The effects of sintering temperature on the mechanical properties and toughening mechanisms of carbon fibre-reinforced HfB$_2$-SiC composites

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Abstract
HfB$_2$-SiC composites were fabricated by the introduction of carbon fibres to meet the mechanical requirements, and hot pressing was the sintering route. Experiments were carried out to study the effects of the sintering temperature on the mechanical properties and microstructure of HfB$_2$-SiC composites with 15 vol% carbon fibres. In this study, the straight carbon fibres became curved during the pressing process, and the reasons were discussed. The mechanical results showed that curved fibres enhanced the fracture properties when the composites were sintered at temperatures below 1900 °C, and the toughening mechanisms, interfacial debonding, crack bridging and pull-out from the matrix were valid. When fibres are employed to improve the fracture toughness of other ceramics, bent fibres might be a common phenomenon, and this paper can provide important guidance to other researchers.

1. Introduction

Thermal protection systems (TPSs) are used to mitigate the effects of aerothermal heating on aerospace vehicles [1, 2]. Hafnium boride (HfB$_2$) is an important component of TPSs because of its thermophysical properties [3–17], such as its high melting point (>3300 °C), high thermal conduction (104 W m$^{-1}$ K$^{-1}$), low coefficient of thermal expansion (5.7*10$^{-6}$/K), and excellent oxidation resistance (10 times greater than that of ZrB$_2$ when used in the atmosphere from 2000 °C to 2200 °C). These advantages make HfB$_2$ a perfect candidate for high-temperature aerospace applications, such as hypersonic flight or rocket propulsion systems [3, 4]. Thus, HfB$_2$-based ceramics have attracted more attention from researchers in recent years. However, the unsatisfactory toughness of HfB$_2$-based ceramics, not more than 3.5 MPam$^{1/2}$ [4, 15], still presents an obstacle to sophisticated applications.

Introduction of a toughening phase into the matrix is a main approach to improve the fracture toughness of ceramic matrices. The toughening phase may enhance the resistance of the matrix to fracture or crack propagation by mechanisms such as crack bridging, crack deflection, interfacial debonding and/or pull-out from the matrix [18–37].

The toughening phase includes fibres, particles, whiskers, graphite flakes and nanotubes [18–37]. Carbon fibres, approximately 5–10 μm in diameter, are composed mostly of carbon atoms bonded in microscopic crystals. Alignment of the crystals is responsible for the outstanding mechanical and physical properties of these fibres [18–32]. Hence, the addition of carbon fibres to HfB$_2$-based ceramic matrices is recognized as a better solution.

The number of carbon fibres, their distribution in the matrix and the manufacturing process all influence the mechanical properties of carbon fibre-reinforced ceramic matrix composites. Moreover, the sintering temperature determines the strength of the matrix and the strength of the interface between the fibres and matrix. A higher sintering temperature (above 2000 °C) increases the strength, but too great an interfacial strength prevents crack bridging, crack deflection, interfacial debonding and/or pull-out from the matrix.
Previous studies have demonstrated that the introduction of silicides, such as SiC, MoSi2 and TaSi2, has positive effects on the oxidation, densification and mechanical properties of borides [38, 39]. Therefore, in this study, certain amounts of micro-scale SiC and nano-scale SiC powders were added to HfB2-based ceramics while hot pressing at temperatures below 2000 °C. Excellent oxidation resistance of HfB2-based ceramics is also essential for sophisticated applications, and SiC can form a boride-silicide solid solution with HfB2, which may improve oxidation resistance in air.

The optimum sintering temperatures for the matrix and appropriate interfacial bonding between the matrix and carbon fibres would not be the same; the sintering temperatures should not ensure only the maximum strength of the matrix or interfacial bonds but appropriate strengths of both. Therefore, in this paper, the sintering temperatures were 1800 °C, 1850 °C, 1900 °C and 1950 °C, and the focus was the effect of sintering temperature on the mechanical properties and toughening mechanisms of carbon fibre-modified HfB2-SiC-based ceramics.

