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Preparation and mechanic properties of multi-wall carbon nanotube reinforced alumina matrix composites by spray drying and hot-pressing sintering

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Abstract
The multi-wall carbon nanotube (MWCNT) reinforced alumina (Al₂O₃) matrix composites were fabricated by spray drying and vacuum hot-pressing sintering. The mechanical properties of the composites with different mass fractions of MWCNT were studied. The flexural strength and fracture toughness of the composite were 498.3 MPa and 5.69 MPa·m¹/², respectively, which were about 55.3% and 84.7% higher than that of pure Al₂O₃. With the increase in the content of MWCNT, the Vickers hardness and relative density of the composite decreased gradually. The correlation between the microstructure and the mechanical properties of the composite was analyzed.

1. Introduction

Alumina-based ceramic materials show excellent mechanical performance, corrosion resistance, and thermal stability and are widely used as structural ceramic materials for decades. With the development of new functional composite materials, alumina ceramic materials have a very broad prospect in some new applications, such as high-speed cutting tools, biological materials, insulating materials, anti-wear components, etc. However, the poor fracture toughness limits its applications. To improve the fracture toughness and enlarge the application field, specific reinforcement phases such as chromium (Cr), zirconia (ZrO₂), magnesia (MgO), silicon carbide (SiC), carbon fibers and whiskers, are added to the alumina matrix [1–4].

Carbon nanotubes (CNTs) were first discovered by Iijima in 1991, and due to the excellent mechanical and electrical properties, CNTs are extensively studied by various researchers for several applications [5]. According to previous research, CNTs have an average modulus of elasticity (1.8TPa) and flexural strength (14.2GPa), but the tensile strength is about 10 to 100 times of steel with 1/6th the density of the steel density. These excellent properties make CNTs an ideal reinforcement for composite materials [6–10]. There are many reports on the applications of CNTs as a reinforcing phase to improve the strength and fracture toughness of alumina-based ceramic materials. Guodong Zhan prepared the single-wall carbon nanotube (SWCNT) reinforced alumina matrix composite that has nearly twice the fracture toughness of pure alumina. Zhan prepared CNT/Al₂O₃ composite powders by ball milling and produced the composite by hot process sintering, for which the fracture toughness was three times higher than the pure Al₂O₃ matrix [11, 12]. An et al used the ball milling method to prepare 4 wt% CNT reinforced Al₂O₃ composites, and the hardness was increased by 30%. Tong et al prepared a 1 wt% CNT/Al₂O₃ composite material by vacuum hot pressing sintering, and the fracture toughness was increased by 103%. The fracture toughness of the MWNT reinforced Al₂O₃ composites prepared by Siegel was increased by 24% [13–15].

However, some results showed that the addition of carbon nanotubes deteriorated the bending strength and fracture toughness of the matrix. Sun reported that the mechanical properties of the CNT/Al₂O₃ composite, prepared at 1500 °C, decreased significantly due to the CNT addition. Mo prepared 1.5 vol% CNT reinforced Al₂O₃ composite and showed that the fracture toughness increased by 10% than pure Al₂O₃ [16–18].
deteriorated material performance can be attributed to the following reasons: the first reason is that the CNTs are more prone to agglomeration owing to their one-dimensional nature and high aspect ratio (1:1000), which makes it difficult to disperse in the ceramic matrix uniformly. The second reason is that the CNTs have poor physical and chemical wettability with other materials leading to poor interfacial bonding between the materials. The third reason is that the structure of the CNTs is easily disrupted during the preparation process (such as ball milling, purification, high-temperature treatment, high pressure, etc.), which further deteriorates the properties of the CNTs [19–23].

Hence, in this paper, the spray drying process is used to disperse the MWCNTs in the Al2O3 matrix uniformly, and the powder is sintered by the vacuum hot-pressing sintering. The effect of mass fraction of MWCNT on the hardness, relative density, flexural strength, and fracture toughness of the alumina matrix is studied.

