Effects of TiO$_2$ Content on Microwave-Attenuating Properties of TiO$_2$-Al$_2$O$_3$ Composite Ceramics

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Abstract. Microwave attenuation ceramic is a kind of dielectric loss material, which is used to absorb some unnecessary microwave electromagnetic field energy. For this attenuation material, it is required to have a large attenuation ratio, a sufficient mechanical strength and a good thermal stability. In this work, TiO$_2$-Al$_2$O$_3$ composite ceramics were prepared via the conventional pressureless sintering method. The addition of CuO as liquid phase sintering aid was used to lower the sintering temperature of TiO$_2$-Al$_2$O$_3$ composite ceramics. The effects of TiO$_2$ content on sintering properties, phase composition, microstructure, mechanical properties and microwave-attenuating properties were investigated. With the increase of TiO$_2$ content, the sintering temperature decreased from 1300°C to 1100°C, meanwhile the dielectric constant rose from 15.42 to 23.80 and the dielectric loss increased from 0.042 to 0.314, which improved the attenuation of the TiO$_2$-Al$_2$O$_3$ attenuation ceramics. When the content of TiO$_2$ was 10 wt%, TiO$_2$-Al$_2$O$_3$ composite attenuation ceramics with good properties could be obtained.

1. Introduction

Microwave attenuation materials is a kind of dielectric loss material which have attracted more and more attention with the widespread use of microwave electron tubes. In order to make the microwave tube work normally under the specific required parameters, the microwave attenuating materials is an indispensable key material for making the microwave tube working stably and reliably, which can suppress the electromagnetic wave in the non-design mode of the microwave tube, prevent the self-excited oscillation, increase the working bandwidth of the resonant cavity, absorb all signals, reduce reflection and improve the electromagnetic matching performance of the terminal [1]. The main requirements for attenuation materials are as follows: 1. sufficient attenuation, which is the key to enable attenuation materials to work normally and withstand enough high power. 2. good thermal conductivity, which can transmit the heat generated by microwave attenuation in time to maintain the normal working state of vacuum tubes. 3. sufficient mechanical strength which ensure the long-term operation of devices [2].

Compared with metal-based, SiC-based, porous ceramics and other microwave attenuation ceramics, Al$_2$O$_3$-TiO$_2$ composite attenuation ceramic is a desiring microwave attenuation material owing to the advantages of easy preparation and high dielectric loss at high frequencies [3]. However, according to resent research, the phase composition, microstructure and attenuation properties of Al$_2$O$_3$-TiO$_2$ composite attenuation ceramic with different content of TiO$_2$ are not very clear. Besides, the sintering temperature of this ceramics is relatively high (1500°C) [4], so it is necessary to reduce its sintering temperature to make it better to be applied. The most common and economical method to
achieve low temperature sintering of ceramics is to add low melting point compounds as sintering aids. CuO was widely used for low temperature sintering process in many ceramic systems and it could effectively reduce the sintering temperature of ceramics [5-7]. Therefore, CuO was added into the Al$_2$O$_3$-TiO$_2$ composite attenuation ceramic system to reduce the sintering temperature. At the same time, the effects of TiO$_2$ content on sintering properties, phase composition, microstructure, mechanical properties and microwave-attenuating properties were studied in this work.

2. Experimental procedures
All samples were prepared via traditional solid reaction method. High-purity Al$_2$O$_3$(99.9), TiO$_2$(99.9), CuO (99.9) powders purchased from Sinopharm Chemical Reagent Co., Ltd. were used as initial ingredients, and the mixture was prepared according to the mass ratio shown in Table 1, which the content of TiO$_2$ ranged from 1 to 10wt% while that of copper oxide was 2 wt%. The mixed powder was ball milled for 4 hours using alcohol as milling medium, then quickly dried at the temperature of 70 °C and sieved through 200 mesh. Afterwards, the mixed powder was pressed together with 5 wt% polyvinyl alcohol (PVA) into pellets of 10mm diameter and 1 mm in thickness under the pressure of 220 MPa. The green pellets were sintered at 1100 °C - 1350 °C for 4 h with a heating rate of 5°C/min.

