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The influence of Fe content on the magnetic and electromagnetic characteristics for $\text{Fe}_x(\text{CoNi})_{1-x}$ ternary alloy nanoparticles

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$\text{Fe}_x(\text{CoNi})_{1-x}$ ($x = 0.14, 0.20, 0.25$) ternary alloy nanoparticles were fabricated by a self-catalyzed reduction method at a low temperature. The investigation of static magnetic properties revealed both saturation magnetization and coercive force enhanced with increasing Fe content. By dispersing alloy nanoparticles into paraffin matrix homogeneously, the electromagnetic properties of them were investigated experimentally and the electromagnetic absorption performances were calculated according to transmission line theory. Significant dielectric relaxation was found in the low Fe content sample, which is dominant in dielectric loss. The magnetic loss was attributed to natural resonance and the resonance peaks' shift to high frequency region with increasing Fe content. The enhanced electromagnetic absorption performances were obtained by adjusting Fe content to balance electromagnetic parameters, because the electromagnetic parameters can be varied by structural and magnetic properties. © 2011 American Institute of Physics. [doi:10.1063/1.3556762]

Recently, the development of radar-absorbing materials for commercial and military applications has become a cutting-edge issue. Much effort has been given to seeking suitable electromagnetic wave absorption (EMA) materials, such as carbon-based materials,^{1,2} ferrites,^{3,4} and carbonyl iron powder.^{5,6} However, some disadvantages restrict their further applications. For instance, carbon-based materials have particularly outstanding dielectric properties, but low permeability. So their impedance matching characteristic is poor due to the high permittivity and low permeability. Although ferrites possess perfect low frequency electromagnetic performance, their permeability decreases rapidly at high frequency region due to Snoek's limit. On the other hand, metallic and alloy magnetic materials have high permeability, large saturation magnetization, and high Snoek limit at high frequency band. Consequently, metal or alloy nanoparticles are candidate materials for the fabrication of thin absorbers and are especially promising for the excellent EMA performances in the gigahertz range.^{7,8}

According to transmission line theory, for EMA materials, the balance between complex permittivity and permeability is dominant in their reflection and attenuation characteristics. The electromagnetic parameters should be controlled in an appropriate range for improving EMA performances of absorbers. Compared with single-element metal, ferromagnetic alloys have advantage in the respect of matching complex permittivity and permeability by adjusting the component and microstructures of alloys.^{9,10} However, the high conductivity of metal and alloy materials leads to the rapid decrease of high frequency permeability owing to eddy current losses induced by the electromagnetic wave.^{8,11,12} If particle size decreases to nanometer, eddy current effect can

be effectively restrained due to small particle size and high resistivity. Nanoparticles present relatively low permittivity owing to their high resistivity, and enhanced permeability and natural resonance frequency due to the increase of effective anisotropy field. For achieving ferromagnetic alloy nanoparticles, several methods have been investigated, such as sol-gel process, chemical vapor deposition, hydrogen thermal, and standard and modified arc-discharge techniques.^{7-9,13-16} However, most of these methods require high temperature and a vacuum or atmosphere environment, which typically leads to high costs, operational complexity, or difficulty in terms of practical applications. Herein, a simple low temperature reduction was reported to prepare the ferromagnetic ternary alloy nanoparticles.¹⁰

$\text{Fe}_x(\text{CoNi})_{1-x}$ ternary alloy nanoparticles were prepared in solution at 80 °C using $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ as reducing agent. High frequency electromagnetic properties were measured by a vector network analyzer (VNA, Agilent N5230A) using transmission/reflection mode. The paraffin composite specimen with cylindrical shape containing 20 vol. % alloy particles as fillers was prepared for the measurement of EM parameters.¹⁰

Figure 1 shows XRD patterns of the as-prepared samples which are FeCoNi alloy solid solution phase with a mixture of hcp and fcc crystalline structures.⁵ With the increase of Fe content, the diffraction peaks shift to lower angle zone, which is attributed to the distinction of atomic radius among cobalt (1.67 Å), nickel (1.62 Å), and iron (1.72 Å). SEM images reveal that particle size decreases with the enhancement of Fe content. $\text{Fe}_{0.25}(\text{CoNi})_{0.75}$ and $\text{Fe}_{0.20}(\text{CoNi})_{0.80}$ samples have spherical morphology and an average diameter about 180 and 260 nm, respectively. The $\text{Fe}_{0.14}(\text{CoNi})_{0.86}$ sample has a flowerlike morphology and larger particle size with an average diameter about 1 μm . The average grain size was calculated using Debye-Scherrer's formula.^{10,17} The

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FIG. 1. (Color online) XRD patterns of $\text{Fe}_x(\text{CoNi})_{1-x}$ ($x = 0.14, 0.20, 0.25$) ternary alloy nanoparticles.

calculated results show the average grain diameter for $x = 0.14, 0.20, 0.25$ samples is about 17, 14, and 9 nm, respectively. So the $\text{Fe}_x(\text{CoNi})_{1-x}$ ($x = 0.14, 0.20, 0.25$) ternary alloy nanoparticles should be polycrystalline aggregates and consist of nanograins.

