Preliminary study of in situ transformed carbon fibers/Al$_2$O$_3$ ceramic matrix composites

J.J. Cao*, H.H. Chen, F. Du, H.C. Zhao, L. Fan

Department of Materials Science and Engineering, China University of Mining & Technology, Beijing 100083, China

Abstract

The fabrication process, formation of carbon fibers and mechanical properties of in situ transformed carbon fibers/Al$_2$O$_3$ ceramic matrix composites prepared by hot-press sintering were investigated. In the sintering process, pre-oxidized polyacrylonitrile fibers (below named as pre-oxidized PAN fibers) were used as the precursors of the in situ transformed carbon fibers at the sintering temperature of 1700 °C. Twice grade heating was employed respectively at 444 °C and 1070 °C for 10 min before reaching the sintering temperature in order to encourage the transformation of pre-oxidized PAN fibers into carbon fibers. XRD analysis shows that the composites present an apparent diffraction peak at 26.3°, which corresponds to (002) crystal face of carbon fibers. By EDX analysis the carbon content of the in situ transformed carbon fibers is 92.68%. These evidences certificate the PAN fibers have been in-situ transformed to carbon fibers during the sintering process. The fracture toughness of the composites with 20 vol. % pre-oxidized PAN fibers reaches 6.29 MPa m$^{1/2}$. Compared with 4.75 Mpa m$^{1/2}$ of alumina, it is clear that the in-situ transformed carbon fibers remarkably improve the fracture toughness of the composites and the toughening mechanisms contribute to fiber pull-out and crack bridging.
© 2013 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Keywords: B. Composite; C. Fracture toughness; In situ transformed carbon fiber; Pre-oxidized PAN fiber

1. Introduction

Carbon fiber toughened ceramic matrix composites have high toughness, high specific strength, high specific modulus, good thermal stability, etc. [1,2], which have been used in various fields such as aviation, aerospace, transportation, sports and health [3–5]. At present, carbon fiber toughened ceramic matrix composites are prepared mainly by the addition of commercial carbon fiber into ceramic powder, then mixing them uniformly and sintering. During the mixing process, the carbon fibers can be damaged [6,7]. The high cost of carbon fibers contributes to the high cost of carbon fiber toughened ceramic matrix composites. In this paper, the authors propose that pre-oxidized polyacrylonitrile fiber can be used as a precursor to prepare in situ transformed carbon fiber toughened alumina ceramic matrix composite by hot-press sintering in vacuum. The preparation process of the composites,

formation, microstructure of carbon fiber, and the mechanical properties of the composites were investigated.

2. Experimental details

2.1. Raw materials

Alumina powder was selected as the matrix powder. The powder average size is about 2 μm and purity is 99.8%. Its density is 3.96 g/cm^3. Pre-oxidized PAN fiber was used as the precursor of carbon fiber. The average diameter and density of the precursor fiber are 14 μm and 1.4 g/cm^3, respectively.

2.2. Structural analysis

Thermal analysis of the pre-oxidized PAN fibers was carried out using TG/DTA differential thermal analyzer. During the thermal analysis test, the fibers were heated up to 1300 °C in an Ar gas environment at a heating rate of 10 °C/min. The XRD analysis was used to identify the

*Corresponding author. Tel./fax: +86 10 62339081.
  E-mail address:* caojingjing1105@163.com (J.J. Cao).

crystal phase of the pre-oxidized PAN fibers and the in-situ carbon fibers (C_f)/Al_2O_3 composites, using Cu target k_α radiation and Ni filter at 0.02°/s scanning rate in the range of 10–75°. The elemental composition of the in-situ C_f/Al_2O_3 composites was determined by EDX. The microstructure and fracture morphology of the in-situ C_f/Al_2O_3 composites were observed using SEM. On the basis of previous research [13], the content of pre-oxidized PAN fiber and sintering temperature used in the experiment are shown in Table 1. Samples were gold-coated for 1 min.