The buck density of the sintered ceramics was tested using Archimedes methods. The phase structure of ceramics was identified by X-ray diffraction (XRD, Rigaku, DMAX-RB, Japan) with Cu Kα radiation. The microstructure of the ceramics was observed by a scanning electron microscopy (SEM, JSM-6710F, JEOL, Japan). The thermal conductivity of ceramics was conducted with the help of a thermal conductivity measuring instrument (LFA-467, NETZSCH, Germany). The mechanical properties (bending strength) of ceramics were measured by electronic universal testing machine (WDW-100, BAIROE, China). The microwave-attenuating properties were investigated by a network analyser (8720ES, Agilent, USA) using Hakki-Coleman's dielectric resonator method, which was modified and improved by Courtney and Kobayashi et al [8-10], and all measurements were conducted in the frequency of 5-9 GHz at room temperature.

Table 1. Component ratio of the mixture powder.

| Sample group | Al$_2$O$_3$ (wt%) | TiO$_2$ (wt%) | CuO (wt%) |
|--------------|-------------------|---------------|-----------|
| A            | –                 | 1             | 2         |
| B            | –                 | 5             | 2         |
| C            | –                 | 10            | 2         |

3. Results and discussion
3.1. Sintering behaviour
Figure 1 shows the buck density of the Al$_2$O$_3$-TiO$_2$ composite ceramics with different TiO$_2$ content. For samples with the same composition, the curve of the buck density increased at first and then decreased after reaching the maximum value at the optimum sintering temperature. For samples with different compositions, it could be clearly seen that the optimum sintering temperature of ceramics decreased with the increase of TiO$_2$ content. Since the high sintering temperature of Al$_2$O$_3$ ceramics (1750°C) [11], CuO was added at the time of preparing Al$_2$O$_3$- TiO$_2$ ceramics to lower the sintering temperature. When the content of TiO$_2$ was 1 wt%, the sintering temperature of ceramics was 1300°C. Compared with the pure Al$_2$O$_3$ ceramics, the sintering temperature decreased by 450 °C, which proved that CuO could effectively reduce the sintering temperature of this system. In addition, when TiO$_2$ content was 10 wt%, ceramic samples possessed the highest density and the sintering temperature reduced to 1100 °C. This result shows that TiO$_2$ and CuO might form a combined sintering aid which could reduce the sintering temperature of the Al$_2$O$_3$-TiO$_2$ composite ceramics system and the optimum ratio of TiO$_2$ to CuO was 5:1 in this work. This was due to the formation of low melting point liquid phase during the sintering process, which promoted the sintering of Al$_2$O$_3$-TiO$_2$ composite ceramics.
3.2. Phase analysis

Figure 2 is the XRD patterns of the Al₂O₃-TiO₂ composite ceramics with different TiO₂ content sintered at their optimum temperature. All diffraction peaks could be matched well with Al₂O₃ (JCDPS: #80-0786), TiO₂ (JCDPS: #78-2485), Cu₆Al₂O₄ (JCDPS: #78-1605) and an unknown Cubic-type phase (JCPDS: #70-0609). When the content of TiO₂ was 1 wt%, as shown in Figure 2(a), the main crystal phase of the ceramics was Al₂O₃, and there was also a small amount of Cu₆Al₂O₄ which was due to the reaction between Al₂O₃ and CuO as liquid phase sintering aid at high temperature. With the increase of TiO₂ content, the Cu₆Al₂O₄ decreased gradually until it disappeared, and the appearance of TiO₂ led to the formation of TiO₂-Al₂O₃ composite ceramics. In Figure 2(c), as the amount of TiO₂ reached 10 wt%, the ceramics was mainly composed of Al₂O₃ and TiO₂.
Figure 3. SEM images of Al$_2$O$_3$-TiO$_2$ composite ceramics with (a)-(c) 1wt% TiO$_2$, (e) 5wt% TiO$_2$, and (g)-(h) 10wt% TiO$_2$. BSE images of Al$_2$O$_3$-TiO$_2$ composite ceramics with (b)-(d) 1wt% TiO$_2$ and (f) 5wt% TiO$_2$.