2. Experimental procedure

In this study, the HfB2 powders (purity >99.5%, purchased from Northwest Institute for Nonferrous Metal Research, China) were approximately 5.0 μm thick. Micro SiC powders (purity >99%, approximately 2.5 μm) were also purchased from Northwest Institute for Nonferrous Metal Research (China). Nano SiC powders (purity >99%, approximately 0.1 μm, purchased from Northwest Institute for Nonferrous Metal Research, China) were treated with aqueous hydrofluoric (HF) acid solution for 15 min. The carbon fibres (purity >99%) had a length of approximately 200 μm (product T300 from Toray Industries, Inc.). The raw materials, HfB2, 15 vol% micro SiC, 15 vol% carbon fibre and 5 vol% nano SiC, were wet ground in a polyethylene bottle for 10 h, using ethanol as the grinding medium. The slurry was dried in a rotary evaporator. Then, the mixtures were hot pressed at 30 MPa for 60 min, while the sintering temperatures were 1800 °C, 1850 °C, 1900 °C and 1950 °C in a N2 atmosphere. The obtained composites were named HfB2-SiC-Cf-1800, HfB2-SiC-Cf-1850, HfB2-SiC-Cf-1900 and HfB2-SiC-Cf-1950. Each sample was ground and polished with diamond slurries to a 1 μm finish.

The polished surface microstructure was observed with scanning electron microscopy (SEM) (JSM-6510, Japan). The interfacial images were obtained by transmission electronic microscopy (TEM) (Philips CM12/STEM, Japan). The bulk density of the samples was measured using Archimedes’ principle, and the theoretical density was calculated according to the rule of mixtures. The relative density was the ratio of bulk density to theoretical density. The flexural strength was surveyed with a three-point bending test on 3 mm by 4 mm by 36 mm bars using a 22 mm span with a crosshead speed of 0.5 mm min−1. The fracture toughness (KIC) was evaluated by a single-edge notched beam test using 2 mm × 4 mm × 22 mm test bars on the same jig used for flexural strength, with a 16 mm span and a crosshead speed of 0.5 mm min−1. All flexural bars were fabricated with the tensile surface perpendicular to the hot pressing direction, and a minimum of five samples were tested under each experimental condition.

3. Results

Figure 1 presents TEM images of the interfaces and SEM micrographs of the polished surfaces of HfB2-SiC-Cf composites with different sintering temperatures. As shown in figure 1a, there were some carbon fibres in the polished surface of the HfB2-SiC-Cf-1800 composites. The distinct interface between the matrix and fibre can be easily examined, and the gaps were approximately a few nanometres. In addition, boundaries in the matrix were easily examined, and the gaps were approximately a few nanometres. In addition, boundaries in the matrix were unclear, and it was not easy to identify them. In addition, the interfaces between the matrix and the fibres became thin lines. Many differences were observed in figure 1(d). It was difficult to distinguish the borders in the matrix, and it was not easy to observe the interfaces between the matrix and the fibres.

For hot-pressed HfB2-SiC-Cf composites, the chemical reaction between the carbon fibres and matrix influenced their interfaces, and thermal diffusion was also a very important factor that affected the interfaces. The XRD patterns of sintered composites with different sintering temperatures and the raw materials (carbon fibres, SiC and HfB2) are plotted in figure 2; carbon fibre peaks were not detected in the sintered composites. A similar phenomenon also existed in the ZrB2 ceramic matrix modified with carbon fibres [40]. The
disappearance of the carbon fibre peaks may be ascribed to their poor degree of graphitization, and the diffraction angles of the carbon fibres were similar to the \((0001)\) peak of HfB\(_2\).

Only peaks for HfB\(_2\) and SiC were found in the sintered composites, and no other materials, such as HfC or B\(_4\)C, were found. These results might mean that no apparent chemical reaction occurred between the carbon fibre and matrix during the sintering process, and thermal diffusion might have resulted in the interfacial differences of the HfB\(_2\)-SiC-C\(_f\) composites with different sintering temperatures, as shown in figure 1.

