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SiC_f/SiC composites reinforced by randomly oriented chopped fibers prepared by semi-solid mechanical stirring method and hot pressing

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Abstract SiC short fibers, with an average diameter of 13 μm, length of 300–1,000 μm and chopped from SiC continuous fibers, were surface modified by the semi-solid mechanical stirring method to produce a discrete coating of aluminum particles. Then the starting mixtures, which consist of SiC short composite fibers, aluminum powder less than 50 μm and α-SiC powder of an average diameter of 0.6 μm, were mechanically mixed in ethanol for about 3 h, dried at 80 °C in air, and hot pressed under 30 MPa pressure at 1,650, 1,750 and 1,850 °C with 1 h holding time to prepare SiC_f/SiC composites. Volume fraction of SiC short fibers in the starting powder for SiC_f/SiC composites was about 25 vol.%. The composites were characterized in terms of bulk density, phase composition, and mechanical properties at room temperature. In addition, the distribution of SiC short fibers in the matrix and the cracking pattern in the composites were examined by optical microscope. Fracture surface of the composites were performed by a scanning electron microscope (SEM). The effect of hot-pressing temperature on bulk density and mechanical properties was investigated. The results indicated that SiC short fibers were uniformly and randomly distributed in the matrix, bending strength and bulk density of the composites increased with increasing sintering temperature. The composite, hot-pressed at 1,850 °C, exhibited the maximum bulk density and bending strength at room temperature, about 3.01 g/cm^3 and 366 MPa, respectively. SEM analyses showed that there were a few of fiber pullout on the fracture surface of samples sintered at 1,650 °C and 1,750 °C, which was mainly attributed to lower densities. But few of fiber pullout was observed on the fracture surface of sample sintered at 1,850 °C, the combined effects of high temperature and a long sintering time were considered as a source of too severe fiber degradation because of the large amount of oxygen in the fibers.

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Introduction

Silicon carbide fiber reinforced silicon carbide composites (SiC_f/SiC) have been extensively studied over the past few years, which are one of the best promising structural materials for high temperature applications in different fields including advanced engines, gas turbines for power/steam co-generation, heat exchangers, heat treatment and materials growth furnaces, and nuclear reactors of the future. SiC_f/SiC composites exhibit significant improvement of mechanical (ductile) properties or they are tough although their constituents are brittle in comparison with the monolithic SiC ceramic [1–2].

A number of studies have been conducted on the SiC_f/SiC composites reinforced by continuous fibers, which are generally arrayed in 1D, 2D or 3D woven cloths, and SiC matrix were prepared by chemical vapor infiltration (CVI) [3], polymer impregnation/pyrolysis (PIP) [4–6], liquid silicon infiltration (LSI) also called (reactive) melt infiltration (RMI or MI) processes [7–8] and nano infiltration and transient eutectics (NITE) process [9–11]. However, a few investigations have been carried out on SiC_f/SiC composites reinforced by SiC short fibers [12–13]. For SiC_f/SiC composites reinforced by randomly oriented ceramic short fibers, such as Al_2O_3 or SiC short fibers which are in cotton-like shape, the short fibers can not be easily introduced and uniformly distributed into SiC matrix with the conventional powder processing techniques such as ball milling. On the other hand, most of the interfaces between the matrix and fibers are thin films or continuous coating in different thickness, whose main function is to arrest or/and deflect the matrix microcracks [2]. For short-fiber-reinforced composites, short fibers usually oriented randomly, a detailed toughening process appears to be more complicated, because it would be sensitive to the orientation and volume fraction of short fibers.

In the present work, SiC_f/SiC composites reinforced by randomly oriented chopped fibers were prepared by semi-solid mechanical stirring method and hot pressing. The composites were characterized in terms of bulk density, phase composition, bending strength and fracture toughness at room temperature. In addition, the distribution of SiC short fibers in matrix and the cracking pattern in the composites was examined using by optical microscope. Fracture surface of the composites were performed by a scanning electron microscope (SEM). Feasibility of Al powder as a sintering additive for SiC matrix and degree of influence resulting from sintering temperature were evaluated. The reinforcing mechanics of SiC short fibers in SiC matrix were discussed too.

