Mechanical and dielectric properties of short carbon fiber reinforced $\text{Al}_2\text{O}_3$ composites with MgO additive

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Abstract

A series of short-carbon-fiber/Al$_2$O$_3$ composites with MgO as sintering additive were fabricated by pressureless sintering process. The effects of short carbon fiber (Csf) content on the mechanical, dielectric and microwave absorbing properties of the composite were investigated. The results show that the addition of MgO enhances the density, hardness and the flexural strength of the alumina ceramic. However, these mechanical properties of the Csf/Al$_2$O$_3$–MgO composite decrease with increasing Csf content. Both the real and imaginary parts of the complex permittivity increase with increasing Csf content in the frequency range of 8.2–12.4 GHz, which is attributed to the increasing electron polarization and associated polarization relaxation, respectively. When the Csf content is 0.3 wt%, the reflection loss less than −10 dB and the minimum value of −27 dB are obtained with the coating thickness being 1.4 mm. The results indicate that the Csf/Al$_2$O$_3$ with MgO is an excellent candidate for microwave absorbing material with favorable mechanical property.

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Keywords: C. Dielectric property; C. Mechanical property; MgO–Al$_2$O$_3$; Short carbon fiber; Microwave absorbing property

1. Introduction

Electromagnetic absorbers (EMA) are currently gaining much attention especially in the field of microwave frequency applications for protecting sensitive circuits, wireless communication systems and military equipments [1–3]. In comparison with traditional EMA, which consists of organic binder and microwave absorbing fillers, such as carbonyl iron [4,5], carbon materials [6–8] and complex absorbing fillers [9,10], ceramic EMA possesses important performance of good durability at room and high temperature. $\alpha$-$\text{Al}_2\text{O}_3$ ceramic is well known for the low cost, high hardness and flexure strength, which has been proven as an ideal candidate for structural application [11]. On the other hand, these excellent properties also make it an ideal candidate matrix for the ceramic EMA application. Short carbon fiber with excellent mechanical property and proper dielectric property, such as high strength, high modulus, low thermal expansion, and high electrical conductivity [12,13], are often used as reinforcement and absorbing fillers [14]. Many research works have been carried out to study the dielectric property, electromagnetic interference shielding and microwave absorption of the EMA using short carbon fibers as absorbing fillers [15]. These research works showed that the composites containing short carbon fiber possess attractive microwave absorbing property and potentially practical applications both in room and high temperature microwave absorption. Therefore, Csf/Al$_2$O$_3$ composite has attracted increasing interest because of the good combination performance.

Pressureless sintering is an ideal preparation method for mass production because of its cost effectiveness. However, the primary limitation of the sintered product prepared by pressureless sintering is the relative poor mechanical property of the ceramic [16–19]. Adding sintering additives into the ceramic, such as MgO and rare earth oxide, is a classical and effective approach to eliminate the decline of mechanical properties of the products fabricated by pressureless sintering [20,21]. In the present work, MgO is added in order to enhance the mechanical property and ensure the dielectric property of the composite simultaneously. Csf/Al$_2$O$_3$ composites with MgO as sintering additive were prepared by pressureless sintering at 1500 °C for 2 h. The effect of the Csf
content on microstructure, mechanical and microwave dielectric properties of the composites was investigated in detail.

2. Experimental

2.1. Materials and sample preparation

The raw material of PAN based carbon fibers were purchased from Nantong Sengyou Carbon Fiber Company, Jiangsu, China. The diameter of 5–7 μm and the length is 2 mm. α-Al₂O₃ powders were purchased from Huatai Ceramic Company Ltd, Tangshan, China. The diameter of the α-Al₂O₃ powders is about dₜ=0.66 μm and the purity is above 99.99%. MgO powders were provided by Xi’an chemical reagent Co. Ltd., Shaanxi, China, and the purity is above 98%.