2.3. Properties evaluation

Density of the in-situ C_f/Al_2O_3 composites was measured by the Archimedes method. Vickers hardness (HV) measurement was carried out at 9.8 N load for 15 s by microhardness tester. The fracture toughness (K_{IC}) was evaluated using the single edge notched beam (SENB) method. The notched samples were prepared with the specimen size of 30 ± 1 mm (length) $\times 4 \pm 0.1$ mm (breath) $\times 6 \pm 0.2$ mm (height). The ratio of the notch depth to specimen height is $a/W \approx 0.45$–0.55, and the notch was cut by diamond inner circle section (0.2 mm thickness). Three-point bent tests were performed at a loading speed of 0.05 mm/min. The fracture toughness was calculated using the following equation [8]:

$$K_{IC} = \frac{3PL}{2BW^{3/2}\alpha^{1/2}Y} \qquad (1)$$

where P is the breaking load during three-point bending test, L is the bending span, 24 mm, B is the specimen breath, W is the specimen height and a is the notch depth, α is the ratio between a and W, and Y is the calibration factor which was calculated by the following equation [8]:

$$Y = \frac{1.99 - \alpha(1-\alpha)(2.15 - 3.93\alpha + 2.7\alpha^2)}{(1+2\alpha)(1-\alpha)^{3/2}} \qquad (2)$$

3. Preparation of the composites

3.1. Preparation procedure

The pre-oxidized PAN fibers were cut into short fibers (the length between 3 and 5 mm), then they were mixed with the alumina powder and milled for a certain time. The mixtures of the pre-oxidized PAN fibers and alumina

Table 1
Composites groups.

Specimens designated	Pre-oxidized PAN fiber content (vol%)
AF00	–
AF15	15
AF20	20
AF25	25
AF30	30

powder were hot-pressed in a graphite die (placed in the sintering furnace) under a pressure of 40 MPa and at 1700 °C for 120 min in vacuum, and then cooled in the furnace to room temperature. Monolithic Al_2O_3 specimens were also prepared by hot-press sintering in order to compare with the in-situ C_f/Al_2O_3 composites. The content of pre-oxidized PAN fiber is in the range of 0–30 vol% and the specimens were designated as in Table 1. The specimen sizes were 55 mm $\times$ 10 mm $\times$ 6 mm.

3.2. Sintering parameters optimizing

In carbonization process of pre-oxidized PAN fibers a series of cyclization, cross-linking, and pyrolysis chemical reactions take place along with the release of a large number of small molecules. Differential thermal analysis was used to determine the structural evolution of the pre-oxidized PAN fibers during the carbonization progress in order to determine optimization parameters for the sintering process.

The DTA curve, as shown in Fig. 1, exhibits an endothermic peak at about 102 °C which is due to the evaporation of the moisture absorbed from air. An exothermic peak at around 444 °C is caused by cyclization reaction of unreacted PAN molecules. An endothermic peak at about 1073 °C is due to the complex carbonation reaction and the release of small molecules [9].

The TG curve shows a rapid weight loss below 102 °C, which is caused mainly by the moisture loss of the fibers. Between 102 and 444 °C, the curve exhibits a plateau, which indicates that there are not small molecules released during the reaction process of non cyclization chain structures. Between 444 and 1300 °C, the fibers exhibit almost uniform weight loss due to the release of small molecules.

Based on the above differential thermal analysis results of the pre-oxidized PAN fibers and combined with the sintering temperature of Al_2O_3 powder, the sintering process parameters for the pre-oxidized PAN fibers and
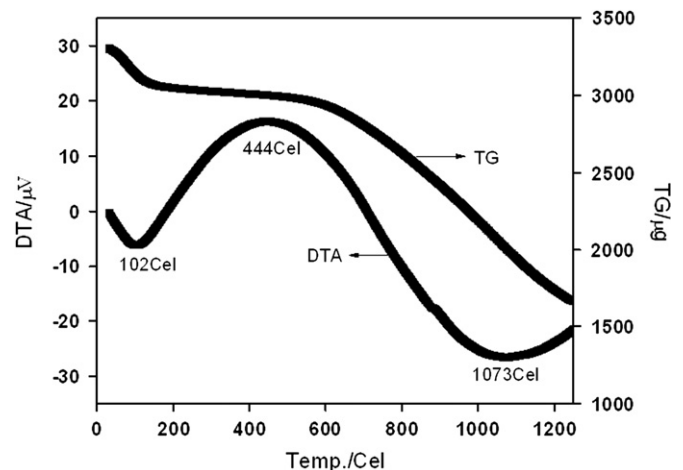

Fig. 1. DTA/TG curves of the pre-oxidized PAN fibers.

alumina composite were optimized, as shown in Fig. 2. The temperatures of 444 °C and 1070 °C are maintained for 10 min each to insure that the pre-oxidized PAN fibers could smoothly transform into carbon fibers. Initial pressure is 20 MPa, and the pressure begins to increase when the temperature reaches 1070 °C and finally the sintering pressure is held at 40 MPa.

