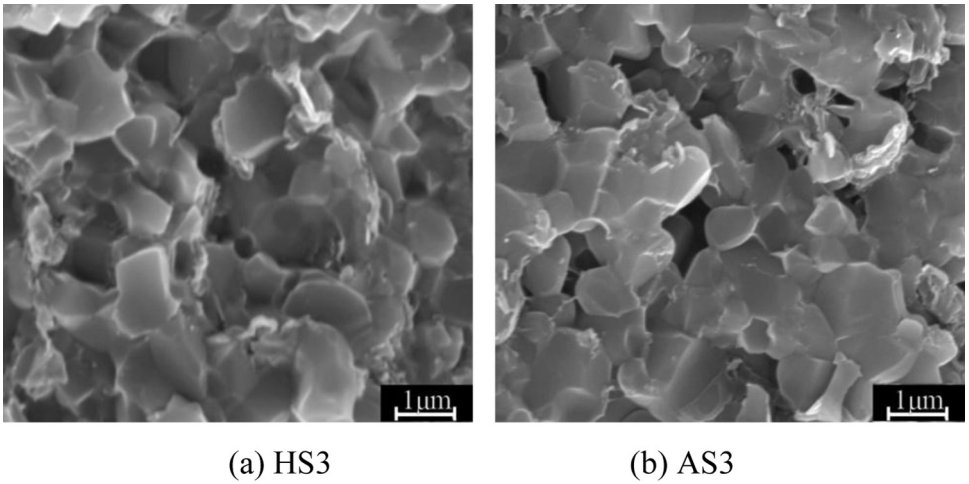

Fig. 2. The matrix surface morphology of the HS3 and AS3 specimen.

degree of the damaged carbon fibers, the number of the macroscopic poles and the distributed condition of the SiC nanowires would play an important role on the mechanical properties of the C_{sf}/SiC composites.

3.3. The growth mechanism of SiC nanowires

Some catalytic balls were observed at the tips of the SiC nanowires (Fig. 4), which implied that these nanowires might grow in the vapor–liquid–solid (VLS) mechanism. The morphology of the SiC nanowires on the fracture surface in the AS3 was relevant with the distribution of sintered additive and annealed condition. SiC nanowires without the catalytic balls at the tips in other areas (omitted) implied that the growth of SiC nanowires was controlled by vapor–solid (VS) mechanism. The results indicated that VLS mechanism and VS mechanism were responsible for the formation mechanism of SiC nanowires.