Figure 4. EDS on the grain of (a) A point, (b) B point, and (c) D point for Al$_2$O$_3$-TiO$_2$ composite ceramics.

Table 2. The EDS analysis of Al$_2$O$_3$-TiO$_2$ composite ceramics marked in Figure 3.

| Spot | Atom(%) |
|------|---------|
|      | A       | B       | C       | D       | E       | F       | G       |
| Al   | 29.01   | 43.80   | 29.58   | -       | -       | -       | -       |
| Cu   | 14.01   | -       | 15.57   | -       | -       | -       | -       |
| Ti   | -       | -       | -       | 35.57   | 37.62   | 32.92   | 30.81   |
| O    | 54.40   | 54.94   | 51.18   | 61.46   | 60.37   | 65.60   | 67.46   |
| Au   | 3.58    | 1.26    | 3.67    | 2.97    | 2.01    | 1.49    | 1.73    |
| Total| 100     | 100     | 100     | 100     | 100     | 100     | 100     |

3.3. Microstructure

Figure 3 illustrates the SEM and BSE images of the Al$_2$O$_3$-TiO$_2$ composite ceramics. As can be seen from Figure 3, there was no pore on the surface of the ceramic samples and the observed compact microstructure demonstrated that all samples were sintered well. If there were a large number of pores in the ceramics, it would seriously affect the dielectric properties of ceramic samples, leading to a poor matching performance of attenuated ceramics. As the sample reached compact sintering, good attenuation performance would be obtained and it was also instrumental in the improvement of thermal conductivity. When the TiO$_2$ content was 1 wt%, as shown in Figure 3(a) and 3(c), the average grain size was about 2 μm. In addition, there was obvious second phase existed from the BSE images in Figure 3(d), suggesting that A point and B point were two kinds of grains. The EDS was carried out to analyze the composition of these two points. Figure 4 gives the EDS results on the grain...
of Al$_2$O$_3$-TiO$_2$ composite ceramics. Through the analysis from Figure 4(a) and 4(b), the composition of A point was consistent with CuAl$_2$O$_4$, while that of B point was Al$_2$O$_3$. When the TiO$_2$ content was 5 wt%, as could be noticed from Figure 3(e) and 3(f), there were three kinds of grains existing in the ceramics. The EDS results showed that point C and D were CuAl$_2$O$_4$ and TiO$_2$ respectively, which was consistent with the XRD results. As for 10 wt% TiO$_2$ content, a large amount of TiO$_2$ (E, F, and G points) were presented in the Al$_2$O$_3$-TiO$_2$ composite ceramics shown in Figure 3(g) and 3(h). The EDS analysis of Al$_2$O$_3$-TiO$_2$ composite ceramics marked in Figure 3 were summarized in Table 2.

3.4. Microwave attenuating properties

The microwave attenuating properties of samples with different content of titanium dioxide at microwave frequencies were listed in Table 2. It was reported that the dielectric constant of pure phase Al$_2$O$_3$ was 8.5–11 [12] and the dielectric constant of composite ceramics reached 15.42 when 1 wt% TiO$_2$ was added. At this time, the ceramic samples were composed of matrix (Al$_2$O$_3$) and the second phase (CuAl$_2$O$_4$), thus the increase of dielectric constant might be explained by the existence of CuAl$_2$O$_4$ ($\varepsilon_r' = 20–23$) [13]. As TiO$_2$ content increasing, the dielectric constant increased gradually. When the content of TiO$_2$ reached 10 wt%, the dielectric constant was 23.80. The dielectric constant of the composites materials generally satisfies the logarithmic mixing rule shown as following [14]:

$$\log \varepsilon = V_1 \log \varepsilon_1 + V_2 \log \varepsilon_2$$  \hspace{1cm} (1)

where $\varepsilon$ was the dielectric constant of composites, $\varepsilon_1$ and $\varepsilon_2$ were the dielectric constant of components 1 and 2, and $V_1$ and $V_2$ were the volume percentage of components 1 and 2. According to the equation, the increasing dielectric constant of Al$_2$O$_3$-TiO$_2$ composite ceramics was owing to high dielectric constant of TiO$_2$.

