Journal of Magnetism and Magnetic Materials 391 (2015) 172–178

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

The studies of high-frequency magnetic properties and absorption characteristics for amorphous-filler composites

Z.W. Li*, Z.H. Yang

Temasek Laboratories, National University of Singapore, 5A Engineering Drive 1, Singapore 117411, Singapore

ARTICLE INFO

Article history:
Received 14 August 2014
Received in revised form
26 February 2015
Accepted 5 April 2015
Available online 7 April 2015

Keywords:
EM materials
Amorphous-filler composites
High-frequency magnetic properties
Magnetic resonances

ABSTRACT

Pure amorphous flake fillers and amorphous flakes coated by ferrite nanoparticles with core–shell-like structure were fabricated using mechanical ball-milling. The later with core–shell-like structure can greatly decrease permittivity and improve the absorption properties, as compared to the former. The absorption of all amorphous-filler composites has its origin in a quarter-wavelength resonator. Based on the resonator model, absorption frequency f_A and the corresponding return loss *RL* are calculated, which are well consistent with observed values. It is also found that the resonance frequency is proportional to effective resistivity, based on William–Shockley–Kittel's eddy model.

1. Introduction

Electromagnetic (EM) composites can strongly attenuate EM energy that propagates into the composites, thus achieving reflection reduction at the boundary between the composites and free space. In recent years, the EM composites have attracted much attention, due to their extensive applications in industry, commerce and defence. The composites consist of magnetic fillers and polymer. Much valuable work has been published for the composites with various fillers, such as spinel ferrite fillers [1,2], hexaferrite fillers with c-axis and c-plane anisotropy [3–6], and metallic fillers [7–12].

Ferromagnetic amorphous materials have relatively high saturation magnetization (10–15 kGs), very low coercivity (<1 Oe) and low electric resistivity (~10^{-4} Ω cm). Therefore, it can be predicted that the amorphous has large initial permeability. The dc permeability of amorphous ribbons can be as high as hundreds of thousands, as shown in Table 1. However, two drawbacks limit the amorphous ribbons for use as EM materials. For one, the eddy loss of conductive amorphous ribbons leads to very low resonance frequency. To decrease the eddy loss, amorphous fillers with sizes of smaller than the skin depth are usually obtained from mechanical grinding of their ribbons. The resonance frequency f_R with GHz can be achieved [12]. For two, amorphous-filler composites have considerably large permittivity, about 60–120 [12]. The large permittivity and relatively small permeability lead to a mismatch between EM composites and free space, thus deteriorating the absorption properties. In order to decrease permittivity, composites with a core–shell structure, in which metallic particles are isolated by a thin layer of silica (SiO_2), are often used [13–16]. However, the non-magnetic SiO_2 shell causes an undesired decrease in permeability. Therefore, ferrite nanoparticles are used as the shell and can make compensation for the decrease [17].

In this work, amorphous flakes covered by ferrite nanoparticles with a core–shell-like structure were prepared by mechanical ball-milling for use as fillers in composites. The experiments show that the composites with the core–shell structure fillers can greatly decrease the permittivity and therefore, significantly improve EM absorption properties of amorphous-filler composites.

2. Experiment

Co-based amorphous ribbon with thickness of 25 μm was purchased from MetGlas Company, model number 2714A with composition $Co_{66}Fe_4Ni_1Si_{14}B_{15}$. The main parameters are listed in Table 1. Spinel ferrite, $Ni_{0.23}Cu_{0.1}Zn_{0.67}Fe_2O_4$ (NiZnCu), nanoparticles were prepared using sol-gel technology and particle sizes are 50–100 nm [18].

The ribbon was cut into small pieces with dimension of about 5 mm and followed by ball-milling for 270 min to obtain amorphous flakes. Using a set of sieve, the amorphous flakes are classified into samples #1, #2 and #3, respectively, according to their sizes, 125–300, 75–125 and smaller than 75 μm. The amorphous flakes with size of smaller than 75 μm were mixed with the

* Corresponding author. Fax: +65 68726840.
E-mail address: tsllizw@nus.edu.sg (Z.W. Li).

http://dx.doi.org/10.1016/j.jmmm.2015.04.027
0304-8853/

Table 1
Magnetic parameters of amorphous ribbon of 2714A.

Saturation induction (Tesla)	0.57
Maximum D.C. permeability:	
Annealed	600,000
As cast	290,000
Saturation magnetostriction (ppm)	<0.5
Electrical resistivity (μΩ cm)	136
Curie temperature (°C)	365

NiZnCu nanoparticles and followed by ball-milling for another 60 min. The weight ratios of the amorphous and ferrite are 90:10 and 80:20, which are known as samples #4 and #5, respectively.

X-ray diffraction (XRD) was performed using a ULTIMA IV diffractometer with Cu K_α radiation. The microstructure and the size of amorphous flakes were observed using a JOEL JSM-6701F scanning electron microscope (SEM). The magnetization curves and M–H loops were measured with applied fields of 0–20 kOe, and between −20 and +20 kOe, respectively, at room temperature using EV-9 VSM (Vibrating Sample Magnetometer). Demagnetizing correction was considered. The coercivity H_c was obtained from the M–H loops. The saturation magnetization M_s is defined as the value at H=20 kOe. The electric resistivity was obtained from the resistance measured using BMM80 multimeter as well as the section area and thickness of composites. The results are listed in Table 2.