The Cₜf/Al₂O₃ composites with fixed content of MgO powders (2 wt%) and different contents of Cₜf (0, 0.1, 0.2, 0.3, 0.4 and 0.5 wt%) were prepared. The short carbon fibers were first ultrasonically dispersed for 30 min in ethanol to remove the impurity on the fiber surface. Al₂O₃ and MgO powders were mixed by ball-milling using ethanol as mediums for 1 h. After adding the pure fibers into the mixture slurry of α-Al₂O₃ powder and MgO powder, the final mixture slurry was mechanically stirred for 45 min to obtain uniform mixture slurry. Then the mixture slurry was dried at 70 °C and sieved to obtain fine powders. The fine powders were compacted into discs (Φ70×6 mm²) under a uniaxial pressure of 100 MPa. Finally, according to the sintering condition shown in the literatures [11,18–20,22] and preliminary experiments, the Cₜf/Al₂O₃–MgO discs were sintered by pressureless sintering in vacuum (10 Pa) at 1500 °C for 2 h with the heating rate of 10 °C/min. The samples without Cₜf were also prepared by the same method without addition of Cₜf. The circular sintered disks were cut into rectangular specimens and polished by diamond grinding wheel for three-point bending test (3×4×36 mm³) and dielectric property test (22.86×10.16×2 mm³). The components and the mechanical properties of the composites are listed in Table 1.

2.2. Characterization

The cross-section morphology of the sample was observed by scanning electron microscopy (TESCAN VEGA 3 SBH, Czech Republic). The phase composition of the sintered samples was identified by X-ray diffraction (XRD, pert MPD pro, The Netherlands) using CuKα radiation with a step size of 0.03° over the 2θ range from 20° to 90°. The bulk density of the sintered sample was measured according to Archimedes’ principle with deionized water as immersion medium and the relative density was calculated as the bulk density divided by the theoretical density. The 500RA (Wilson-Wolpert, Northwood, MA) hardness tester was used for HRA (Rockwell Hardness A scale) measurement. The specimens with the dimension of 3×4×36 mm³ was used to measure the flexural strength by three-point bending test with a span of 30 mm and a crosshead speed of 0.5 mm/min. The test was conducted following the general guidelines of ASTM standard C 1341. The σ was calculated by the following equation:

\[ \sigma = \frac{3PL}{2wt^2} \]

where P is the load at a point of deflection of a load–displacement curve in test, L is the outer support span, w is the specimen width, and t is the specimen thickness.

The complex permittivity of Cₜf/Al₂O₃ samples was tested using a network analyzer (Agilent, E8362B PNA, USA). The samples cut into rectangular plate with the size of 22.86×10.16×2 mm³ were used to measure the complex permittivity, which is based on the measurements of the reflection and transmission module in the frequency range of 8.2–12.4 GHz (X-band), in the fundamental rectangle wave-guide mode TE₁₀. In the test, the space between the specimens and the flange was avoided to ensure the accuracy of the dielectric property of the composites [2].

2.3. Calculation of microwave reflection loss of the composites

The calculation of the reflection loss (RL) was carried out to obtain the microwave absorbing property of the composites. According to the electromagnetic parameters and transmission line theory, the reflection loss for a single layer absorber backed by a perfect conductor is given by the following formula [15]:

\[ RL (dB) = 20 \log \left| \left( Z_m - Z_0 \right) / \left( Z_m + Z_0 \right) \right| \]

where Z₀ is the impedance of the free space; Zₘ is the input impedance of the coatings, which can be expressed as the following equation:

\[ Z_m = Z_0(\mu_r/\varepsilon_r)^{1/2} \tanh \left[ (2\pi f d/c)(\mu_r \varepsilon_r)^{1/2} \right] \]

Table 1

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Fiber content (wt%)</th>
<th>MgO content (wt%)</th>
<th>Al₂O₃ content (wt%)</th>
<th>Relative density (%)</th>
<th>Hardness (HRA)</th>
<th>Flexure strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A0</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>97.0</td>
<td>92.1±1.2</td>
<td>195±10</td>
</tr>
<tr>
<td>B0</td>
<td>0</td>
<td>2</td>
<td>98</td>
<td>97.8</td>
<td>93.0±2.6</td>
<td>270±21</td>
</tr>
<tr>
<td>B1</td>
<td>0.1</td>
<td>2</td>
<td>97.9</td>
<td>97.2</td>
<td>92.3±1.4</td>
<td>322±23</td>
</tr>
<tr>
<td>B2</td>
<td>0.2</td>
<td>2</td>
<td>97.8</td>
<td>96.8</td>
<td>91.7±1.2</td>
<td>319±18</td>
</tr>
<tr>
<td>B3</td>
<td>0.3</td>
<td>2</td>
<td>97.7</td>
<td>96.6</td>
<td>91.4±2.1</td>
<td>301±22</td>
</tr>
<tr>
<td>B4</td>
<td>0.4</td>
<td>2</td>
<td>97.6</td>
<td>95.5</td>
<td>90.8±1.8</td>
<td>298±23</td>
</tr>
<tr>
<td>B5</td>
<td>0.5</td>
<td>2</td>
<td>97.5</td>
<td>95.1</td>
<td>89.7±0.7</td>
<td>281±15</td>
</tr>
</tbody>
</table>
where $\mu_r$ and $\varepsilon_r$ are the relative permeability and permittivity of the coatings, respectively; $j$ is the imaginary unit; $f$ is the frequency of the electromagnetic (EM) wave; $d$ is the thickness of the coatings; $c$ is the velocity of light in free space. Here, the real and imaginary part of $\mu_r$ could be taken as 1 and 0, respectively, because of the weakly magnetic property of the composite.