2. Experimental

2.1. Preparation

Figure 1 shows the schematic of the composite powder preparation method, in which MWCNT was used as reinforcement in the alumina (MWCNT/Al2O3) matrix. Initially, a certain mass of AlCl3 · 6H2O (AR) was dissolved in the deionized water, and MWCNTs (OD: 25–50 nm, length: 10–20 μm) with different mass fraction x (x = 0.0, 0.5, 1.0, 1.5, 2.0, 2.5) were added into the solution. Then the solution was sonicated for 30 min and the mixed suspension was stirred for 2 h. Subsequently, NH4 · H2O was added slowly to adjust the pH ≈ 9 with magnetic stirring. With the addition of NH4 · H2O, the Al(OH)3 · H2O particles were generated in the solution and were adsorbed on the surface of the carbon nanotubes. This process is beneficial to inhibit the re-agglomeration of the MWCNTs during the subsequent processing [24, 25]. The NH4+ and Cl− ions were removed from the suspension by filtration and were washed with deionized water. Then the filtered cake was placed in the deionized water and magnetically stirred again to form a hydrated alumina suspension. The suspension of the Al(OH)3 · H2O and MWCNT was atomized with high-speed nitrogen gas (N2) and then passed into a glass container at 300 °C to remove the free water to obtain spherical particles of MWCNT/Al(OH)3 · H2O composite. The composite powder was heat-treated at 1000 °C in Argon ambience for 1 h to prepare the MWCNT reinforced α-Al2O3 composite powder. Finally, the composite powder was sintered at 1500 °C, 50 MPa for 1 h in a vacuum hot press sintering furnace (HP HIGH-MULTI 500, Fuji Electric Industrial Co., Ltd), and then cooled naturally.

2.2. Characterization

In this study, the microstructural analyses of the samples were conducted using the following instruments: Raman scattering (LabRAM HR Evolution, HORIBA JOBIN YVON Corp.), transmission electron microscope (TEM) (Tecnai G2 TF30, S-Twin, FEI, USA), X-ray diffraction (XRD) (RINT, Japanese Rigaku), field emission scanning electron microscope (FE-SEM) (HITACHI SU8010), AG-X plus (Shimadzu), Vickers hardness tester (HV-5, Yanrun Company, Shanghai). The samples were cut into 20 mm × 4 mm × 3 mm dimension by the diamond wire cutting machine. The flexural strength was measured by a universal mechanical testing machine.
The fracture toughness of the nanocomposite was evaluated using the Antis equation. In this method, ten indentations were developed using a 5 kg load for 15 s, and the crack length was measured. The average of 10 measurements was taken as the Vickers hardness as well as the average crack length. Subsequently, the fracture toughness was calculated using formula (1) [26, 27]:

\[
K_c = \chi \left( \frac{E}{H} \right)^{1/2} \frac{P}{C^{3/2}}
\]

where \( P \) is the load, \( E \) is the elastic modulus, \( H \) is the Vickers hardness, \( C \) is the radial crack length (measured from the center of indent), and \( \chi \) is the constant.

3. Results and discussion

TEM images show the morphology and surface characteristics of the MWCNTs, as shown in figure 2. The length of the MWCNT is of few microns, and the outer diameter and inner diameter values are about 25–50 nm and 5–10 nm, respectively. Figure 2(a) shows the unagglomerated graphitized CNTs with no metallic catalyst particles on the surface. However, a small number of amorphous carbon particles attached to the surface of the CNTs are detected from figure 2(b).

Figure 3 shows the morphology of the composite particles after spray pyrolysis and heat treatment, respectively. As shown in figures 3(a), (b), after spray drying, the MWCNTs are found to be covered by the hydrated alumina, which can prevent the re-agglomeration of CNTs. The spherical shape of the composite powder may result in better liquidity, which can make it easier to mold. After heat treatment, the crystallized water of \( \text{Al(OH)}_3 \cdot \text{H}_2\text{O} \) was dislodged and formed many pores in the composite particles (figure 3(d)), and eventually, \( \alpha-\text{Al}_2\text{O}_3 \) was generated from the \( \text{Al(OH)}_3 \cdot \text{H}_2\text{O} \) particles.

Raman spectrum was used to characterize the integrity of the CNT structure. Figure 4 shows the Raman spectra of the CNTs before and after vacuum hot pressing sintering at 1500 °C. In the Raman spectrum, the area integral of the D band shows the structural disorder of the CNTs, and the G band shows the stretching vibrations of sp² hybridized carbon atoms of graphene. Therefore, the ratio of D band to G band can roughly describe the integrity of the CNTs. The \( I_D/I_G \) ratio of the original MWCNT is 0.68, and after vacuum hot press sintering at 1500 °C, 50 MPa pressure, the value is 0.85, which means the high temperature and high-pressure sintering partially destroyed the structure of the CNTs, which is hardly conducive to the improvement of the composite performance.