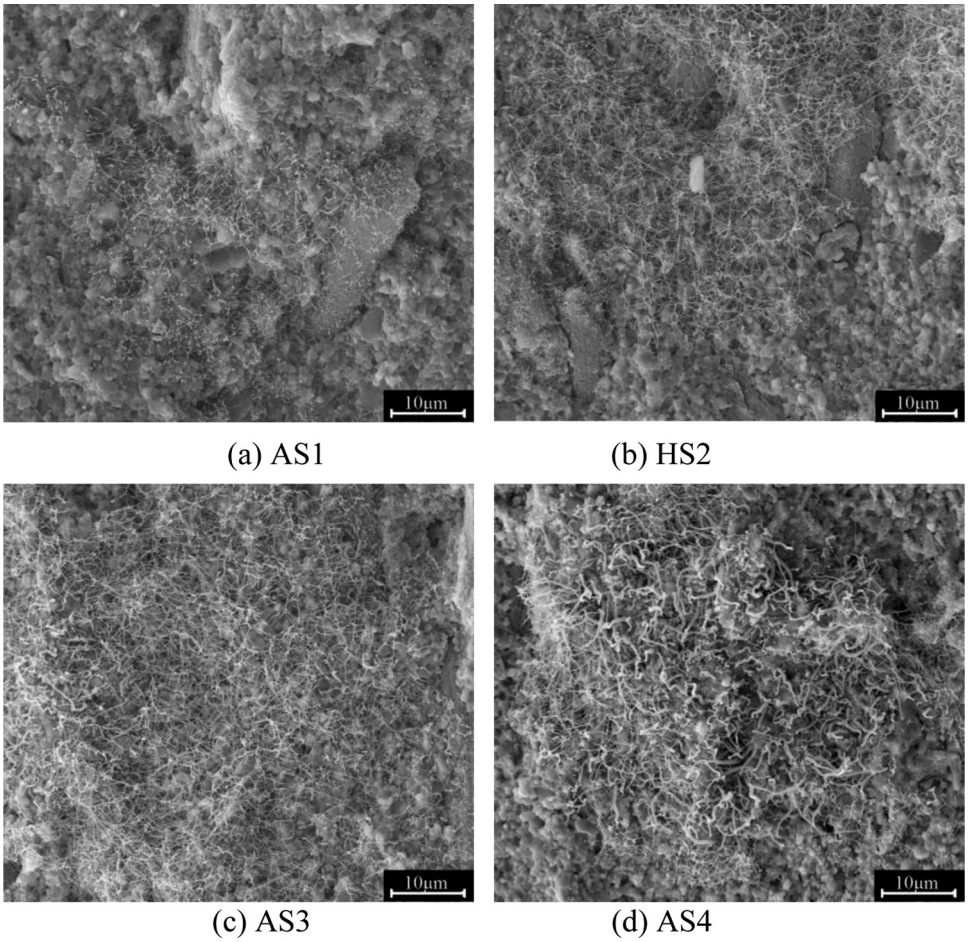

Fig. 3. The typical fracture surface of the annealed materials of the C_{sf}/SiC composites.

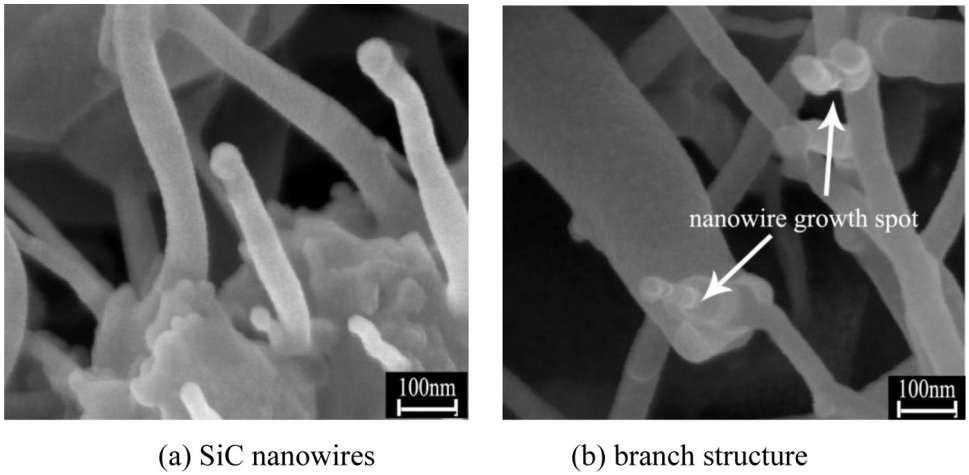

Fig. 4. The different morphology of SiC nanowires in the AS3 composites.

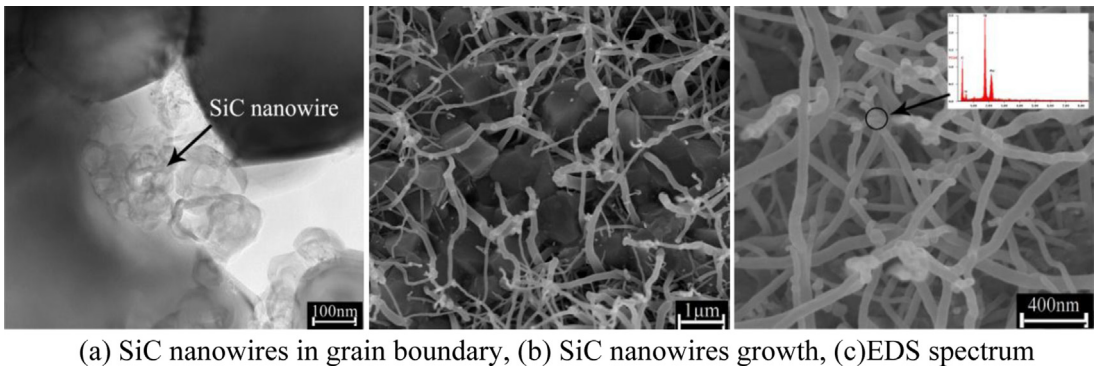

Fig. 5. The typical fracture surface of C_{sf}/SiC composites after annealed treatment at 1750 °C.