3. Results and discussion

3.1. Microstructure and XRD patterns

The X-ray diffraction pattern of the C_{sf}/Al_{2}O_{3}–MgO composites with 0.3 wt% short carbon fibers is shown in Fig. 1. The pattern exhibits peaks of $\alpha$-Al_{2}O_{3} as the major crystalline phase and magnesia–alumina spinel as a secondary phase in the composites. It is well known that spinel can inhibit the process of secondary phase recrystallization and eliminate pores by slowing down grain boundary migration, which is beneficial to the grain refining and the densification of the composite. Therefore, the addition of MgO promotes the densification of the ceramic which is favorable for improving the mechanical properties of the composite. Typical cross-section morphologies of the samples are represented in Fig. 2. It is obviously observed that the Al_{2}O_{3} matrix is dense and the grain size is uniform. The grain size of the Al_{2}O_{3} ceramic decreased by small additions of MgO, as illustrated in Fig. 2a and b. Fig. 2d shows that the fibers dispersed uniformly in the matrix, which have great influence on the dielectric and mechanical properties of the composite. The reason is that the dispersion state of the conductive fillers in an insulating matrix directly determines the electrical conductivity of the absorbers, which is a crucial factor for determining the complex permittivity of the absorber [2]. Nevertheless, the phenomenon of agglomeration appeared when the fiber content is high, as shown in Fig. 2e.

3.2. Mechanical properties

The relative density and mechanical properties of the composites are given in Table 1. Based on literature review and preliminary experiments, 2 wt% MgO was added to Al_{2}O_{3} ceramic as sintering aid. Compared the properties of samples named A0 and B0, it can be seen that the density, hardness and flexure strength of the sample increase with the addition of MgO. The flexure strength of the Al_{2}O_{3} ceramic with MgO is 270 MPa, which is 38.5% higher than the pure Al_{2}O_{3} ceramic. It is attributed to the formation of a small amount of liquid with the addition of MgO at high temperature, which promotes the sintering process and densification of the composite. The results indicate that the MgO plays an important role in the sintering process of the composite, which is beneficial to the densification and enhancement of the mechanical properties of the Al_{2}O_{3} ceramic. Therefore, 2 wt % MgO was added into all the samples containing short carbon fibers to obtain C_{sf}/Al_{2}O_{3} absorbing material with better mechanical properties. The mechanical properties of the series samples named B0–B5 show that both the relative density and hardness of the samples decrease slightly with increasing C_{sf} content. This is probably due to that the hardness and relative density of the composite is closely related to the microstructure of the composite [26]. The addition of the C_{sf} inevitably introduces pores into the composite, as shown in Fig. 2d. The amount of the pores increases with increasing fiber content, which results in the decrease of the hardness and relative density of the composite, similar to that observed in other investigations [27]. The flexural strength of the composites given in Table 1 shows that all of the C_{sf}/Al_{2}O_{3}–MgO composites exhibit higher flexural strength than the ceramic without C_{sf} and the flexural strength of C_{sf}/Al_{2}O_{3}–MgO composite decreases slightly as the content of C_{sf} increases from 0.1 to 0.5 wt%. The maximum value of 322 MPa is obtained from the sample containing 0.1 wt% C_{sf}, which is about 19.3% higher than the Al_{2}O_{3}–MgO ceramic without C_{sf}. The flexure strength of the fiber/matrix composites is strongly dependent on the interfacial bonding between the fiber and the matrix. The strong interfacial bonding between the fiber and the matrix (seen from Fig. 2c) makes the fibers effectively bear the load applied to the composite, which promotes the increasing of the flexure strength. However, it is difficult for the C_{sf} to disperse uniformly in the matrix with the C_{sf} content increase and the high C_{sf} content resulted in C_{sf} agglomeration, as seen in Fig. 2e. Therefore, the decrease density and the agglomeration of the fibers with the increasing C_{sf} content is responsible for the decrease of the flexure strength.