Experimental procedures

The properties of SiC continuous fiber (KD-I, National university of defence technology, Changsha, China, 410073) used in this investigation are summarized in Table 1. SiC short fibers used as the reinforcement agent in this paper were chopped from continuous fiber, with an average length of 300–1,000 μm. Average diameter of matrix SiC powder was 0.6 μm.

Table 1 Properties of SiC continuous fiber (KD-I) at room temperature

Density, g/cm^3	2.5
Average diameter, μm	13
Tensile strength, GPa	2.0–2.4
Young's modulus, GPa	170–180
C/Si ratio, atomic	1.27
Chemical composition (wt.%)	Si:C:O = 53.72:29.1:17.18

The Al/SiC_f composite powder, which was a mixture of SiC short composite fibers and aluminum powder prepared by semi-solid mechanical stirring method as reported in the previous works in detail [14–15], was passed through a sieve with 50 μm holes. The composite powder below sieve was mechanically mixed with SiC powder in ethanol for about 3 h. Then the starting mixtures for preparation of SiC_f/SiC composites were dried at 80 °C in air, put in a carbon die and hot pressed under 30 MPa pressure in an argon gas atmosphere at 1,650, 1,750 and 1,850 °C, with a holding time of 1 h. Thus the basic constituents of starting mixtures for SiC_f/SiC composites were SiC short composite fibers, aluminum powder less than 50 μm and SiC powder. The sample size was $30 \times 20 \times 4$–5 mm. The reinforcing phase in the composite was SiC short fibers. Aluminum powder less than 50 μm was used as sintering additives for SiC_f/SiC composite in present work. The volume fractions of SiC short fibers in the starting mixtures for SiC_f/SiC composites were about 25 vol.%.

To investigate the distribution of SiC short fibers in the matrix, Vickers hardness and fracture toughness, the samples were ground with a diamond wheel and polished using a diamond pastes. The final diamond lap had an abrasive particle size of 0.5 μm. The Vickers hardness and fracture toughness were estimated by indentation fracture (IF) method on an Akashi (AVK-A) hardness tester with an applied load of 98 N for 10 s. Both Vickers diagonals and crack lengths were measured in the profile projector using a suitable magnification. At least five valid indentations were made for each data point reported in this study. For mechanical testing, samples were cut and ground into rectangular bar specimens ($3 \times 2 \times 30$ mm) and measured by the three-point bend test with a crosshead speed of 0.1 mm/min and a span of 20 mm at room temperature in air. All data of bending strength were averages of four tests. Microstructure and fracture surface after bending test was observed by optical microscope and scanning electron microscope (SEM). The bulk densities of sintered samples were measured by the Archimedes method.

Results and discussion

In the previous study [14], we have prepared the short SiC composite fibers by semisolid mechanical stirring method for the first time, a discrete single layer of aluminum particles of nanometer, submicron and micron sizes coated on the surface of SiC short fibers. Figure 1 shows the axial sections of composite powder on and below the sieve with 50 μm holes. It can be seen that the composite powder below the sieve is a mixture of SiC short composite fibers and aluminum powder less than 50 μm, and most of SiC short composite fibers are below the sieve and they are isolated from each other or they are in powder-like shape. This change was thought to be due to the surface modification of SiC short fibers by the semi-solid mechanical stirring method and it is very important in present work. Firstly, SiC short fibers which are in cotton-like shape can converted into powder-like shape, thus they can be easily introduced into SiC matrix with the conventional powder processing techniques. Secondly, aluminum powder less than 50μm is thought to be the candidate of sintering aids during hot pressing and interface material for the composites.