According to classical nucleation theory, there was a substantial barrier associated with the formation of the critical nucleation cluster at a random position on the substrate. The catalyst (such as metal La) may decrease nucleation barrier at the particle/nanowire interface and facilitate the growth of SiC nanowire. During the hot-pressd process, the La–Si–Al–C grain boundary phase was easy to form and the smaller SiC particles were precipitated. Finer carbon fiber and powder reacted with metal oxides to form La and Al metal atoms which acted as catalyst during annealed process. During the annealed process, more silicon and carbon atoms adhered to grain boundary and the preferential growth of SiC nanowires can occur as the metal La and Al catalyst was formed at low vacuum. This result was consistent with the work reported by Verspui and Knippenherg [10]. They reported that lanthanum had important effect on growth and morphology of α-SiC whisker and the addition of lanthanum resulted in the growth of thinner elongated crystal with an increasing growth rate in the longitudinal direction and a decreasing growth rate in the radial direction. The relative reports also proved that SiC nanowires would grow along the plane {1 1 1} direction with the lower energy [13].

3.4. The toughened mechanics

The pullout and de-bond effect of the short cut carbon fiber were the mainly toughened mechanics for the C_{sf}/SiC composites. When the C_{sf}/SiC composites were annealed at 1750 °C for 1 h, the SiC nanowire grew from the grain boundary phase. Fig. 5(a) and (b) proved that the SiC nanowire distributed uniformly around the SiC grains. The SiC nanowire would alter the performance of the grain boundary phase. When the flaw encounters the SiC nanowire, the expanded cracking path would become longer and the more energy was consumed, so the fracture resistance would be enhanced. At the same time, the SiC nanowire would interlace with each other and form the network in the three dimensional direction (Fig. 5(c)). The EDS analysis proved that the composition of nanowires was SiC phase. As we all know, the mechanical properties of SiC nanowire were better than the SiC bulk materials, so the network shape SiC nanowire would improve the mechanical properties of the C_{sf}/SiC composites.

The grain bridging could always be detected at the wake of the propagating crack for the investigated materials, which was a toughened mechanics of the C_{sf}/SiC composites. The debonding and pullout of carbon whisker also played a significant role in improving mechanical properties. Carbon fiber reacted with sintered additives during annealed process, then the pull-out effect of carbon fiber reduced. When the contribution of in situ SiC nanowires exceed the contribution of damaged carbon fiber on mechanical properties, the total mechanical properties of C_{sf}/SiC composites increase. As a result, AS3 material possessed a high fracture toughness. The main toughened mechanisms included grain bridging, crack deflection, pullout of carbon fiber and bridging of SiC nanowires in the C_{sf}/SiC composites after annealed treatment. In present work, the in situ SiC nanowire was considered to be an important factor for improving fracture resistance.

4. Conclusion

In the present work, The commercial α-SiC powder instead of expensive β-SiC powder and bargain price La_2O_3–Al_2O_3

additives were utilized to fabricate the SiC matrix composites with high toughness. A novel and simple method, namely annealing treatment, was put forward to fabricate the in situ SiC nanowire toughened C_{sf}/SiC composites. Appropriate annealed treatment was favorable for the growth of SiC nanowire. Compared with hot-pressed materials, the superior mechanical properties can be obtained in the annealed C_{sf}/SiC composites with rich-lanthanum additive due to in situ SiC nanowire. The La_2O_3 content had a significant effect on the morphology and distribution of the SiC nanowire. The multi-toughening mechanics including grain bridge, crack deflection, whisker de-bonding and pullout, and nanowire bridge were responsible for improvement of fracture toughness.

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