3.3. Dielectric properties

The effect of the C_{sf} content on the complex permittivity of the composite is presented in Fig. 3. It is found that the addition of C_{sf} significantly enhances the complex permittivity of the composites in X-band. The real ($\varepsilon'$) and the imaginary ($\varepsilon''$) parts of the complex increase from about 9 and 0 to 43~31.5 and 16~23.6 with the C_{sf} content increasing from 0 to 0.5 wt%, respectively. In addition, $\varepsilon'$ decreases with the increasing frequency, while $\varepsilon''$ increases with the increasing frequency when the fiber content is higher than 2 wt%, which
is called frequency response effect and it is beneficial to broaden absorption band of the absorbers.

The real part \((\varepsilon')\) of the complex permittivity represents the polarization ability of the material. It is mainly related to the electronic relax polarization in a gigahertz frequency range for the material with carbon fiber as absorbing fillers. It is due to that the free electrons in carbon fibers respond rapidly to an alternating electromagnetic field \([22,28]\). The increasing Csf content means more free electrons are introduced into the composite and then the electronic relax polarization increases proportionally. Therefore, \(\varepsilon'\) increases with the increasing Csf content ultimately. In addition, the capacitance of the material is a function of its dielectric constant \(\varepsilon'\) and the electrical model proposed by Saib and co-authors can be also used to explain the effect of Csf content on the permittivity of the composite \([29]\). The model assumed that a network of mini-capacitors formed by separating conductive fibers and the insulating matrix. According to this model, it is believed that the increase of Csf content means the decrease of the distance between the conductive fibers and the decrease of the distance leads to a larger capacitance of the system and a higher \(\varepsilon'\).

The imaginary part \((\varepsilon'')\) of complex permittivity represents the dielectric loss of the materials. In order to overcome the electrical resistance when the composite is applied an alternating electromagnetic field, the electromagnetic energy is converted into thermal energy and dissipates in the composite because the free electrons would shift with the alternating electric field. It is mainly dependent on two different factors: electrical conductivity and an eventual relaxation. It can be expressed by the equation \([2]\):

\[
\varepsilon'' \approx \varepsilon''_{\text{relax}} + \frac{\sigma}{\omega \varepsilon_0}
\]

where \(\varepsilon''_{\text{relax}}\) is relaxation polarization, \(\sigma\) is the electrical conductivity, \(\varepsilon_0\) is the dielectric constant in vacuum, and \(\omega\) is the angular frequency. It can be seen that \(\varepsilon''\) is proportional to \(\varepsilon''_{\text{relax}}\) and \(\sigma\). The increasing carbon fiber content means more quantity electronic relax polarization and associated polarization relaxation expressed \(\varepsilon''_{\text{relax}}\) in Eq. (4). On the other hand, carbon fiber is well known for its good electrical conductivity and it is also shown by much research that the conductivity of the composite containing Csf increases with the increasing Csf content \([14,30]\). Therefore, it is reasonable that \(\varepsilon''\) increases with increasing fiber content because both the \(\varepsilon''_{\text{relax}}\) and \(\sigma\) increase. The phenomenon of the complex permittivity varies with the frequency is due to that the polarization of the free

Fig. 2. SEM photographs of composites (a) A0, (b) B0, (c) B1, (d) B2, and (e) B5.
3.4. Microwave absorbing property

The effects of the Csf content and the thickness of the absorber on the reflection loss are shown in Fig. 4. Fig. 4a shows the relationship between the reflection loss and frequency for the coatings with different coating thicknesses as the Csf content is 0.3 wt%. It can be seen that the reflection loss peak shifts from 12.1 GHz to 9.8 GHz with the thickness increasing from 1.3 mm to 1.6 mm and the value less than −10 dB (90% microwave absorption) is obtained for all the thickness. The composite with the thickness of 1.4 mm exhibits that the RL less than −10 dB in the frequency of 10.2–12.4 GHz and the minimum value of −27 dB is obtained. Fig. 4b shows the relationship between reflection loss and frequency for the coatings of different Csf contents (d = 1.3 mm). It can be seen that the reflection loss peak of the composite also shifts to lower frequency with the Csf content increase.