The relative densities, flexural strength and fracture toughness of the HfB\(_2\)-SiC-C\(_f\) composites with different sintering temperatures are listed in figure 3. According to figure 3(a), the relative density and flexural strength of the HfB\(_2\)-SiC-C\(_f\) composites tended to increase as the sintering temperature increased from 1800 °C to 1950 °C.

For ceramic materials, the flexural strength increases as the porosity decreases. For the HfB\(_2\)-SiC-C\(_f\) composites, the relative density increased slightly from 96.1\% to 99.2\% as the sintering temperature increased from 1800 °C to 1950 °C, which increased the flexural strength.

As shown in figure 3(b), the fracture toughness of the HfB\(_2\)-SiC-C\(_f\)-1800 composites was 4.27 MPa.m\(^{1/2}\), and the fracture toughness value was 5.37 MPa.m\(^{1/2}\) when the sintering temperature was 1850 °C. When the sintering temperature increased to 1900 °C and 1950 °C, the fracture toughness values were 5.14 MPa.m\(^{1/2}\) and 4.79 MPa.m\(^{1/2}\), respectively. This implied that the fracture properties of the composites did not always increase with the sintering temperature.

To discuss the fracture behaviour of HfB\(_2\)-SiC-C\(_f\) composites with different sintering temperatures, the fracture surface was carefully analysed. Therefore, the microstructure of the initial carbon fibres used in this research is shown in figure 4, and micrographs of the fracture surface are given in figure 5. As shown in figure 4, there were some small sagging stripes on the surface of the carbon fibre, and the diameter was approximately 6 \(\mu\)m.

Figures 5(a) and (b) show the fracture surfaces of the HfB\(_2\)-SiC-C\(_f\)-1800 composites. In figure 5(a), two long pitted fibres, stripped partly from the matrix, were observed, and one fractured fibre was pulled approximately 10 \(\mu\)m out from the matrix. Furthermore, the end of this pulled-out carbon fibre and its surrounding matrix debonded. In figure 5(b), although almost no carbon fibres existed in the fracture surface, there were two obvious grooves whose lengths were identical to those of the fibres marked in figure 5(a). In addition, the grooves and the carbon fibres were all slightly bent. These results provided evidence that the grooves were the
tracks left by fibres that were stripped from the matrix during three-point bending fracture toughness tests. In addition, in figure 5(b), we found some sheet-like substances, which were not raw materials used in this experiment, in the matrix.

Figure 5(c) shows the fracture surface of the HfB$_2$-SiC-C$_f$-1850 composites. As depicted in figure 5(c), two or three fibres were pulled out of the matrix, and their lengths ranged from 8 $\mu$m to 35 $\mu$m. Moreover, the ends of these pulled-out carbon fibres partly separated from the surrounding matrix, and sheet-like substances, like those in figure 5(b), were also found in this matrix. Figure 5(d) shows the fracture surface of the HfB$_2$-SiC-C$_f$-1900 composites. We found two fractured carbon fibres that were pulled out of the matrix, and the exposed lengths of these fractured carbon fibres were 10 $\mu$m and 25 $\mu$m. Other fractured carbon fibres were not separated from the surrounding matrix or dragged out of the matrix. In addition, a slightly curved long carbon fibre with a seriously damaged surface was seen, and sheet-like materials remained present. Figure 5(e) shows the fracture surface of the HfB$_2$-SiC-C$_f$-1950 composites. In figure 5(e), there was very little evidence of the behaviour, interfacial debonding and fibre pull-out from the matrix, although some fractured carbon fibres were present. In addition, we found pits on the surface of the carbon fibre in figure 5, compared with figure 4.
4. Discussion

In this study, the raw materials were powders and short fibres, and hot pressing was the fabrication method. During the pressing process, the force might transfer by contact between raw materials, and at the same time, the powder particles might slide or turn. Therefore, there is sliding friction between powder particle, which may change the value of the applied force. All these factors can cause unequal forces on carbon fibres, which bend, as shown in figures 5(a) and (d). This analysis is illustrated in figure 6.

Although the fibres were slightly curved by the mechanical forces shown in figure 3, carbon fibres can enhance the resistance of HfB₂ ceramics to fracture or crack propagation, while the toughening effects are strongly controlled by the sintering temperature.

