Ferrite multiphase/carbon nanotube composites sintered by microwave sintering and spark plasma sintering

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Ni-Carbon nanotube (CNT)-Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ multiphase composites were successfully prepared using microwave sintering (MWS) and spark plasma sintering (SPS) techniques. The obtained samples were characterized by scanning electron microscopy, electrical conductivity, and physical properties measurement system with vibrating sample magnetometer. The SPS prepared composites exhibited higher density, fine grain size, and to maintain favorable three-dimensional conductive network of CNTs compared with the microwave sintered (MWS) ones. Whether use MWS or SPS, both the density and the grain size are increasing with the CNT content increment. The increasing of density and grain size is the main contribution of the saturation magnetization increasing. In the composites of high content of CNTs (such as 5wt%), the spinel structure of ferrite was totally destroyed, as indicated by a considerable decrease in the saturation magnetization. Interestingly, it is found that the Curie temperature increases with the increment of CNT content while the high saturation magnetization was maintained, which has implication that the multiphase ferrite composites will find application in a broad temperature range.

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1. Introduction

In recent years, with the purpose of improving the effectiveness of microwave attenuation capability of ceramics at cryogenic temperature (such as liquid He temperature) especially for application as on-beam-line higher-order-mode (HOM) load in advanced particle accelerators based on superconducting radio frequency (RF), some experimental investigations have been focused on the design of novel materials with the properties of broad-frequency microwave absorption, selective microwave absorption capability, excellent chemical and physical stability at cryogenic temperatures, and appropriate direct current (DC) electrical conductivity for charge drainage (the traditional ferrite-based absorber materials were found inevitably to be insulator at cryogenic environment).1,2

Ni–Zn ferrites have been commonly used in the microwave devices, transformers in power supplies, multilayer chip inductors (MLCI), rod antennas and read/write heads for high speed digital tape, etc.3–7 In the application of attenuation of HOM microwave in the resonant chamber of accelerator, however, the unacceptable high resistivity at liquid Helium temperature make ferrite ceramics a trap to collect the charged particles which build up an extra electric field and disturb the basic beam current. One of the simplest and most effective ways to do so is to incorporate conductive filler to improve the electrical conductive of ferrite. CNTs have been used to form conductive network in some composites for their remarkable chemical inertness, thermal, mechanical, and electrical properties.8–13

It is well known that the properties of multiphase composites are strongly influenced by the dispersion homogeneity and structure integrity of fillers.10–12 Both of the MWS and SPS are fast and effective technique for fabricating materials.13,14 For the MWS method, the microwave power energy can be transferred into heat within the whole volume of the bulk, and the homogeneous temperature would be efficiently improving the densification rate of ceramics and control the growth of grain size. In the SPS processing, the composite powders are pressed uniaxially in a graphite die then sintered by Joule heat and by hypothetical plasma generated in the gap between powder materials. SPS promotes matter diffusion and enables the manufacture of dense materials in a short time at low sintering temperatures compared with conventional methods.15 Although the mechanism of SPS is not yet fully understood, it has been widely employed to fabricate ferrite materials.16–18

In the present work, the MWS and SPS technique were used to fabricate CNT-Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ bulks. Ni nanoparticles were also synthesized and evenly distributed in the composites through in-situ carbothermal reduction approach. The phase composition, microstructure, electrical conductivity, hysteresis loop and Curie temperature of composite ceramic were investigated. A specific attention has been paid on the comparison between of SPS and MWS sintering methods.

2. Experimental

2.1 Materials

Multiwalled CNTs (diameters: 50–60 nm, length: 2–10 μm, purity of 95%) were purchased from ShenZhen Nanoport Ltd.
powders were purchased from China National Medicines Corporation Ltd. Analytical grade of concentrated nitric acid and sodium hydroxide were purchased from China national medicines corporation (China). Analytical grade of concentrated nitric acid and sodium hydroxide were purchased from China national medicines corporation Ltd.

2.2 Functionalization of CNTs and Synthesis of CNT-Ni0.5Zn0.5Fe2O4 Nanopowders

CNTs were functionalized by the combination of covalent and non-covalent bond modification method. High density hydrophilic groups were grafted on the carbon nanotube surface to obtain a high concentration stable CNTs suspension. A combined precipitation-hydrothermal method was used to synthesize Carbon nanotube/Ni0.5Zn0.5Fe2O4 ferrite composite powders.

2.3 SPS Sintering of Ni/CNT/Ni0.5Zn0.5Fe2O4 Multiphase Ceramics

SPS techniques were used to synthesize Ni/CNT/Ni0.5Zn0.5Fe2O4 composite powders. The important sintering parameters were used as follows: heating rate of 10°C/min, target temperature of 1000°C, holding time of 1 h, in Ar2 atmosphere.