In order to understand the distribution of SiC short fibers in the matrix, cross-sections of SiC_f/SiC composite samples were prepared by grinding and polishing, and were observed by optical microscope, as shown in Fig. 2. From this figure, it can be seen that SiC short fibers are uniformly and randomly distributed in the matrix indicating that it is easy for SiC short fibers to be uniformly distributed into α-SiC matrix after surface modification by semi-solid mechanical stirring method.

Figure 3 shows the X-ray diffraction pattern of SiC_f/SiC composites. As shown in the figure, in the region of XRD-resolution, the composites were composed of α-SiC, β-SiC and Al_2O_3. The presence of Al_2O_3 in the composites indicates that almost all of aluminum particles in the starting mixture were oxidized in air or by oxygen in the fiber during preparations of the composites. Figure 4 is the elemental distribution graphs of O and Al by line scanning along radial direction of interface between SiC short fiber and SiC matrix. It can be recognized that there are obvious O and Al peaks, the result strongly support the idea that there is a discrete interphase between the matrix and SiC short fibers and it is suggested that the interphase was formed in situ resulting from chemical reaction at the fiber-matrix interface between aluminum particles on the surface of SiC short fibers and the oxygen in the fibers during high temperature of composite processing.

The bulk densities and mechanical properties of SiC_f/SiC composites as a function of sintering temperature are shown in Table 2. It can be seen that the bulk densities of SiC_f/SiC composites increase with increasing sintering temperature. Although it is difficult to calculate the theoretical bulk density of the composite, it is obvious that there are porosities in samples sintered at 1,650 °C and 1,750°C as shown in Fig. 2a–b, and nearly full dense SiC_f/SiC composite can be achieved at 1,850°C under a pressure of 30 MPa as shown in Fig. 2c–d.

The average bending strength of SiC_f/SiC composites sintered at different temperature are shown in Table 2. The results indicate that bending strength increased with increasing sintering temperature. The average value of bending strength of the composite sintered by HP at 1,850°C is 341.67 MPa and the maximum value is 366 MPa at room temperature. The change of bending strength with increasing sintering temperature can be mainly attributed to the change of bulk density. The bulk densities of samples sintered at 1,650 °C and 1750 °C are lower than that of sample sintered at 1,850 °C.

The mechanism of densification of SiC using mixtures of Al_2O_3, Y_2O_3 and CaO as sintering additives has been reported as liquid-phase-assisted sintering [7–8]. The low temperature eutectic mixture of the oxides based on Si–Al–Y–Ca–O is an effective densification additive for the fine-grained SiC at relatively low temperature. In present work, the sintering aids

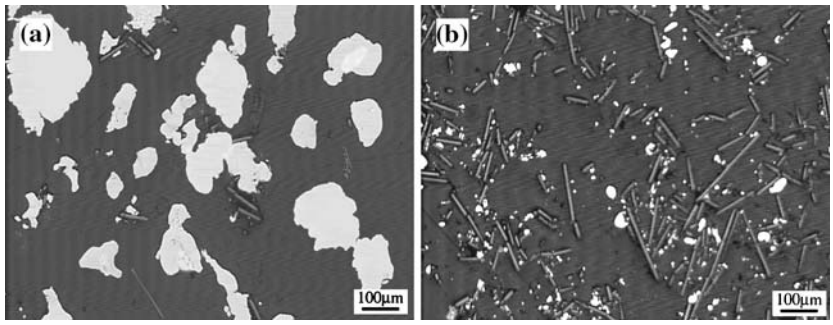

Fig. 1 Axial sections of Al/SiC_f composite powder on and below the sieve of 50 μm: (**a**) on the sieve, (**b**) below the sieve

