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Mechanical properties and microstructure of two-dimensional carbon fiber reinforced zirconia composites prepared by hot-pressing

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Abstract

Two-dimensional carbon fiber reinforced zirconia matrix composites have been fabricated by slurry infiltration and hot pressing techniques. The room temperature mechanical properties were investigated and the fracture features of composites were observed. The results showed that with the increase of temperature the relative density of as-prepared C_f/ZrO_2 composites increased. But the mechanical properties of composites on fiber configuration firstly increased and then decreased. Higher mechanical properties were obtained for the composite hot-pressed at 1500 °C i.e. the flexural force and fracture energy were 136.0 N and 31.3 kJ · m^{-2} respectively. SEM observation revealed fiber pull-out in the composite sintered at ≤1500 °C. For the composite sintered at a higher temperature, however, chemical diffusion between fiber and ZrO_2 was found by HRTEM, which indicates the formation of strong bonding. Also the reduced nonlinear region and short pullout length of fiber suggest a strong interfacial bonding between the fiber and matrix. The strong interfacial bonding and large thermal residual stress mainly contribute to the degradation of mechanical properties above 1500 °C.

Keywords: A. Hot-pressing processes; B. Microstructure; C. Mechanical properties; C_f/ZrO_2 composites

1. Introduction

Continuous fiber reinforced ceramic matrix composites have inherited outstanding attributes of the matrix and fiber. They have become indispensable key materials that are applied in aerospace craft [1], missiles [2], and supersonic vehicles [3]. In severe environment, hot structural parts need not only high temperature resistance but also oxidation resistance and thermal shock resistance. Currently, C_f/SiC [4], SiO_{2f}/SiO_2 [5], and C_f/SiO_2 [6] composites have attained widespread application in aviation and national defense fields owing to their lightweight, anti-ablation, good heat insulation and load bearing performances. However, C_f/SiC composites will be oxidized in the presence of oxygen at high temperature [7], and for SiO_2 based composites softening can easily occur above 1100 °C due to lower melting point of SiO_2.

Zirconia composites have been considered potential materials for hot structural parts on the basis of their high melting point, high strength, excellent toughness and unique wear resistance for structural application [8,9]. Furthermore, integration of two-dimensional carbon fiber may greatly improve the thermal shock resistance of zirconia ceramics. Up to now, little research has been done on ZrO_2–matrix composite reinforced with continuous fibers. Zhou et al. [10] reported unidirectional carbon fiber reinforced zirconia composite prepared by slurry infiltration and hot-pressing sintering methods. The flexural strength and fracture toughness were more than 500 MPa and 15 MPa · $m^{1/2}$, respectively. However, severe anisotropy remained in this composite. Pujari and Jawed [11] reported chopped alumina fiber–TZP matrix composites prepared by a conventional powder metallurgy route. They found that the alumina fibers did result in a two fold increase in

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toughness with respect to the monolithic TZP but the failure mode remained brittle. Minet et al. [12] prepared ZrO_2–based composites by CVI densification from 2D carbon fibers consolidated with pyrocarbon. The mechanical behaviors of the 2D C–C/ZrO_2 were studied under compression loading. The results indicated that the stress–strain curves exhibit general features which are typical of 2D ceramic composites on the basis of three strain domains. Compared with the CVI procedure, the traditional slurry infiltration and hot-pressing methods have some advantages such as low cost, short processing time and easy adaptability to conventional manufacturing techniques.

In the present work, two-dimensional carbon fibers reinforced zirconia-based composites (C_f/ZrO_2) were prepared by hot-pressing. The effects of hot-pressing temperature on microstructures and mechanical properties of composites were investigated. To clarify the fiber strengthening and toughening mechanism, SEM and HRTEM were employed to analyze fracture surface and microstructural features of fiber/matrix interface.