2.4 Microwave Sintering of Ni/CNT/Ni0.5Zn0.5Fe2O4 Multiphase Ceramics

In the MWS process, the CNT/Ni0.5Zn0.5Fe2O4 composite powders were sintered by MWS technique, using the HAMiLab-HV3 Type microwave sintering furnace (Synotherm Corporation, China). The important sintering parameters were used as follows: heating rate of 10°C/min, target temperature of 1000°C, holding time of 1 h, in Ar2 atmosphere.

2.5 Characterization

Multiphase bulk ceramics apparent density was measured by the Archimedes technique. The sintered microstructures were characterized by scanning electron microscopy (SEM, Hitachi S-4800, Japan). The electrical conductivity and saturation magnetization of the composites were measured by physical properties measurement system (PPMS, Quantum Design, USA). The high temperature magnetization of multiphase composites was investigated by SQUID-VSM (Quantum Design, USA) equipped with a high temperature stage. The range of the test temperature is from 300 to 1000 K.

3. Results and discussion

3.1 Microstructure and phase analyses of multiphase composites

In our previous work,2,20) the phase evolution and microstructure of multiphase composites fabricated by MWS and SPS have been discussed respectively. Table 1 shows the physical property of composites fabricated by MWS and SPS. It can be seen that, whether use MWS or SPS technology, compared with the sample of pure Ni0.5Zn0.5Fe2O4, the samples with CNTs have higher density. The experimental results are indicating that the introduction of the CNTs can promote the sintering kinetics of the ferrite ceramics. However, compared with the MWS method, the grain growth kinetics has been inhibited through SPS technique and the grain size become finer.

In order to clearly observe the phase composition and distribution in the composite ceramics, Backscattered electron (BSE) image analyses of the fracture surface were performed. Figures 1(a) and 1(b) present the BSE images of the samples with CNT content 2 and 5 wt% respectively. The similar phenomena of the carbothermal reduction were observed in both MWS and SPS treated samples. It is obvious to find that, there are some nanosized “white” ball-like grains (low Z contrast phase) embedded between the larger ferrite grain [Fig. 1(a)], and these “white” ball grains become more prominent in the 5 wt% sample [Fig. 1(b)]. The average diameter of the “white” ball-like grain is about 200 nm. Energy dispersive spectrometer (EDS) contents

| CNTs contents | Grain size (µm) | Density (g/cm³) | M6 (emu/g) | σ (S m⁻¹) (300 K) | σ (S m⁻¹) (70 K) |
|---------------|----------------|----------------|------------|------------------|------------------|
| CNTs-free     | 500 nm         | 75 nm          | 4.89       | 4.96             | 4.60             |
| 0.5 wt.%      | 800 nm         | 400 nm         | 4.96       | 5.22             | 4.89             |
| 1 wt.%        | 1.5 µm         | 500 nm         | 5.12       | 5.19             | 4.89             |
| 2 wt.%        | 2.5 µm         | 600 nm         | 5.23       | 5.27             | 4.89             |
| 5 wt.%        | N/A            | 1 µm           | 5.45       | 5.065            | 4.89             |

Table 1. Physical property of composites fabricated by MWS and SPS

Fig. 1. BSE image of the fracture surface of samples fabricated by SPS at 800°C for 5 min: (a) 2 wt%; (b) 5% CNTs. The insets are magnification images showing the uniform size of metal particles.
analysis indicated the composition of ‘white’ ball-like grain is composed of Ni element (not shown here).

3.2 Electrical and magnetic properties of multiphase composites

Compared with the CNT/Ni0.5Zn0.5Fe2O4 composites fabricated by MWS, the maximum electrical conductivity value of SPS samples has increased of about 650 times (Fig. 2), and the electrical conductivity at liquid helium temperature is improved of nearly three orders of magnitude (Table 1). The unexpected electrical conductivity at liquid helium temperature is improved strongly depends on the weight ration of the CNTs.12),20) As described in the previous papers, the electrical conductivity of the composites strongly depends on the weight ration of the CNTs.12),20) Theoretically, when the contents of the CNTs in the composites are the same, the electrical conductivity should be in the equal orders of magnitude, if the CNTs three-dimensional networks maintained in the matrix are the same in the sintering process. So the electrical conductivity of the SPS samples higher than the MWS samples indirectly indicates that, compared with the MWS, the sintering technique of SPS is beneficial to maintain the three-dimensional conductive network of CNTs in the composites.