With the increase of TiO$_2$ content, the dielectric loss increased from 0.042 to 0.314, which achieved a higher attenuation effect. On the one hand, the increase of dielectric loss was due to the introduction of more oxygen vacancies with the enhancement of TiO$_2$, leading to the formation of conductive loss in high frequency electromagnetic field. The higher the concentration of oxygen vacancies, the higher the polarization loss and the conductive loss. Macroscopically, the attenuation of Al$_2$O$_3$-TiO$_2$ composite ceramics was improved. On the other hand, there were a trace of Mg$^{2+}$, Ca$^{2+}$, Fe$^{3+}$, Mn$^{3+}$, Zr$^{4+}$ and Sb$^{3+}$ presenting in the raw material of TiO$_2$, and most of these impurity ions could displace Ti$^{4+}$ into the lattice of TiO$_2$. Thus, this would also affect the attenuation properties of Al$_2$O$_3$-TiO$_2$ composite ceramics.

Table 3. Properties of Al$_2$O$_3$-TiO$_2$ composite ceramics

| Sample group | St (°C) | Buck density (g/cm$^3$) | dielectric constant ($\varepsilon_r'$) | dielectric loss (tg$\delta_\varepsilon$) | Bending strength (MPa) | Thermal conductivity (W/m K) |
|--------------|--------|-------------------------|-------------------------------------|------------------------------------|-----------------------|-----------------------------|
| A            | 1300   | 3.906                   | 15.42                               | 0.042                              | 72.88                 | 20.90                       |
| B            | 1200   | 3.977                   | 16.28                               | 0.093                              | 188.16                | 21.72                       |
| C            | 1100   | 4.226                   | 23.80                               | 0.314                              | 224.98                | 22.05                       |

Bending strength and thermal conductivity also were two important parameters for the attenuate ceramics. Appropriate mechanical strength provides a stable working condition to ensure the long-term operation of devices. Good thermal conductivity could make attenuation ceramics converting the absorbed energy into Joule thermal energy to dissipate in time which helps to maintain the normal working temperature of the ceramic body and improve its stability. The bending strength and thermal conductivity of Al$_2$O$_3$-TiO$_2$ composite ceramics were also listed in Table 3. In this work, when the content of TiO$_2$ was 10 wt%, the bending strength reached 224.98 Mpa, which indicated that the mechanical properties of composite ceramics will be better with the enhancement of TiO$_2$. In addition, thermal conductivity also rose slightly, seeing from Table 3. With the increase of TiO$_2$ content, TiO$_2$
may contribute less to the thermal conductivity of Al₂O₃-TiO₂ composite ceramics under the action of the second phase. The thermal conductivity mainly depended on the matrix material.

4. Conclusions
In this work, TiO₂-Al₂O₃ composite ceramics were prepared via the conventional pressureless sintering method. The effects of TiO₂ content on sintering properties, phase composition, microstructure, mechanical properties and microwave-attenuating properties were investigated. With the TiO₂ content increasing, the sintering temperature decreased from 1300°C to 1100°C, the dielectric constant rose from 15.42 to 23.80, and the dielectric loss increased from 0.042 to 0.314, indicating that the attenuation of the TiO₂-Al₂O₃ attenuation ceramics could be improved. Meanwhile, the enhancement of bending strength and thermal conductivity suggested that the ceramics possessed higher stability of long-term operation. When the content of TiO₂ was 10 wt%, TiO₂-Al₂O₃ composite attenuation ceramics with good properties could be obtained.

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