4. Results and discussion

4.1. Phase structure analysis of in-situ transformed carbon fibers

The pre-oxidized PAN fibers, monolithic Al_2O_3, and the composites with different content of pre-oxidized PAN fibers were characterized by XRD. The diffraction patterns are shown in Figs. 3 and 4.

From the XRD pattern of the pre-oxidized PAN fibers, shown in Fig. 3, the diffraction peak at 17.9° (100) is the
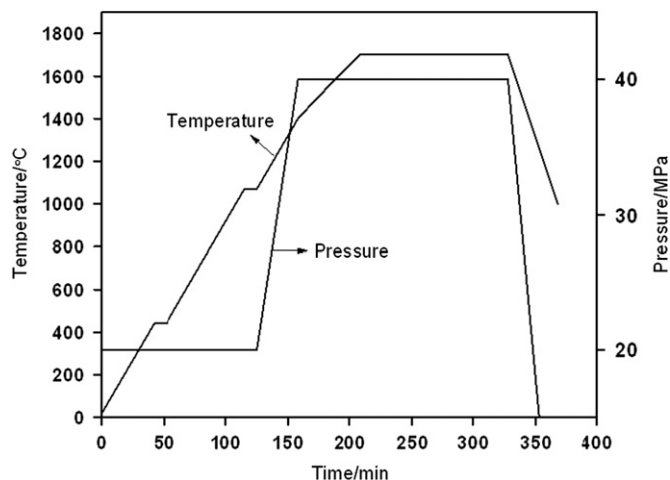

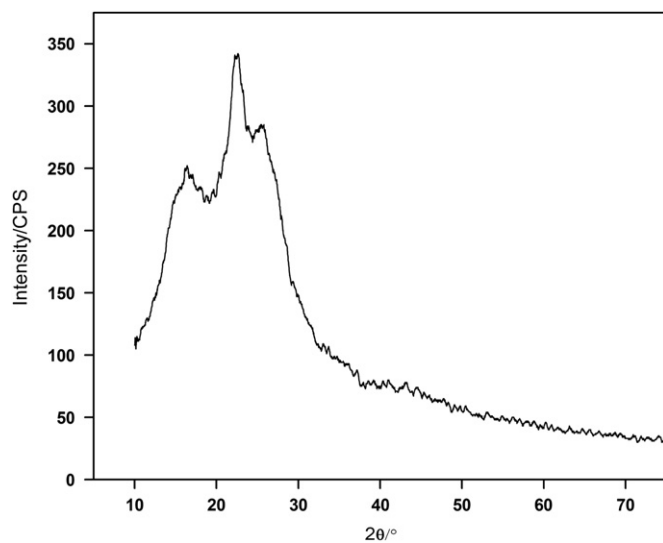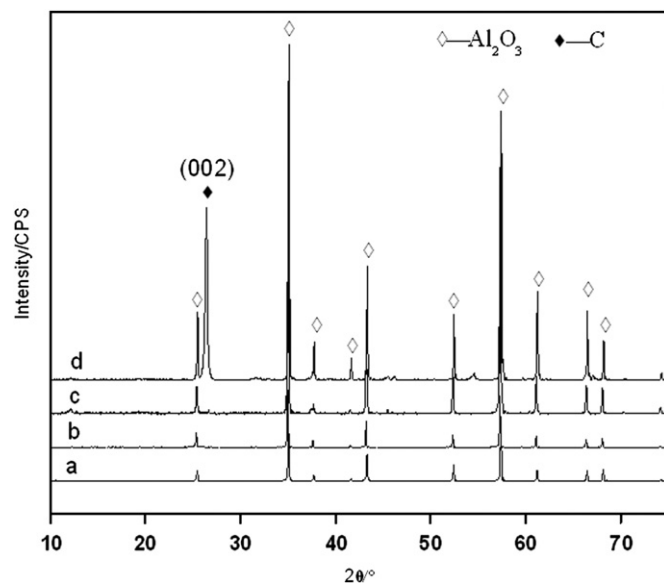Fig. 4. XRD patterns of: (a) monolithic Al_2O_3; (b) AF20 composite; (c) AF25 composite; and (d) AF30 composite.