In this research, the carbon fibre possessed high flexural strength (~3530 MPa), low Young’s modulus (~294 GPa) and high elongation (~1.5%), yet these properties were slightly inferior in the ceramic matrix. Therefore, during the three-point bending test, crack initiation occurred in the ceramic matrix [11, 12, 21], and cracks propagated to the interfaces between the carbon fibres and matrix. Then, a crack could propagate along the interface or in a straight line without any deviation, and the interfacial strength between the fibre and matrix determined the direction of propagation. When composites were sintered at 1950 °C, the interfacial bonds between the carbon fibres and matrix were perfect, which mainly resulted from thermal diffusion between the carbon fibres and matrix, so the crack propagated straight forward because the interfaces were very strong. When composites were fired below 1900 °C, interfacial debonding was the main mechanism of crack propagation. Figure 3 proved that sintering below 1900 °C benefited the fracture toughness of the HfB₂–SiC–Cf composites, and then we investigated how the curved fibres enhanced the fracture toughness.

When a crack increased , it had to propagate along the circumference of a fibre. This meant that the fibre bore the applied load, which resulted in tensile strain, and then the interface debonded along the length of the fibre. The fibre bridged the crack until the load exceeded its tensile strength. Then, the cracked fibre was pulled out, although this was more difficult when the fibre was slightly curved. After that, the crack continued to
Figure 5. SEM micrographs of the fracture surfaces of the HfB$_2$-SiC-C$_f$ composites, with different sintering temperatures (a) 1800 °C, upper fracture surface; (b) 1800 °C, lower fracture surface; (c) 1850 °C; (d) 1900 °C; (e) 1950 °C.

Figure 6. A carbon fibre bends during the pressing process.
propagate forward. The microstructures in figures 4(a)–(d) agreed with these explanations, and the crack propagation process is illustrated in figure 7.

When the composite was sintered at 1800 °C, the strength of the matrix was not high, and the interfacial bond between the carbon fibre and matrix was slightly weak. As a result, although crack bridging, interfacial debonding and/or pull-out from the matrix occurred, the toughening effects were not satisfactory.

Figure 8 shows the micrographs of the carbon fibres used in this test, and the initial length of the fibres was approximately 200 μm. Comparing figure 8 with 5 (especially figures 5(a) and (d)), we found that the carbon fibres were shorter because of the wet ball milling method. Then, we investigated locations of the fragments. The sheet-like substances in the matrix in figure 5 were fragments of carbon fibres, and they might promote the densification of HfB$_2$-SiC-Cf composites [37].

5. Conclusion

In this research, carbon fibres were employed to improve the fracture toughness of an HfB$_2$ matrix by a hot-pressing method. The results showed that the toughening effects were strongly controlled by the sintering temperature, and the fracture properties of the composites did not always increase with the sintering temperature. The fracture toughness of the HfB$_2$-SiC-Cf-1800 composites was 4.27 MPa.m$^{1/2}$, and the fracture toughness was 5.37 MPa.m$^{1/2}$ when the sintering temperature was 1850 °C. When the sintering temperature increased to 1900 °C and 1950 °C, the fracture toughness was 5.14 MPa.m$^{1/2}$ and 4.79 MPa.m$^{1/2}$, respectively.

When composites were sintered at 1950 °C, the interfacial bonding between the carbon fibres and matrix was perfect, so the cracks went straight forward because of the interfacial strength. When composites were fired below 1900 °C, interfacial debonding was the main mechanism of crack propagation, and the toughening mechanisms, interfacial debonding, crack bridging and pull-out from the matrix were valid. When the composite was sintered at 1800 °C, the strength of the matrix was not high, the interfacial bonding between the carbon fibres and matrix was slightly weak, and the toughening effects were not satisfactory.
In our study, we found an interesting phenomenon in which the straight carbon fibres became curved during the pressing process, and the bent fibres may also improve the fracture toughness of other ceramics made by hot-pressing methods. A similar phenomenon might also occur when nanotubes are chosen as the toughening material. Therefore, this paper can provide important guidance to other researchers.

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