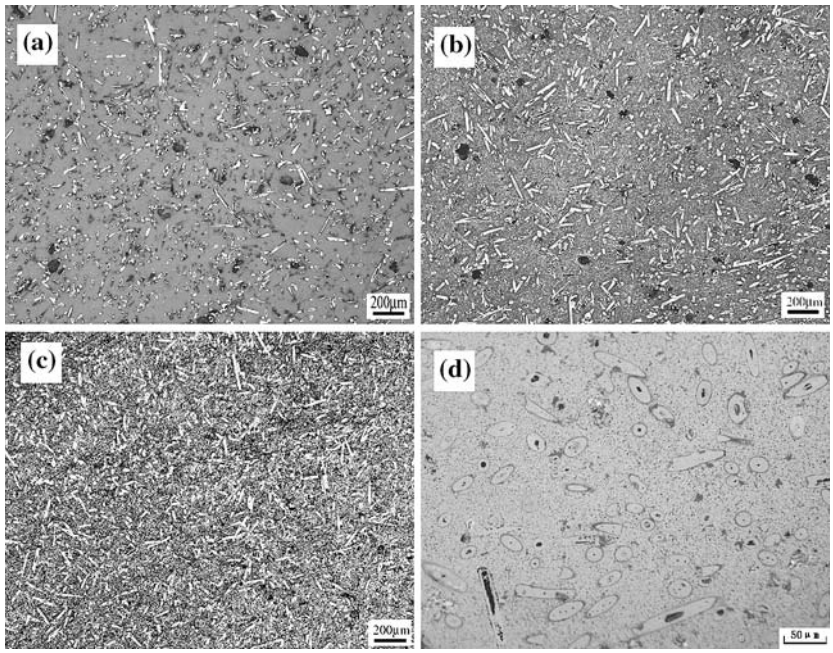

Fig. 2 Distribution of SiC short fibers in SiC_f/SiC composites sintered by HP at different temperature: (**a**) 1,650 °C, (**b**) 1,750 °C, (**c–d**) 1,850 °C

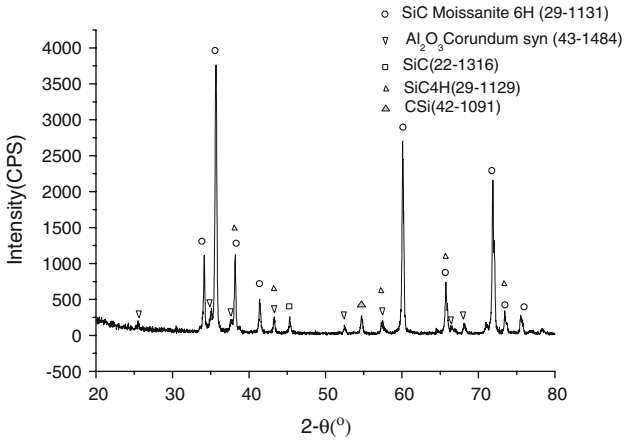

Fig. 3 Typical X-ray diffraction pattern of SiCf/SiC composites sintered by hot pressing

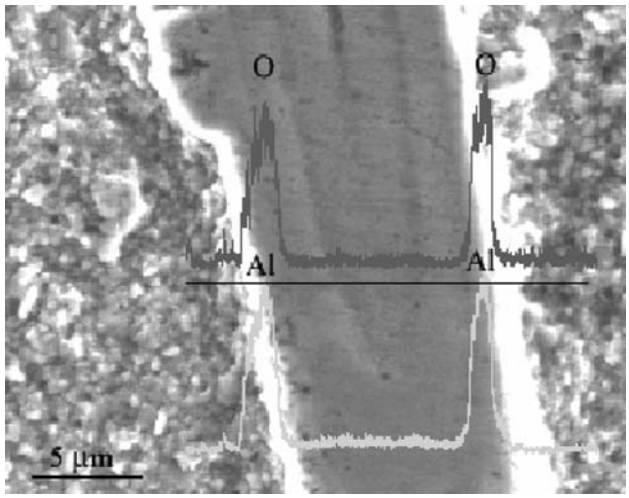

Fig. 4 Elemental distribution graphs of O and Al by line scanning along radial direction of interface between SiC short fiber and SiC matrix

was thought to be the combined effects of aluminum powder at low temperature and alumina which was converted from aluminum particles oxidized by oxygen in the fibers at high temperature and the oxidized aluminum particles on the surface of SiC short fibers will be the interface material between SiC short fiber and SiC matrix.