Fig. 2. The sintering process of the composites.

Fig. 3. XRD pattern of the pre-oxidized PAN fibers.

chain structures of PAN molecules that are not completely transformed into trapezoidal structure at the preoxidation stage. The diffraction peak at 26.3° (002) is the heat-resistant trapezoidal structure. It is the foundation of forming a carbon layer structure [10].

Fig. 4 shows the XRD patterns of sintered monolithic Al_2O_3 and the composite with different fiber content. There are only peaks of crystalline α-Al_2O_3 for monolithic Al_2O_3 in Fig. 4(a). However, the composites with lower content of pre-oxidized PAN fibers (Fig. 4(b, c)) also only exhibit the peaks of Al_2O_3 but not any obvious peaks associated with carbon fibers. To verify the existence of carbon fibers, the composite with 30 vol% pre-oxidized PAN fibers content was prepared and its XRD pattern is shown in Fig. 4(d). In the Fig. 4(d), besides the peaks of Al_2O_3, the typical peak of carbon fibers in (002) crystal face appears at 26.3°. The position of the diffraction peak of carbon fibers is always between 25° and 27° in XRD patterns, which is related to the quality of the pre-oxidized PAN fiber [11]. Fig. 4(d) shows that the pro-oxidized PAN fibers have been in situ transformed into carbon fibers in the sintering process.

The interlayer spacing of standard graphite single crystal (d002) is 0.3354 nm [9]. By Bragg′s law, the calculated (d002) interlayer spacing of the in situ carbon fibers is 0.3425 nm. That is to say that the arrangement of carbon layers may be slightly disordered and the in situ carbon fibers is a polycrystalline turbostratic structure [9,12,13].

In the preparation process of the composites, non cyclization PAN fibers cause the structure to change by the cyclization and cross-linking reaction at the preoxidation stage with temperature increase, which reflects in the diffraction peaks at 17.9° (shown in Fig. 3) but has disappeared in Fig. 4. This change also confirms that the pre-oxidized PAN fibers have transformed into carbon fibers.

The energy spectrum analysis for the fibers in the AF15 sample is shown in Fig. 5. The atomic percentage of carbon element accounts for 92.68%, and there are small amounts of Al_2O_3 and SiO_2 retained on the surface of the carbon fiber. Therefore, the pre-oxidized PAN fibers in the composite have been in situ transformed into carbon fibers after the sintering.

4.2. Microstructure of composites

The microstructure images of the composites with different content of pre-oxidized PAN fibers are shown in Fig. 6(a–c), and (d) is the high magnification image of Fig. 6(b).

The carbon fibers in situ transformed from the pre-oxidized PAN fibers are uniformly distributed in the alumina matrix, however slight interspaces exist in the interfaces between the fiber and matrix as an arrow shown in Fig. 6(d).

4.3. Mechanical properties of composites

The content of pre-oxidized PAN fibers influences the density, microhardness and fractural toughness of the composites, as shown in Figs. 7 and 8.

The density of the composites decreases with the pre-oxidized PAN fiber content increase. This is due to the increase of pre-oxidized PAN fiber content resulting in a slight increase of the interspaces of matrix/fiber interface (as shown in Fig. 6d); also, the density of carbon fibers is lower than that of alumina. The composites then exhibit a lower density. Above 20 vol% pre-oxidized PAN fibers the density of the composites decline due to the fibers agglomeration causing more porosity.