2. Experimental procedure

2.1. Fabrication of composites

ZrO_2 powder (ZrO_2 > 92 wt%, Y_2O_3 ~7.4 wt%, and average particle size around 2 μm) and PAN-based carbon fiber (3500 MPa average tensile strength, and 6–7 μm in diameter) were used as starting materials. The powder was mixed in deionized water with carboxymethyl cellulose (CMC) as a binder and isopropyl alcohol as a dispersant, and then ball-milled with zirconia balls. The prepreg was prepared by infiltrating the continuous carbon fibers into slurry and then dried, stacked in a graphite die and hot-pressed between 1450 °C and 1650 °C under a pressure of 25 MPa in N_2 atmosphere. The content of carbon fiber was about 25 vol% in the composites.

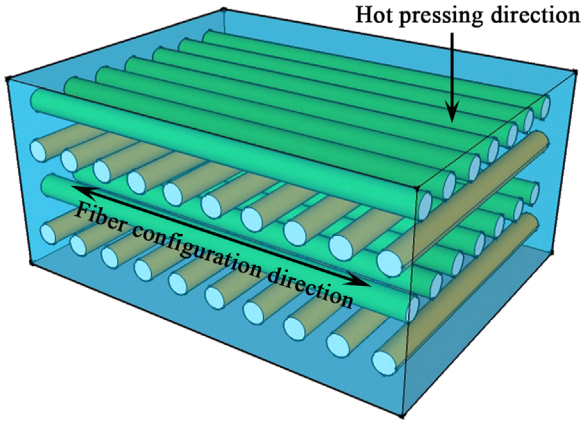

Fig. 1. A schematic diagram of cross-ply structure concerning the C_f/ZrO_2 composites.

2.2. Characterization of composites

The bulk densities of the samples were measured according to Archimedes' principle with deionized water as immersion medium. Fig. 1 shows a schematic diagram of cross-ply structure concerning C_f/ZrO_2 composite and hot pressing direction and fiber configuration direction. The specimens were cut along the fiber configuration direction from composite, and then were machined into bars of 36 mm × 4 mm × 3 mm to measure the flexural strength. The three-point bending method was employed with a span of 30 mm and a cross-head speed of 0.5 mm/min at room temperature in air. Characterization of toughness by fracture energy, the area under flexural force–displacement curve also before maximum force fell about 10%, was used. For all the tests, five or six specimens were tested for each batch of composites.

The fracture surfaces of specimens were observed by a scanning electronic microscope (SEM, Mode JXA-8100, Jeol Co., Tokyo, Japan). The microstructural features of fiber/matrix interface were characterized using a transmission electronic microscope (TEM, Model 200CX, Jeol Co., Tokyo, Japan).

3. Results and discussion

3.1. Mechanical properties of composites

Table 1 shows C_f/ZrO_2 composites physical properties on fiber configuration direction hot-pressed at 1450–1650 °C. It can be seen that the relative density of C_f/ZrO_2 composites gradually increased from 93.1% to 98.3% with hot pressing temperature. However, the mechanical properties firstly increased and then decreased with hot pressing temperature. The top mechanical properties appeared at 1500 °C. That is, the flexural force and fracture energy arrived at their maximums of 136.0 N and 31.3 kJ · m^{-2}, respectively. The 1450 °C-sintered composites exhibited much lower mechanical properties, which was attributed to the poor properties of the matrix

Table 1
Relative densities and mechanical properties of C_f/ZrO_2 composites.

Temperature (°C)	Relative density (%)	Flexural force (N)	Fracture energy (kJ · m^{-2})
1450	93.1 ± 0.2	45 ± 10	9.2 ± 0.4
1500	94.6 ± 0.2	136 ± 18	31.3 ± 0.8
1550	95.9 ± 0.3	93 ± 21	17.5 ± 0.5
1600	97.8 ± 0.1	56 ± 11	10.7 ± 0.3
1650	98.3 ± 0.2	41 ± 10	8.2 ± 0.3

with low density (high porosity). The degraded mechanical properties above 1500 °C may be attributed to the strong interface between carbon fiber and matrix and larger thermal residual stress; density is an unimportant factor in this situation.