Typical indentation images of SiC_f/SiC composite sintered by HP at 1,850 °C are shown in Fig. 5. Radial-median cracks were observed at the corners of the indentation impression. The evolutions of the cleavage front profile of right, left and down corners of the indention are shown in Fig. 5b–d. When the cleavage front encountered one short fiber, as shown in Fig. 5c, it cut through the short fiber and was trapped on the other side of the short fiber. When the cleavage front encountered two short fibers, as shown in Fig. 5d, the two fibers were penetrated and bridged across the

Table 2 Properties of SiCf/SiC composites at room temperature

Sintering temperature, °C	1,650	1,750	1,850
Density, g/cm^3	2.03	2.46	3.01
Average flexural strength, MPa	50.75	155.75	341.67
Microhardness, Hv	–	–	1368
Average fracture toughness, MPam$^{1/2}$	–	–	5.76

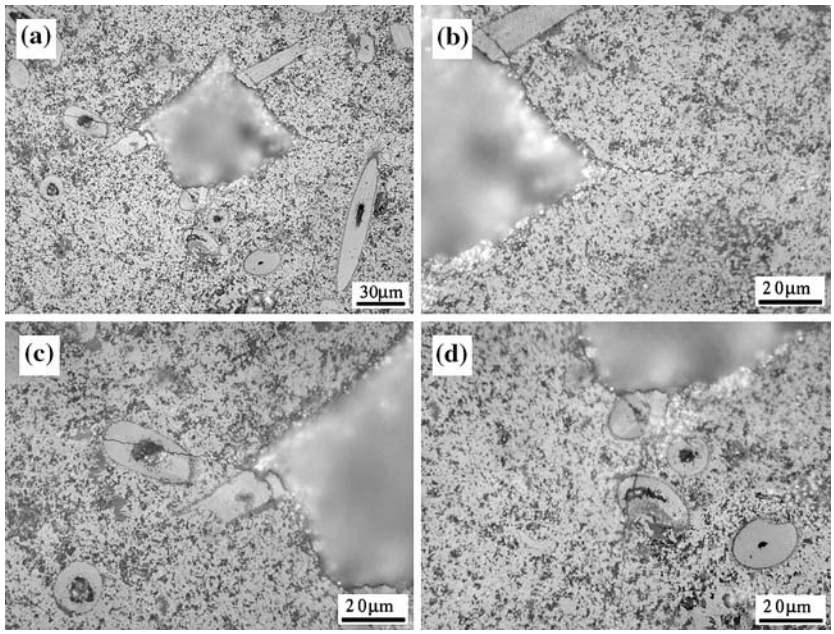

Fig. 5 Typical indentation images of SiC_f/SiC composite sintered by HP at 1,850 °C: (**b**) right corner, (**c**) left corner, (**d**) down corner

crack. The cleavage front shown in Fig.5b did not encounter short fibers and its length was longer than that of cracks shown in Fig. 5c–d, indicating that the short fiber was the crack growth resistance. In the present work, the fracture toughness was estimated by indentation fracture (IF) method, thus the shorter length of the crack growth, the greater value of the fracture toughness. The average value of fracture toughness of the composite sintered by HP at 1,850 °C is 5.76 $MPam^{1/2}$, as listed in Table 2. The fracture toughness values of this sample are between 5.09 $MPam^{1/2}$ and 6.45 $MPam^{1/2}$, which are higher than 3.3 $MPam^{1/2}$ of the fracture toughness of single crystal SiC [16].