From Fig. 8, it can be seen that the average microhardness of the composites decreases with the increase of the pre-oxidized PAN fibers. It is considered that the reduction of microhardness is related to the density of the composites.
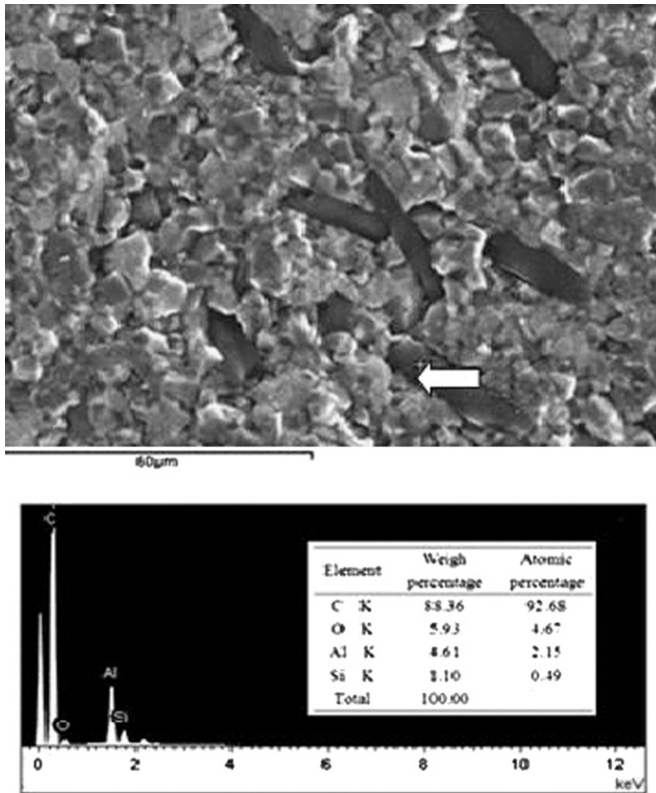

Fig. 5. Energy spectrum analysis for the carbon fiber in AF15.

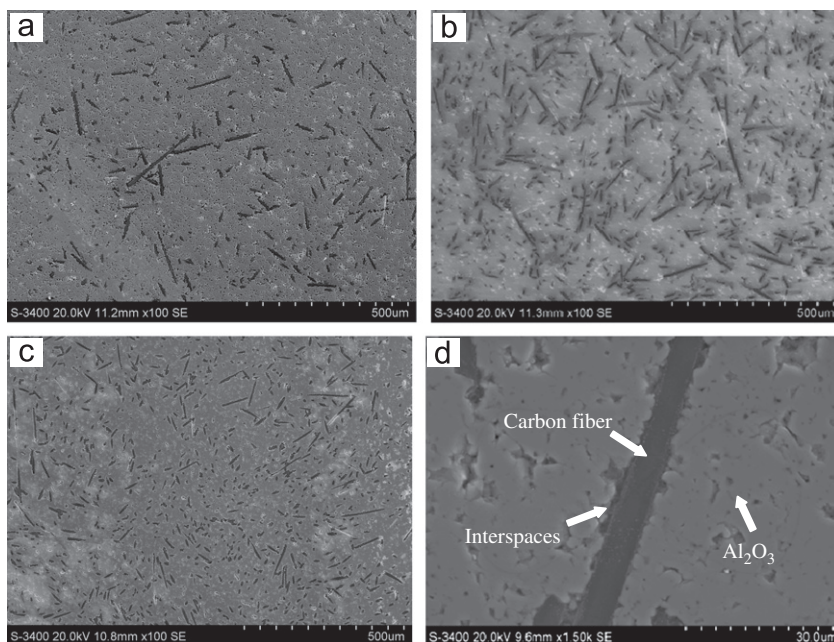| Element	Weigh percentage	Atomic percentage
C K	88.36	92.68
O K	5.93	4.67
Al K	4.61	2.15
Si K	1.10	0.49
Total	100.00	

Fig. 6. Microstructure images of the composites: (a) AF15; (b) AF20; (c) AF25 and (d) high magnification image of (b).