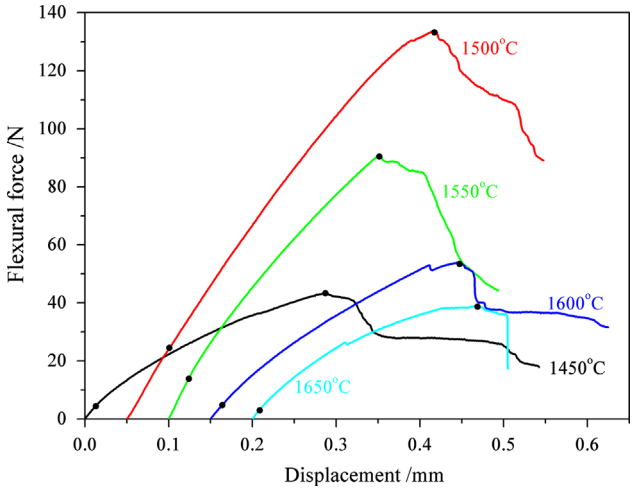

Fig. 2. Flexural force–displacement for the C_f/ZrO_2 composites sintered at various temperatures.

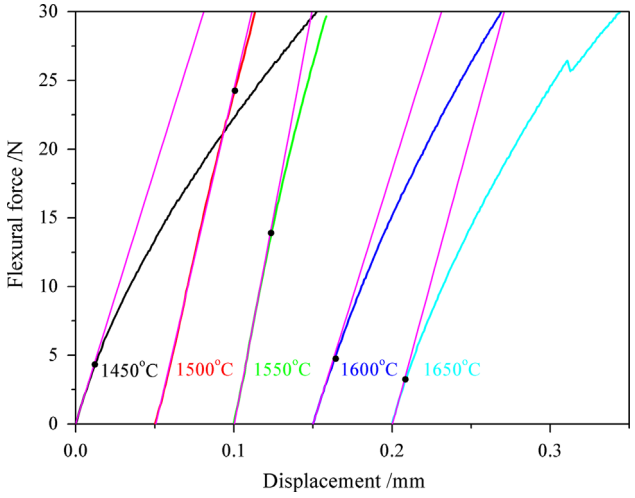

Fig. 3. Magnified flexural force–displacement curves near the linear region.

Six typical flexural force–displacement plots for the C_f/ZrO_2 composites sintered at 1450–1650 °C are shown in Fig. 2. All curves that start from the origin to failure position included two parts. One is a linear region which starts from the origin to first black dot. The other is a nonlinear region between two black dots. From Fig. 2, it can be found that a large nonlinear part is observed up to 1500 °C. However, this part was reduced when the temperature was 1600 °C and 1650 °C, still showing an almost "toughness" behavior different from that of monolithic ceramics.

In order to clearly observe the composites' mechanical behavior, enlarged flexural force–displacement curves were near the linear region. Fig. 3 gives the elastic response of the force–displacement curves. All curves exhibit a linear response from the origin to black dot and a subsequent gradual decrease of the slope upward, that is, nonlinear response. The transition from a linear response to a nonlinear response is always attributed to the initiation of matrix cracking, which was confirmed in other composites (such as C/SiC and SiC/SiC) [13,14].

3.2. Morphologies of fractured surfaces and interface characteristics

In order to clarify the influence of hot pressing temperature on the mechanical properties of composites, fracture surfaces of the C_f/ZrO_2 composites hot pressed at 1500 °C and 1650 °C are shown in Fig. 4a and b respectively. The fracture surface of the sample sintered at 1500 °C exhibited a stepwise feature and fiber pull-out (Fig. 4a). These are caused by the debonding of fiber/matrix interface and deflection of cracks [15]. The pull-out fibers would make contributions to the enhanced mechanical properties of the composite.

However, only small or short pullout of fibers is observed on the fracture surface of 1650 °C-sintered sample, shown in Fig. 4b. The short pullout length of fiber indicates a strong interfacial strength between the fiber and the matrix [16], which is also indicated from the reduced nonlinear deformation in the flexural force–displacement curves, shown in Fig. 2. Evidently, strong fiber/matrix interface bonding formed at such a higher temperature [17]. This is part of the reason why the 1650 °C-sintered sample possessed the highest relative density but exhibited the lowest mechanical properties.