Typical fracture surfaces of SiC_f/SiC composites prepared in the present work are shown in Fig. 6. A few of fiber pullout can be observed on the fracture surface of samples sintered at 1,650 °C and 1750 °C,as shown in Fig. 6a–d, but few of fiber pullout is observed on the fracture surface of sample sintered at 1,850 °C, as shown in Fig. 6e–f. In general, fibers are the principle load-carrying members, while the surrounding matrix keeps them in the desired location and orientation, acts as a load transfer medium between fibers. In SiC_f/SiC composites sintered at 1,650 °C and 1,750 °C, since the density is relatively low and the matrix was loosely formed during HP process, cracks easily propagate along the weak region. Meanwhile, the weak load transfer between matrix and fibers in this composite allows a few of fibers pullout and lower bending strength. But the dense matrix in SiC_f/SiC composite sintered at 1,850 °C would prevent fibers pullout from the matrix and higher bending strength.

It is obvious that the SiC fiber used in present work, whose properties are shown in Table 1, is the production of first generations of SiC based fibers [2, 17], containing significant amounts of free carbon and excess silicon combined with oxygen and carbon as an intergranular phase. Their strength and Young's modulus show little change up to 1,000 °C. Above this temperature, both these properties show a little decrease up to 1,400 °C. Above 1,400 °C, the intergranular phase will begin to decompose, carbon and silicon monoxides are evacuated and a rapid grain growth of silicon carbide grains shall be observed, thus the density of the fiber decreases and the tensile properties exhibit a dramatic fall [18]. Hot pressing can be used to produce SiC/SiC with particular, whisker, chopped fibers or unidirectional fiber composites, but this is not a viable method to prepare SiC_f/SiC composites if the SiC fiber containing high oxygen content. Because the high temperature and high pressures required sintering SiC matrix will cause damage to SiC fibers. The sintering temperatures in present work is relatively high (1,600–1,850 °C), which means that only the fibers with a high thermal stability (such as Tyranno SA from Ube industries, Japan and Sylramic fibers from Dow Corning, USA) can be employed [2]. The combined effects of high temperature and a long sintering time were considered as a source of too severe fiber degradation because of the large amount of oxygen (about 17 wt.%) in the fibers,