The pure amorphous-flake-fillers with various sizes (#1–#3) and amorphous flakes coated by NiZnCu nanoparticles (#4 and #5) were mixed, with silicone to be prepared into composites #1–#5. The composites were annular disks in shape with an outer diameter of 7 mm, inner diameter of 3 mm and thickness of about 2 mm for microwave measurement. The volume concentration p of composites is between 20 and 36%, as listed in Table 2. The scattering parameters $S11$ and $S12$ were measured over 0.1–10 GHz using an HP5230A Vector Network Analyzer with Transmission-Reflection-Line calibration. The measurement fixture is a segment of 7 mm coaxial air-line, with length of 49.96 mm. The complex permeability and permittivity were obtained from algorithms developed by Nicolson–Ross–Weir method [19]. Also, complex permeability was measured from 0.005 to 1 GHz using Agilent E4991A RF impedance/materials analyzer with open-short-load calibration. The measured fixture is 16454A. For comparison, all permeability spectra are reduced to those for composites with volume concentration p=25% of amorphous fillers, using a simple linear relationship between permeability/permittivity and p.

Table 2
Sample number, preparation, ball-mill time, amorphous flake size, saturation magnetization M_s, coercivity H_c, electric resistivity ρ and volume concentration p of fillers in composites.

No	Sample	Time (min)	Size (μm)	M_s (kGs)	H_c (Oe)	ρ (Ω cm)	p (%)
#1	Amorphous flakes	180	150–300	5.72	0.95	0.86	23
#2	Amorphous flakes	180	75–150	5.75	1.2	1.88	25
#3	Amorphous flakes	180	50–75	5.67	1.4	100	21
#4	90%#3+10% NZC	60	~20	5.57	10.2	173	32
#5	80%#3+20% NZC	60	~20	5.23	10.7	236	36

3. Results

3.1. Structure and static magnetic properties

XRD patterns of original amorphous ribbon, pure amorphous flakes after ball-milling and amorphous flakes coated by NiZnCu nanoparticles, are shown in Fig. 1(a), (b) and (c), respectively. In Fig. 1(a), there is only a broad XRD line at 44.6° for amorphous. Fig. 1(b) indicates that, after ball-mill, the amorphous flakes are still amorphous structure. From Fig. 1(c), two sets of XRD lines are observed. The circles point to the XRD lines of ferrite nanoparticles, which are at 30, 35, 57 and 62.5°.

Fig. 2(a), (b) and (c) shows the images of SEM for samples #2, #3 and #5, respectively. The sizes are 75–125, 50–75 and about 20 μm, respectively. Thickness of the flakes is estimated to be about 5–10 μm from the flakes perpendicular to observation surface, as shown in the arrows of Fig. 2(b). Due to the collision of amorphous flakes and NiZnCu nanoparticles during ball-milling, many nanoparticles are bound to the surface of large amorphous flakes to form a core–shell-like structure, as shown in Fig. 2(d) for sample #5.

Fig. 3 shows the saturation magnetization M_s and coercivity H_c of samples from #0 to #5. The sample #0 is the original amorphous ribbon, which has M_s of 5.7 kGs and H_c of only 0.6 Oe. For the pure amorphous flakes after ball-milling (samples #1–#3), M_s is almost unchanged, 5.67–5.75 kGs, and H_c slightly increases to 1.2–1.4 Oe due to stress produced during ball-milling. For the amorphous flakes coated by NiZnCu ferrites, namely samples #4 and #5, M_s decreases to 5.57 and 5.23 kGs, respectively, as M_s of NiZnCu is about 5 kGs that is smaller than M_s of amorphous [20]. H_c significantly increases from 1.4 to 10.2 and 10.7 Oe, respectively, which has its origin in large H_c of ferrite nanoparticles.

3.2. High-frequency permeability and permittivity

Figs. 4, 5, 7, and 8 show the complex permeability and permittivity for composites with the pure amorphous flakes (#1–#3)

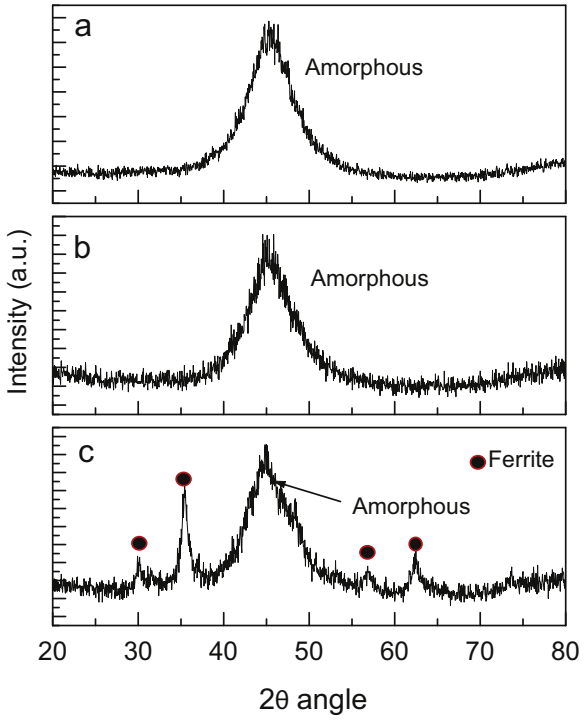

Fig. 1. X-ray diffraction pattern for (a) original amorphous ribbon, (b) amorphous flakes after ball-milling and (c) amorphous flakes coated by NiZnCu nanoparticles.