Ferrite multiphase/carbon nanotube composites sintered by spark plasma sintering

Xiaobing ZHOU,†† Young-Hwan HAN,††† Yongqiang ZHANG, Qian WANG, Jic ZHOU, Lu SHEN, Tongming HUANG,** Weiming PAN,** Changshu XILANG,*** Huiping TANG,*** Jaehyung LEE,†*, So Ik BAE,*, Dong-Yeon LEE**** and Qing HUANG†

Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo, 315201, People’s Republic of China
School of Materials Science and Engineering, Yeungnam University, Gyeongsan, Republic of Korea
Institute of High Energy Physics Chinese Academy of Sciences, Beijing, 100049, People’s Republic of China
State Key Laboratory of Porous Metal Materials, Northwest Institute for Nonferrous Metal Research, Xi’an 710016, China
School of Mechanical Engineering, Yeungnam University, Gyeongsan, Republic of Korea

©2014 The Ceramic Society of Japan. All rights reserved.

Key-words : Multiphase, Spark plasma sintering, Carbon nanotube

1. Introduction

Ni–Zn ferrites are excellent core materials for microwave devices, power transformers in electronics, rod antennas and read/write heads for high speed digital tape, etc. and they have been widespread employed in these areas for their good microwave absorbing performance, high resistivity, low magnetic coercivity and high Curie temperature.¹–⁵ Since their discovery by Iijima in 1991,⁶ CNT incorporated ceramic composites have been widely investigated, and a large number of experimental results has shown that appropriate levels of CNT doping can improve the properties of matrix, such as the mechanical properties, the electrical conductivity and the electromagnetic wave absorption, etc.⁷–¹² Due to the higher Sneck’s limit, the metallic soft magnetic material of Ni nanoparticles have better microwave absorption compared with ferrite absorber.¹³,¹⁴

Zhang X. F. et al.¹⁵ investigated the microwave absorption properties of the carbon-coated Ni nanocapsules. The results showed that the bandwidth with a reflection loss less than −10 dB is from 11.2 to 15.5 GHz and the maximum reflection loss is 32 dB at 13 GHz with 2 mm thickness layer. To achieve broad-frequency microwave absorption, one must take advantage of three major attenuation mechanisms: conductivity loss, dielectric loss and magnetic loss. Therefore it is promising that incorporate both CNTs (conductive-loss phase) and Ni metal (magnetic-loss phase) into ferrite materials (both magnetic-loss and dielectric-loss mechanism) to improved electromagnetic properties of ferrite composites. The spark plasma sintering (SPS) method is an advanced technology for manufacturing ferrite. Compared with conventional sintering method, SPS can promote the sintering kinetics and shorten the sintering time at lower temperature.¹⁶ In order to avoid or minimize the degradation of CNT network formed in the composite ceramics and to preserve structural integrity of CNTs, SPS technique was used to fabricate CNT/Ni₈Zn₄Fe₂O₄ bulks in the present work. Ni nanoparticles were also synthesized and evenly distributed in the composites through in-situ carbothermal reduction approach. The phase composition, microstructure and electrical conductivity were investigated.

2. Experimental procedure

Multi-walled CNTs (diameters: 50–60 nm, length: 2–10 μm, purity of 95%) were purchased from Shenzhen Nanoprt Ltd. Co. (China). Ni(NO₃)₂·6H₂O (98.5%), Zn(NO₃)₂·6H₂O (98.5%), Fe(NO₃)₃·9H₂O (98.5%) and Sodium lignin sulfonate (SLS) (99%) were purchased from Aladdin Industrial Corporation (China). CNT/Ni₈Zn₄Fe₂O₄ composite powders were sintered by SPS technique, using the HDP25 Type SPS furnace (FCT System Gmbh, Germany). Ni/CNT/Ni₈Zn₄Fe₂O₄ multiphase ceramics were synthesized through in-situ carbothermal reduction method. The important sintering parameters were used as follows: 35 MPa of applied pressure, heating rate of 100°C/min, target temperature of 800°C, holding time of 5 min, and cooling rate of 30°C/min.

3. Results and discussion

Figure 1 illustrates the SEM micrographs of the fracture
surface of samples with different CNT contents. With the increase in the amounts of CNTs, the average grain size of the composite ceramic increased gradually. The grain size of pure Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ lies between 50–100 nm [Fig. 1(a)], while for 1 wt % CNT composite, the grain size is five times that of CNT-free sample [Fig. 1(b)]. The grain size distribution in these two samples is relatively uniform. Abnormal grain growth could also be observed when the CNT amount increased [Fig. 1(c)]. At 5 wt % of CNTs, the grain size is greater than 1 micron. Compared with the sample of pure Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$, the samples with CNTs have higher density (Table 1). The experimental results indicate that the introduction of the CNTs can promote the sintering kinetics of the ferrite ceramics.

Figure 2(a) represents XRD patterns of composites with different CNT contents. Both samples of Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ and 0.5 wt % CNT/Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ are composed of pure spinel phase, which characteristic diffraction peaks are well consistent with the standard JCPDS card No.8-234. As the amount of CNTs increased to 1 and 2 wt %, a new phase of Ni appeared; the Ni content increased with the CNT increment. Furthermore, as shown in the XRD patterns of the 20 from 29 to 37 degree in Fig. 2(b), the positions of the (311) and (220) peaks shift to the lower-angle with the increasing of CNT contents. This shift was caused by the expansion of lattice cell due to the reduction of Ni ion from the A site of Ni-Zn ferrite. The lattice parameters increased from 0.8383 to 0.8415 nm, when CNT contents increment from 0 to 2 wt % (see Table 2). Although the characteristic diffraction peaks of Ni metal are not visible in the 0.5 wt % composite due to the detection limit of XRD technique, the peak shift of ferrite in Fig. 2(b) corroborates the liberation of Ni atoms from ferrite and the formation of Ni nanoparticles in the final product that visible in the BSE image (not shown here). During the nucleation and growth of Ni metal in the composites, the liquid state of Ni can act as sintering aid to accelerate the void elimination and grain boundary extension that well explain the grain growth and fully consolidation of ferrite composites as shown in Fig. 1.