It is consistent considering that the mechanism of microwave absorption of the coatings is mainly related to two conditions. First, in order to reduce the reflection of the incident EM wave at the surface of the absorber, the input impedance of the coating (Zin) and the free space impedance (Z0) should match as far as possible, which is called impedance matching characteristic. The impedance match degree can be defined as $\Gamma = |(Z_{in} - Z_0)/(Z_{in} + Z_0)|$, the smaller $\Gamma$ means better impedance matching degree and smaller reflection loss of the coating. The other condition is that the incident EM wave must attenuate rapidly through the material layer named attenuation characteristic. In this work, the absorbing fillers of Csf in the composite transform the incident EM wave energy into heat energy.

According to formula (Eq. (2)) and the previous discussion, the condition of minimum reflection loss is $Z_{in}$ close to $Z_0$. The impedance of the free space ($Z_0$) is constant and the input impedance of the coating ($Z_{in}$) is determined by a combination of the six parameters: $\varepsilon'$, $\varepsilon''$, $\mu'$, $\mu''$, f and d as shown in formula (Eq. (3)). The coatings with different thicknesses possess a maximum peak of reflection loss appears at different frequency, the reason is that the impedance match degree is determined by combination of the thickness and frequency...
when the electromagnetic parameters of the coating is certain. So, the RL peaks appeared at different frequency with different thickness. On the other hand, the coating containing 3 wt% \( C_{sf} \) shows a better microwave absorption at high frequency than other coatings, which indicates the coating containing 3 wt% \( C_{sf} \) possesses better impedance match degree at high frequency when the thickness of the coating is 1.3 mm. When the \( C_{sf} \) content increased to 5 wt%, the microwave absorption was worse than other coatings in the whole frequency range, this can be attributed to the coating with too large a complex permittivity at this frequency range, which can cause additional reflective wave on the coating surface and the energy dissipating in the coating reduce. In other words, \( C_{sf} \) content determines the electromagnetic property of the \( C_{sf}/\text{Al}_2\text{O}_3–\text{MgO} \) composite, which is the intrinsic factors determine the microwave absorption of the \( C_{sf}/\text{Al}_2\text{O}_3–\text{MgO} \) composite. Conclusively, the microwave absorption is determined by the material properties, which refers to the electromagnetic parameters and the thickness of the material. Therefore, the microwave absorption of a single layer \( C_{sf}/\text{Al}_2\text{O}_3–\text{MgO} \) coating can be regulated by controlling the \( C_{sf} \) content and the thickness of the coating, and the optimal combination of the \( \varepsilon' \), \( \varepsilon'' \), \( \mu' \), \( \mu'' \), \( f \) and \( d \) can make input impedance of the coating (\( Z_{in} \)) close to the free space impedance (\( Z_0 \)) and optimal attenuation of the electromagnetic wave, which lead to maximum absorption.

4. Conclusions

\( C_{sf}/\text{Al}_2\text{O}_3–\text{MgO} \) composites with high density and excellent mechanical properties were prepared using MgO as sintering additive by pressureless sintering. Compared to the pure \( \text{Al}_2\text{O}_3 \) ceramic, the addition of MgO promotes the densification and enhancement of the mechanical properties of \( \text{Al}_2\text{O}_3 \) ceramic. The remarkable enhancement of the flexural strength of the \( \text{Al}_2\text{O}_3 \) ceramic with the addition of the \( C_{sf} \) results from the strong interface bonding between the fiber and the matrix in the composites, while the decrease of the flexural strength with increasing \( C_{sf} \) content is due to the poor dispersion of the \( C_{sf} \), which reduce the interface bonding between the fiber and the matrix. Both \( \varepsilon' \) and \( \varepsilon'' \) of the \( C_{sf}/\text{Al}_2\text{O}_3–\text{MgO} \) composites increase with increasing \( C_{sf} \) content, which is attributed to the increasing electron polarization and associated polarization relaxation, respectively. The calculation of the reflection loss shows that proper fiber content and thickness of the \( C_{sf}/\text{Al}_2\text{O}_3–\text{MgO} \) composite is important to obtain preferable microwave absorbing property and the results indicate that the \( C_{sf}/\text{Al}_2\text{O}_3–\text{MgO} \) composite is an attractive microwave absorber with excellent mechanical properties.

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