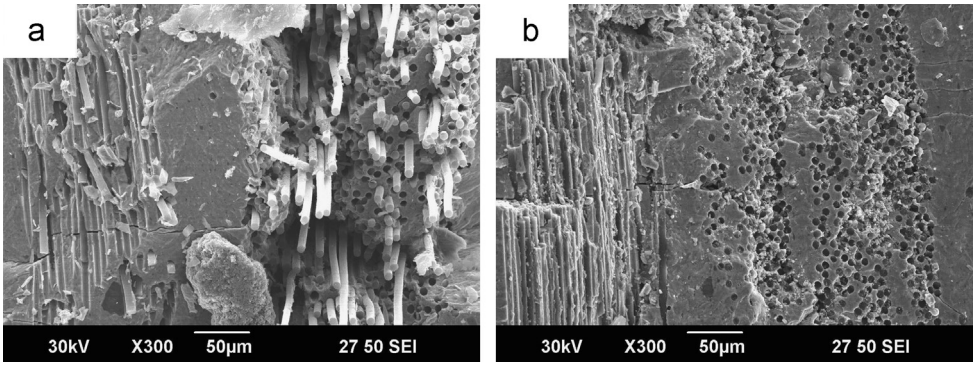

Fig. 4. Fracture surfaces of C_f/ZrO_2 composites sintered at (a) 1500 °C and (b) 1650 °C.

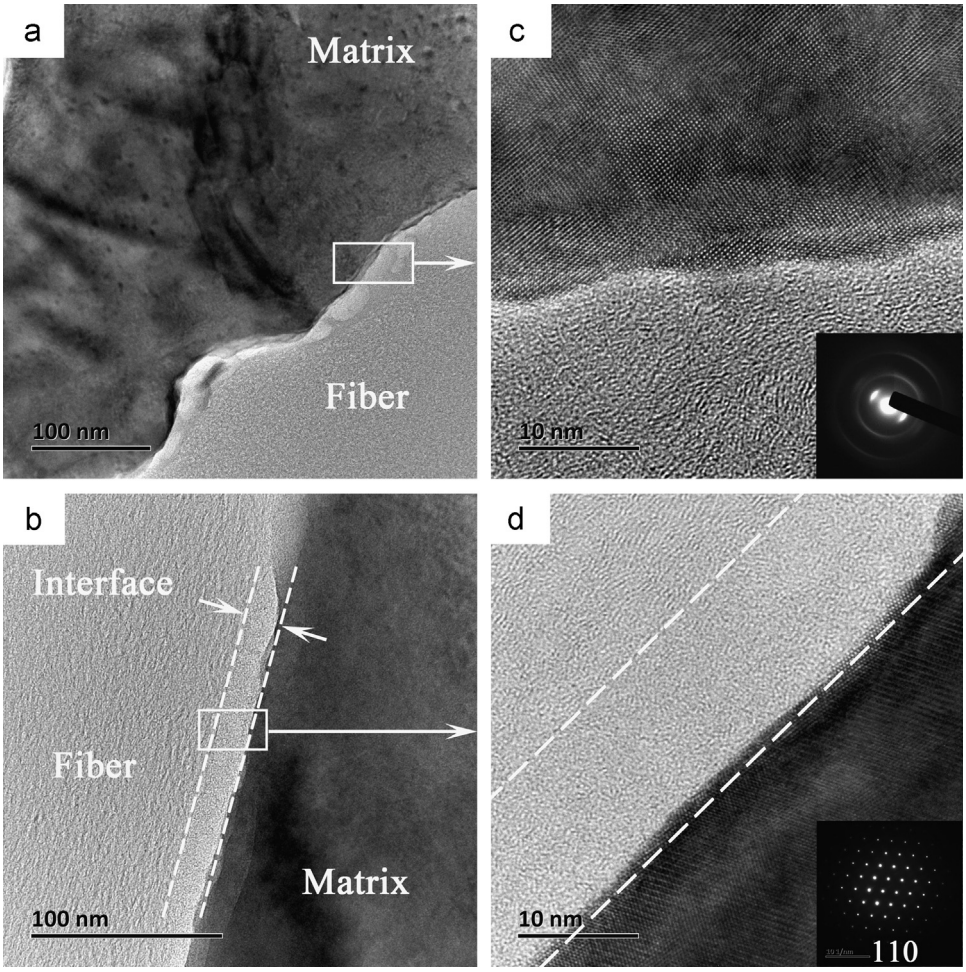

Fig. 5. Magnified TEM images of C_f/ZrO_2 composites hot pressed at (a) 1500 °C, (b) 1650 °C; (c) and (d) high resolution micrographs of interfaces corresponding to (a) and (b).