Regarding to the phase stability of ferrite materials in the presence of carbon material and in the vacuum condition (3 Pa) during SPS sintering, the thermodynamic analysis is performed. Certainly, the analysis is just qualitative comparison among the carbothermal reductions of the nickel oxide, zinc oxide and iron oxide. The difference in the Gibbs free formation energy of the metal from carbothermal reduction of metallic oxide is the key driving force. For a given basic oxidation-reduction reaction, the Gibbs free energy of reaction can be calculated by subtracting the Gibbs free formation energy of all products from that of all reactants. The Gibbs free energy of carbothermal reduction of different oxides was calculated using as shown in Fig. 3 by representing the dependence of calculated Gibbs free energies of three possible reactions on the temperature ranging from 0 to 1000°C. Obviously, The Gibbs free energy of metal formation decreases with the temperature increasing, and the transition points where carbothermal reduction reaction for nickel oxide, iron oxide and zinc oxide carbothermal reduction become thermodynamically favorable are at about 430, 720 and 970°C.

Table 1. Physical properties of composites fabricated by SPS at 800°C for 5 min.

| CNT contents | Grain size (μm) | Density (g/cm$^3$) | $M_s$ (emu/g) | $\sigma$ (S/m$^{-1}$) |
|--------------|----------------|--------------------|--------------|----------------------|
| CNT-free     | 75 nm          | 4.965              | 0.8415       | N/A                  |
| 0.5 wt %     | 400 nm         | 5.224              | 76.49        | 4.36 x 10$^3$       | 1.00 x 10$^{-1}$ |
| 1 wt %       | 500 nm         | 5.193              | 81.21        | 1.14 x 10$^4$       | 6.30 x 10$^{-1}$ |
| 2 wt %       | 600 nm         | 5.227              | 86.89        | 7.00 x 10$^4$       | 8.81 x 10$^{-1}$ |
| 5 wt %       | 1 μm           | 5.065              | 18.43        | 9.11 x 10$^4$       | 1.15 x 10$^{-2}$ |

Table 2. Lattice parameter of Ni-Zn ferrite in the composites with different CNT contents determined from the experimental XRD data.

| CNT contents | Lattice parameters (α nm) | Samples |
|--------------|----------------------------|---------|
|              |                            | CNT-free| 0.5 wt % | 1 wt % | 2 wt % |
| Lattice parameters $a$ (nm) | 0.8383                   | 0.8394  | 0.8399  | 0.8415 |

Fig. 2. (a) XRD patterns of pure ferrite and multiphase composites fabricated by SPS sintered at 800°C for 5 min, and (b) XRD patterns of multiphase composites showing the peak shift phenomena.
It is thus supported by the Chinese Academy of Sciences’ Hundred Talents Programme’ of The Chinese Academy of Sciences (KJCX2-EW-H06), Technological research fund for the public welfare of Zhejiang province (Grant NO.2012C21017), Ningbo Natural Science Foundation (Grant No. 2013A610131), National Natural Science Foundation of China (Grant No. 51172248 and 11005120), State Key Laboratory of Porous Metal Materials (PMM-SKL-1-2013), Yeungnam University research grant in 2014.

Acknowledgements This work was financially supported by The Netherlands Organization for Scientific Research (NWO). The authors thank Prof. Koert Bergman for valuable discussions and for providing helpful suggestions.
8) Q. Huang and L. Gao, *Appl. Phys. Lett.*, **86**, 123104 (2005).
9) X. B. Zhou, L. Shen, L. Li, S. H. Zhou, T. M. Huang, C. F. Hu, W. M. Pan, X. H. Jing, J. Sun and L. Gao, *J. Eur. Ceram. Soc.*, **33**, 2119–2126 (2013).
10) E. T. Thostenson, Z. Ren and T. W. Chou, *Compos. Sci. Technol.*, **61**, 1899–1912 (2001).
11) Y. Q. Liu and L. Gao, *Carbon*, **43**, 47–52 (2005).
12) M. Han and L. Deng, *Appl. Phys. Lett.*, **90**, 011108 (2007).
13) J. Snoek, *Physica*, **14**, 207–217 (1948).
14) V. B. Bregar, *IEEE Trans. Magn.*, **40**, 1679–1684 (2004).
15) X. F. Zhang, X. L. Dong, H. Huang, Y. Y. Liu, W. N. Wang, X. G. Zhu, B. Lv and J. P. Lei, *Appl. Phys. Lett.*, **89**, 53115 (2006).
16) J. J. Sun, J. B. Li, G. L. Sun and W. G. Qu, *Ceram. Int.*, **28**, 855–858 (2002).
17) Q. Huang, D. Jiang, I. Ovid’Ko and A. Mukherjee, *Scr. Mater.*, **63**, 1181–1184 (2010).
18) G. D. Zhan, J. D. Kuntz, J. E. Garay and A. K. Mukherjee, *Appl. Phys. Lett.*, **83**, 1228–1230 (2003).
19) F. Inam, H. Yan, D. D. Jayaseelan, T. Peijs and M. J. Reece, *J. Eur. Ceram. Soc.*, **30**, 153–157 (2010).