Figure 5 shows the XRD of the 2 wt% MWCNT/Al₂O₃ composite material. Partial conversion of amorphous alumina to \( \alpha-\text{Al}_2\text{O}_3 \) after heat treatment at 1000 °C is observed. After hot pressing and sintering, the main phase of the composite material is found to be alumina, which might be due to the low wt.% of the CNTs present in the composite and a low atomic scattering factor of carbon.

Figure 6(a) shows the dependence of the relative density and hardness of MWCNT/Al₂O₃ composite on the content of MWCNTs. The relative density of the composite material is about 96% to 98%, though a slight decrease in the relative density is observed with the increase in the MWCNT content. Similar results are also observed in the case of hardness; as the content of CNTs increases, the Vickers hardness decreases, especially when the mass fraction of CNTs exceeds 2 wt%. This is because, with the increase in the mass fraction, the CNTs...
agglomerate, which leads to the formation of many pores in the composite matrix. So, it further reduces the relative density and the Vickers hardness of the composite.

Figure 7 shows the flexural strength and fracture toughness of the composite material. The results show that when the mass fraction of MWCNT is 2 wt%, the flexural strength and fracture toughness of the composite material is the maximum in both cases. These values are almost 55.3% and 84.7% more, respectively, relative to pure alumina ceramic. It should be noted that when the mass fraction of MWCNT reaches 10 wt%, the performance of the composite material is deteriorated drastically, which is mainly because as the content increases, more agglomeration takes place. It deteriorates the interfacial bond strength between the MWCNTs and the alumina matrix and reduces the mechanical properties.

Introducing whiskers in the ceramic is expected to improve the toughness of the ceramic through the transfer of energy to the whisker fibers during the fracture process. The main toughening mechanisms are crack bridging, crack deflection, interfacial ceramic/whisker binding, and whisker/fiber inter-wall strength. In this paper, a similar toughening mechanism is observed in the MWCNT/Al₂O₃ composite [28].
Figure 8 (b) shows the crystal size of the MWCNT/Al2O3 composite, which is significantly smaller than the pure alumina ceramic (figure 8 (a)). This indicates that MWCNT can inhibit grain growth during sintering, and grain refinement is beneficial to improve the fracture toughness of the composite material. Meanwhile, MWCNTs are mainly distributed at the grain boundaries, with a small number of CNTs passing through the
Al$_2$O$_3$ grains (figure 8(c)). From figure 8(c), many holes are seen on the surface of the Al$_2$O$_3$ grains, which might have formed after the MWCNTs were pulled out from the matrix. Figures 8(d) and (e) shows the crack-bridging and crack-deflecting phenomena by the MWCNTs. MWCNTs use these mechanisms to consume the crack propagation energy and enhance the fracture toughness of the ceramic. The interfacial bond between the MWCNT and the ceramic matrix also contributes to the toughening of the ceramic. During the fracture process, the interfacial bond should have enough stress transfer capability. High interfacial bond strength is beneficial to improve toughness. From figure 8(c), it is seen that due to the strong interfacial bond, a part of the longer MWCNT is broken or torn, while part of the shorter MWCNT is pulled out [29, 30].

4. Conclusion

The MWCNT/Al$_2$O$_3$ composite was prepared by spray drying and vacuum hot-press sintering with the different mass fractions of CNTs. With the increase in the mass fraction of MWCNTs, the relative density and Vickers hardness values of the composite material were reduced. With 2 wt% of MWCNTs, the flexural strength and fracture toughness of the composites were increased by 55.3% and 84.7%, respectively, compared to pure

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Figure 8. SEM images of the fractured surfaces of pure Al$_2$O$_3$ (a) and 2 wt%MWCNTs / Al$_2$O$_3$ composite (b)–(e) Three toughening mechanisms, (f) schematic of three toughening mechanisms.
The addition of MWCNT inhibited the grain growth of the composite material, which played an important role in the improvement of the mechanical properties of the composite. The main mechanisms for enhancing the fracture toughness of the composite were crack deflection, crack bridging, and CNT pullout. The results showed that the spray drying method can inhibit the re-agglomeration of the MWCNTs and can uniformly disperse the MWCNTs in the alumina matrix. In addition, spray drying can also meet the industrial requirement of rapid batch production of powder, and it can prevent the agglomeration phenomenon of the carbon nanotubes during the preparation process, so that the carbon nanotubes can be uniformly dispersed in the matrix.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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