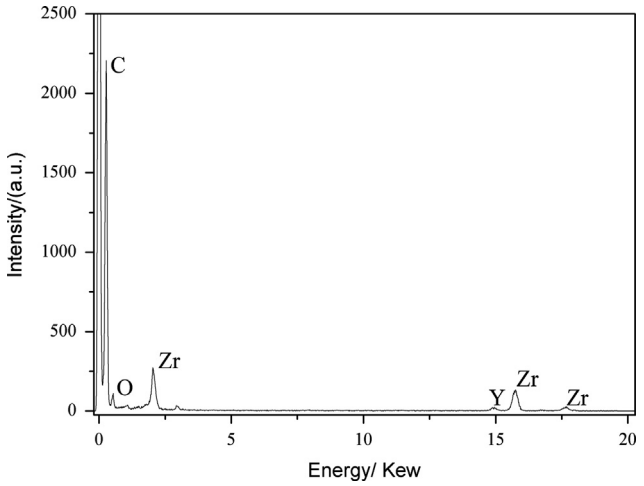

Fig. 6. EDS of interfacial layer between fiber and matrix in Fig. 5d.

HRTEM observations of the fiber/matrix interface reveal that different interfaces form at different hot pressing temperatures. The sample sintered at 1500 °C possesses distinct interface between fiber and matrix without forming an interfacial chemical reaction layer shown as in Fig. 5a and c, which is beneficial to the fiber pull-out.

However, for the C_f/ZrO_2 composite sintered at 1650 °C, interfacial reaction layer can be observed between fiber and matrix, denoted as dotted lines in Fig. 5b and d, which led to the degeneration of carbon fiber and strong interfacial bonding; thus toughening mechanisms such as fiber pullout and interfacial debonding cannot be realized in those composites [18,19]. The EDS-pattern of the interface close to fiber is given in Fig. 6. The result shows that the interfacial layer is enriched by carbon and some amount of Zr, Y and O; it indicates that zirconium, yttrium and oxygen from the matrix have diffused into fibers and some amount of carbon also escaped from fibers and diffused into the neighboring matrix at high temperature. That is, chemical bonding formed, which led to degradation of fibers properties and a strong interface between fiber and matrix. Carbon fiber and cubic zirconia can also be distinguished by SAED shown in Fig. 5c and d. Zhou et al. [10] reported that in unidirectional C_f/ZrO_2 composites strong chemical bonding and even ZrC phase were detected at high hot-pressing temperature. In this case, ZrC phase was not found but a strong interface did exist.