The fracture toughness of the composites with different pre-oxidized PAN fibers content is shown in Fig. 8. It can be concluded that the fracture toughness of alumina ceramics (4.75 MPa m$^{1/2}$) is improved by the addition of
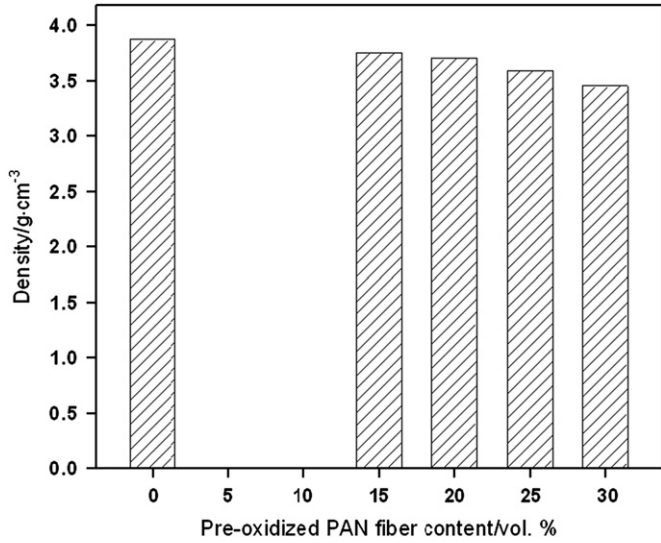
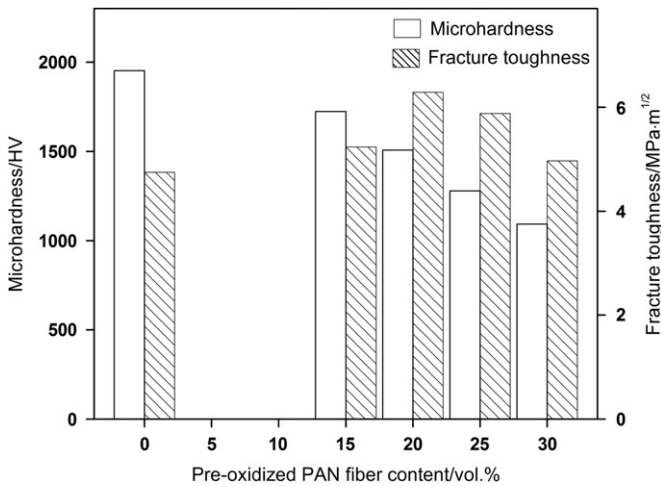

Fig. 7. Density of the composites with different pre-oxidized PAN fibers content.

Fig. 8. Microhardness and fracture toughness of the composites with different pre-oxidized PAN fibers content.

the fibers. The fracture toughness of the composites with 20 vol% pre-oxidized PAN fibers reaches a maximum value (6.29 MPa m$^{1/2}$) and then decreases with the increase of pre-oxidized PAN fiber content. It shows that as the content of pre-oxidized PAN fibers increases in the composites there are more fibers bearing the stress which is transmitted from the ceramic matrix to the fibers, which avoids stress concentration and the emergence of micro-cracks. At higher stress, debonding and pull-out of the fibers from the ceramic matrix contributed to the improvement in toughness via an energy dissipation mechanism. Fig. 9(a) shows the fiber pull-out features, providing evidence for the mechanism. With the increase of fiber volume fraction, more fibers are pulled out from the matrix, and more fracture energy is absorbed in this process thus improving the fracture toughness of the composites. When the content of pre-oxidized PAN fibers is excessive (over 25 vol%), the fracture toughness will decline due to the agglomeration of fibers (Fig. 6(c)) which strongly inhibit the diffusion mechanism, resulting in depressed density (Fig. 7), hardness and weak interfacial connection between carbon fibers and matrix. Thus, the possible toughening mechanisms are not fully operative, resulting in obviously reduced fracture toughness.

It is observed that carbon fibers formed bridges across the alumina matrix, as displayed in Fig. 9(b), which can effectively prevent crack propagation, improving the toughness of composites. SEM images (Fig. 9(a) and (b)) demonstrate the pull-out features and bridging features of carbon fibers, indicating the fiber pull-out and crack bridging toughening mechanism.

5. Conclusions

(1) Well-dispersed in situ transformed carbon fibers/Al$_2$O$_3$ ceramic composites have been prepared in the optimized process parameters. Twice grade heating separately at 444 °C and 1070 °C for 10 min and a sintering temperature of 1700 °C was used to ensure the formation of in situ carbon fibers.
(2) XRD analysis shows that the composites present a typical diffraction peak at 26.3°, which corresponds to the (002) crystal face of carbon fibers, and the interlayer spacing $d_{002} = 0.3425$ nm. The carbon content of the in situ transformed carbon fibers is 92.68%.
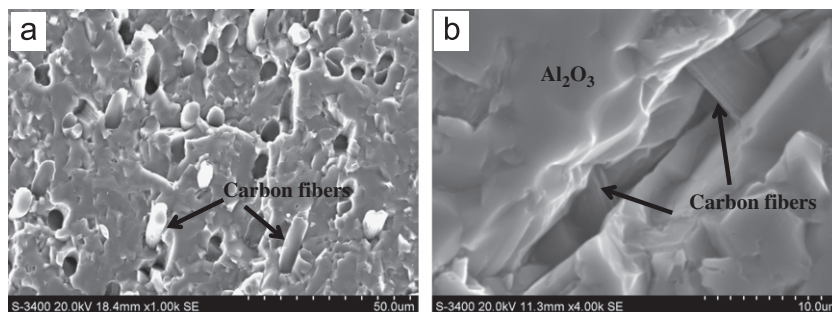