Figure 3(a) shows the hysteresis loop of multiphase composites fabricated by SPS method. Both the residual magnetization and coercive force are nearly zero, which are the characteristic properties of soft ferrite behavior. When the CNT amount is less than 2 wt%, the saturation magnetization increased with the increment of CNT content (Table 1). In the present work, there are some factors could influence the saturation magnetization. With the increase of the CNT contents, the nonmagnetic filler of CNT and the decomposition of Ni0.5Zn0.5Fe2O4 will lead to the saturation magnetization decrease, while the high density and large grain size will improve the saturation. When the CNT content is less than 2 wt%, the influences of the nonmagnetic filler introduce and the decomposition of Ni0.5Zn0.5Fe2O4 caused by it, are very limit. The grain size and the density increases with the CNT content increasing (Table 1), so they should be the primary contributing factors for the saturation magnetization increasing. There are some reports that when the grain size is larger than the single-domain size (~50 nm),22),23) the saturation can be improved with a larger grain size.22),23) S.H. Song et al.22) reports that, high-density submicrometer-sized (100–300 nm) Ni0.5Zn0.5Fe2O4 ferrite ceramics were prepared by spark plasma sintering, the saturation magnetization increases with the grain size/density increasing. They explained that the high density of a soft magnetic material is beneficial to its magnetic properties for a high saturation magnetization.22),24) So the improvement of the saturation magnetization should be partially associated with the density increasing. When the grain size is larger than the single-domain size, the magnetocrystalline anisotropy of local regions within the grains cannot be decreased distinctly with the coupling effect of ferromagnetic exchange between the grains. In this case, the domains in the soft magnetic material have significantly non-uniform states of magnetization. Because of the spin magnetic moments in the boundary regions are freedom distributed, the magnetization of these regions is difficult. Moreover, the randomly distributed magnetic moments can be counteracted each other to some degree.25) In the present work, when the CNT content is less than 2 wt%, the grain size ranges from approximately 75 to 600 nm (SPS) and from approximately 500 to 2.5 μm (MWS). Whether use MWS or SPS, both the density and the grain size are increasing with the CNT content increment. So the increasing of density and grain size is the main contribution of the saturation magnetization increasing.

The density of pure Ni0.5Zn0.5Fe2O4 fabricated by SPS is higher than the same composition of samples fabricated by MWS, but the saturation magnetization is a little lower [Fig. 3(b)]. In Table 1, the average grain size in SPS samples is about 75 nm with a very uniform size distribution,20) contrary to MWS samples which showed larger grains (about 500 nm) with abnormal grain growth.12) As discussion in the relationship between the grain size and saturation magnetization, the larger grain size is, the better saturation magnetization become.

It is obvious that the saturation magnetization of 5 wt % composite decreased remarkably. As discussed in the phase evolution section,12),20) Ni0.5Zn0.5Fe2O4 has been decomposed to Ni, Fe-Ni alloy, and Fe-scarce ZnXFe0.85O ferrite, so that the change in atoms distribution of “A” and “B” sites in AB2O4 spinel structure seriously affects the exchange interaction of A and B sites in the spinel ferrite. The Ms of 5 wt % composite is only 18.43 emu/g, which is lower than for the same composition of samples fabri-
intercept of $M$ versus temperature over Curie temperature. In the Fig. 4(a), the abscissa of magnetization and the temperature can be derived at the magnetization $M$ versus temperature $T$ was performed in a equipped with a high temperature stage and shown in composites on the temperature was investigated by SQUID-VSM high density interface. The dependence of magnetization of contents and Curie temperature of multiphase composites with technology to maintain CNT structure.

It is interesting to understand the correlation between CNT contents and Curie temperature of multiphase composites with high density interface. The dependence of magnetization of composites on the temperature was investigated by SQUID-VSM equipped with a high temperature stage and shown in Fig. 4. The magnetization $M$ versus temperature $T$ was performed in a constant field of 30 kOe. For this applied field, the magnetization at room temperature has reached saturation according to Fig. 3. It is observed that the magnetization decreased with the temperature increase, and tended to zero when the temperature was close to the Curie temperature of the ferrite. When the temperature was higher than the Curie temperature, the magnetization followed a Curie–Weiss law. A linear relationship between the reciprocal of magnetization and the temperature can be derived at the temperature over Curie temperature. In the Fig. 4(a), the abscissa intercept of $M^{-1}$–$T$ from the linear part of the curve is the Curie temperature. From Fig. 4(b), the Curie temperatures of bulks with different CNT contents can be determined. It is interesting to observe that the Curie temperature increases with the CNT content. For the pure Ni$_8$Zn$_{12}$Fe$_2$O$_{19}$ sample, the Curie temperature is only 550 K, while it has remarkably increased to 650 K for 2 wt % composite. One possible mechanism is due to the grain size increment and the resultant large number of phase interfaces and voids forming in the multiphase composites, which affect the exchange interaction of A and B sites in the spinel ferrite. On the other side, the Ni-scarce in the ferrite phase may also influence the Curie temperature.

The multiphase ferrite composites obtained by SPS technique exhibits a promising application as HOM load materials. For example, in the 2 wt % composite, the electrical conductivity at room temperature is largely magnified for ten orders more than that of pure ferrite material and keeps a reasonable value at 300 K. It is interesting to notice that the Curie temperature rises with the increment of CNT content in these multiphase composites.

Fig. 4. (a) The magnetization-temperature curves and (b) corresponding Curie temperatures of products with different CNT contents.

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