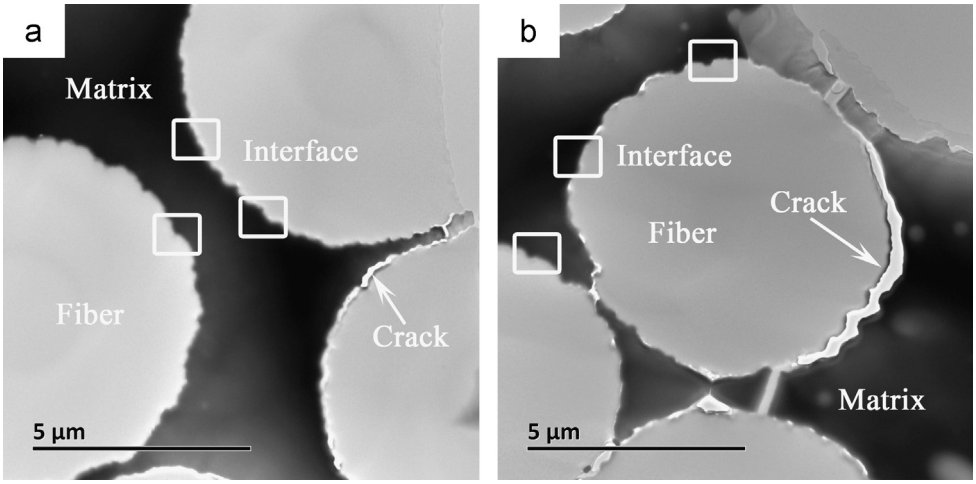

Fig. 7. TEM micrograph of C_f/ZrO_2 composites hot pressed at (a) 1500 °C and (b) 1650 °C.

3.3. Effect of thermal mismatch

The different coefficients of thermal expansion (CTE) between carbon fiber and zirconia and changeable temperature are essential reasons for residual thermal stress of the composite. And the residual thermal stress can affect the situation between fiber and matrix, resulting in different mechanical properties of composites.

Fig. 7 shows TEM images of the C_f/ZrO_2 composites hot pressed at 1500 °C and 1650 °C. It is found that most interfaces of C_f/ZrO_2 hot-pressed at 1500 °C are intact corresponding to Fig. 5a and c. This kind of distinct interface has been denoted by squares in Fig. 7a; a short and narrow crack is also seen between the fiber and matrix. However, long and wide crack between the fiber and matrix was found in the sample sintered at 1650 °C (Fig.7b). Only a small interface of the 1650 °C-sintered composites is intact shown by squares, this interface corresponds to Fig. 5b and d.

This crack would worsen the mechanical properties of C_f/ZrO_2 composite. The reason for formation of crack in C_f/ZrO_2 composite is ascribed to thermal mismatch. Carbon fiber exhibits anisotropic thermal properties. The axial and radial CTE of carbon fiber between room temperature and 900 °C are about $1.1 \times 10^{-6}\,°C^{-1}$ and $8 \times 10^{-6}\,°C^{-1}$ respectively [20,21], both smaller than that of Y–TZP ($9.6–10.4 \times 10^{-6}\,°C^{-1}$) [22]. The residual thermal stress can be calculated according to the following equation [21]:

$$\sigma = E_f E_m V_2(\alpha_f - \alpha_m)(T_0 - T)/(E_f V_f + E_m V_m) \quad (1)$$

Where T is hot pressing temperature, T_0 is room temperature, V is volume fraction, E is elastic modulus, α is thermal expansion coefficient, m and f represent matrix and fiber respectively. From Eq. (1), it is estimated that the higher the hot-pressing temperature, the larger residual stress. For the 1650 °C-sintered sample, the easily formed long and wide crack may be due to thermal residual stress being greater than interfacial bonding strength, despite strong interface bonding. In addition, for the sample sintered at 1500 °C, its residual thermal stress is small owing to lower temperature. So it is found that the interface between fiber and matrix is most intact and distinct, despite weak interface bonding. Therefore excessive hot-pressing temperature is harmful not only to mechanical properties of the C_f/ZrO_2 composites, but also formation of strong interface bonding, due to production of large thermal residual stress.

4. Conclusions

1. The flexural strength and fracture energy of the C_f/ZrO_2 composites firstly increased and then decreased at 1450–1650 °C. The 1450 °C-sintered composites exhibited much lower mechanical properties, which was attributed to the poor properties of the matrix with low density (high porosity). The interfacial bonding and thermal residual stress mainly contribute to the variation of mechanical properties above 1500 °C. The 1500 °C-sintered sample possessed distinct interface and smaller thermal residual stress, which result in top mechanical properties, while the strong fiber–matrix bonding and larger thermal residual stress mainly lead to the decrease of mechanical properties at excessive hot-pressing temperature (1600 °C and 1650 °C).
2. All flexural force–displacement curves that start from the origin to failure position included a linear region and a nonlinear part. The results showed that a large nonlinear part is observed up to 1500 °C. However, this part was reduced when the temperature was 1600 °C and 1650 °C, still showing an “almost tough” behavior different from that of monolithic ceramics.

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