Fig. 9. SEM images of AF20 composites: (a) carbon fibers pull-out and (b) crack bridging.

(3) The fracture toughness of the composites with 20 vol% pre-oxidized PAN fibers reaches 6.29 MPa m$^{1/2}$. Compared with 4.75 Mpa m$^{1/2}$ of alumina, it is clear that the in situ transformed carbon fibers remarkably improve the fracture toughness of the composites and the toughening mechanisms contribute to fiber pull-out and crack bridging.

(4) The density and microhardness decrease with the addition of pre-oxidized PAN fibers, which may be due to slight interspaces between the fiber/matrix interfaces. Therefore, the next work will focus on improving the interfacial bonding between the carbon fibers and alumina matrix.

Acknowledgments

References

[1] J.K. Guo, The brittleness problem of ceramic material, Journal of Fudan University 42 (2003) 822–827.

[2] F.Y. Yang, X.H. Zhang, J.C. He, S.Y. Du, Characterization of hot-press short carbon fiber reinforced ZrB$_2$–SiC ultra-high temperature ceramic composites, Journal of Alloys and Compounds 472 (2009) 395–399.

[3] M. Santi, L. Paveena, K. Jutharatana, V. Amornkitbamrung, Carbon nanofiber-reinforced alumina nanocomposites: fabrication and mechanical properties, Materials Science and Engineering: A 447 (2007) 44–50.

[4] W. Zou, K.Zh. Zhang, L.T. Zhang, L.T. Zhang, Application of ceramic matrix composites to rocket motor, Journal of Solid Rocket Technology 32 (2000) 60–65.

[5] E. Fidancevska, G. Ruseska, J. Bossert, Y.M. Lin, A.R. Boccaccini, Fabrication and characterization of porous bio-ceramic composite based on hydroxyapatite and titania, Materials Chemistry and Physics 103 (2007) 95–100.

[6] J.K. Zhu, F. Luo, P. Li, D.M. Zhu, W.C. Zhou, Effect of short carbon fiber content on the properties of C$_{sf}$/Al$_2$O$_3$ composites, Materials Reviews 24 (2010) 23–25.

[7] L.J. Guo, H.J. Li, K.Z. Li, Review on fiber homogenization techniques in fabrication of short carbon fiber reinforced composites, Ordnance Material Science and Engineering 26 (2003) 50–53.

[8] ASTM E399, Standard test method for plain strain fracture toughness of metallic materials. Annual Book of ASTM Standard, V.03. 01. ASTM, Philadelphia, USA, 1991.

[9] H.Y. Ge, J. Chen, H.Sh. Liu, C.G. Wang, Structural evolvement of PAN oxidized fiber during carbonization and microstructure of carbon fiber, CIESC Journal 60 (2009) 238–243.

[10] Harald Rennhofer, Dieter Loidl, Stephan Puchegger, Herwig Peterlik, Structural development of PAN-based carbon fibers studied by in situ X-ray scattering at high temperatures under load, Carbon 48 (2010) 964–971.

[11] Zh.M. Gao, Y. Gao, X.Sh. Li, Several new X-ray diffraction quantitative techniques in the study on the microstructure of carbon fiber of PAN-based precursor and preoxidized fiber, Materials Engineering 2 (2009) 45–51.

[12] R. Harald, L. Dieter, P. Stephan, H. Peterlik, Structural development of PAN-based carbon fibers studied by in situ X-ray scattering at high temperatures under load, Carbon 48 (2010) 964–971.

[13] L. Wang, J.F. Tong, B.W. Li, H. Huang, Crystal structures of PAN-based carbon fibers during graphitization, Materials Engineering 2 (2009) 363–367.