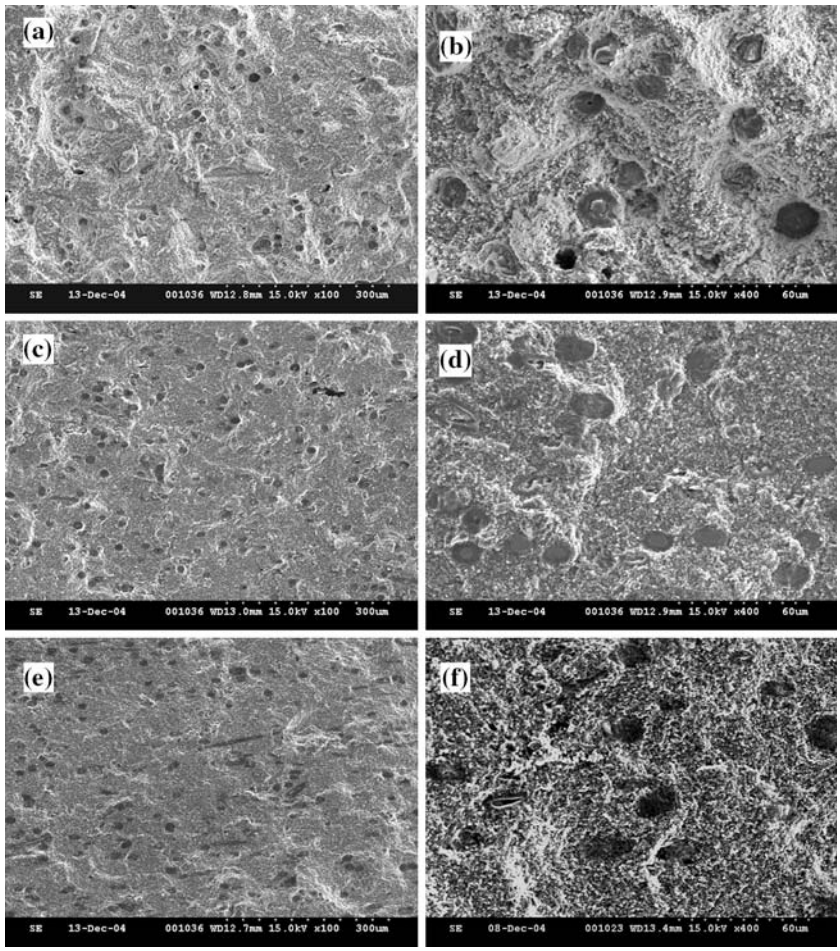

Fig. 6 Fracture surfaces of SiC_f/SiC composites reinforced by randomly oriented chopped fibers and sintered by hot pressing at different temperature: (**a–b**) 1,650 °C, (**c–d**) 1,750 °C, (**e–f**) 1,850 °C

thus the properties of SiC_f/SiC composites prepared in this work are not exciting. It is necessary to reduce the oxygen content of the fiber to improve the thermal stability of SiC_f/SiC composites.

Conclusion

A method for developing a uniform dispersion of SiC short fibers in SiC matrix powder to fabricate SiC_f/SiC composites was investigated on the basis of the resulting microstructure and properties in the present work. The sintering aids was thought to be the combined effects of aluminum powder at low temperature and alumina which was converted from aluminum particles oxidized in air and by oxygen in the fibers at high temperature. It is suggested that the oxidized aluminum particles on the surface of SiC short fibers are the interphase material between SiC short fiber and SiC matrix. Nearly full density can be achieved at 1,850 °C. It was easy for SiC short composite fibers to be uniformly distributed and randomly oriented in the matrix after surface modification by semi-solid mechanical stirring method. The bulk densities and bending strength increased with increasing sintering temperature. The composite, hot pressed at 1,850 °C, exhibited the maximum bending strength and enhanced toughness. The change of bending strength was mainly attributed to the change of bulk density. The large amount of oxygen is responsible for the degradation of the fibers at high temperature.

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References

1. Capoto AG, Lackey WJ (1984) Ceram Eng Sci Proc 5:654
2. Naslain R (2004) Compos Sci Technol 64:155
3. Naslain R, Pailler R, Bourrat X, Bertrand S, Heurtevent F, Dupel P, Lamouroux F (2001) Solid State Ionics 141–142:541

4. Takeda M, Kagawa Y, Mitsuno S, Imai Y, Ichikawa H (1999) J Am Ceram Soc 82:1579
5. Zheng G, Sano H, Uchiyama Y, Kobayashi K, Suzuki K, Cheng H (1998) J Ceram Soc Japan 106:1155
6. Tanaka T, Tamari N, Kondo I, Iwasa M (1998) Ceram Int 24:365
7. Luthra KL, Singh RN, Brun MK (1993) Amer Ceram Soc Bull 72(7):79
8. Hilling WB (1994) Am Cera Soc Bull 73:56
9. Kohyama A, Dong SM, Katoh Y (2002) Ceram Eng Sci Proc 23(3):311
10. Katoh Y, Kohyama A, Dong SM, Hinoki T, Kai JJ (2002) Ceram Eng Sci Proc 23(3):363
11. Katoh Y, Dong SM, Kohyama A (2002) Ceram Trans 144:77
12. Lee JS, Imai M, Yano T (2003) Mater Sci Eng A 339:90
13. Lee JS, Yano T (2004) J Eur Ceram Soc 24:25
14. Qin XH, Jiang DL, Dong SM (2004) Surf Rev Lett 11:205
15. Qin XH, Jiang DL, Dong SM (2004) Mater Sci Eng A385:31
16. Yin L, Vancoille EY, Ramesh K, Huang H (2004) Int J Mach Tool Manu 44:607
17. Jones RH, Steiner D, Heinisch HL, Newsome GA, Kerch HM (1997) J Nucl Mater 245:87
18. Ishikawa T, Sato M, Kajii S, Tanaka Y, Suzuki M (2001) Ceram Eng Sci Proc 22:471