The magnetization hysteresis loops at room temperature were measured by a Physical Property Measurement System (PPMS, quantum design), which present typical ferromagnetic behavior. With the increase of Fe content, both coercive force (H_c) and saturation magnetization (M_s) increase correspondingly. $\text{Fe}_x(\text{CoNi})_{1-x}$ ($x = 0.14, 0.20, 0.25$) ternary alloy nanoparticles have $H_c = 48.1, 70.5, 105.5$ Oe and $M_s = 111.0, 122.3, 131.9$ emu/g, respectively. The increase of H_c results from the smaller grain and particle size of the high Fe content sample, which has a larger anisotropy field and weaker magnetic couple between magnetic particles. The enhancement of M_s for iron-rich samples results from the larger atomic magnetic moment of iron than that of nickel and cobalt.

Figure 2(a) shows the real part (ϵ') and imaginary part (ϵ'') of complex permittivity. The real part ϵ' has an continuous decrease tendency with increasing frequency for $x = 0.14$ and 0.20 samples. However, $x = 0.20$ sample possesses smaller decrease extent. On the contrary, the real part ϵ' of the $\text{Fe}_{0.25}(\text{CoNi})_{0.75}$ sample is almost constant ($\epsilon' = 7.6$) in the whole 2–18 GHz range. The imaginary parts ϵ'' for all the $\text{Fe}_x(\text{CoNi})_{1-x}$ ($x = 0.14, 0.20, 0.25$) samples present the same tendency in the 2–18 GHz range, i.e., ϵ'' gradually increases from 0.9, 0.3 and 0.2 to 4.2, 3.9 and 2.4 for $x = 0.14, 0.20$ and 0.25 samples, respectively. As we reported in FeNi_3 alloy sub-microspheres system, the prepared $\text{Fe}_x(\text{CoNi})_{1-x}$ nanoparticles with this method have small size, a large amount of lattice defects, and a slight oxide layer on the particle surface, all of which may result in a high resistivity. The relative low permittivity comes from the high resistivity.¹⁰ In addition, the values of ϵ' decrease with the increase of Fe content, which is consistent with the reported results of Fe–Ni core shell structured nanoparticles and Co–Fe films systems.^{9,18} Compared with low Fe content samples, iron-rich samples have smaller particle and grain size, and consequently, higher resistivity and lower permittivity. Besides, Fe is more easily oxidized than Co and Ni, which may be another reason for the higher resistivity of iron-rich samples. The $\text{Fe}_{0.14}(\text{CoNi})_{0.86}$ sample

FIG. 2. (Color online) Frequency dependence of complex permittivity (a) and permeability (b) of the $\text{Fe}_x(\text{CoNi})_{1-x}$ -paraffin composites.

has a significant dielectric relaxation feature. Real and imaginary parts have reverse tendency, namely, the real part increases and the imaginary decreases with the increasing frequency, meanwhile, ϵ'' shows a resonance peak around 7 GHz.^{19,20} The dielectric relaxation may come from the higher conductivity and special morphology of the $\text{Fe}_{0.14}(\text{CoNi})_{0.86}$ sample. Compared with iron-rich samples, the real and imaginary parts of complex permittivity for the $\text{Fe}_{0.14}(\text{CoNi})_{0.86}$ sample have larger values and fluctuation, which indicate larger dielectric loss.²¹

Figure 2(b) presents the real part (μ') and imaginary part (μ'') of complex permeability. The real part μ' decreases from 2.27, 2.01 and 2.33 to 1.25, 0.99 and 1.02 for the $x = 0.14, 0.20$ and 0.25 samples, respectively. The imaginary part μ'' shows significant broad resonance feature. The resonance peak of $\text{Fe}_{0.14}(\text{CoNi})_{0.86}$ sample locates around 2–8 GHz. For the $x = 0.20, 0.25$ samples, the resonance peak shifts to the higher frequency region of 5–11 GHz, and μ'' values of the $x = 0.25$ sample are larger than that of the $x = 0.20$ sample. The resonance peaks should arise from natural resonance.^{9,10} The iron-rich sample has enhanced natural resonance frequency. According to the natural resonance equation:²²

$$2\pi f_r = \gamma H_a, \quad H_a = 4|K_{\text{eff}}|/3\mu_0 M_s,$$

$$K_{\text{eff}} = K'_v + 6K'_s/d,$$

where f_r is the resonance frequency, γ the gyromagnetic ratio, H_a the surface anisotropic field, K_{eff} the effective anisotropic coefficient, K'_v and K'_s the volume and surface anisotropy energy constants, and d the diameter of nanoparticles. It can be seen that the smaller d , and larger K'_v and K'_s will result in

the enhancement of f_r . In addition, the surface anisotropy K'_s in ferromagnetic nanoparticles originates from broken symmetry at the surface and becomes the main contributor to the effective anisotropy constant K_{eff} .^{9,11} The iron-rich samples with smaller particle and grain size have larger f_r .

The reflection loss (RL) of the $\text{Fe}_x(\text{CoNi})_{1-x}$ -paraffin matrix composites was calculated using transmission line theory.^{23,24} Figure 3 presents the calculated results of the curves for frequency dependence of RL. For the $\text{Fe}_{0.14}(\text{CoNi})_{0.86}$ -paraffin composites, RL values less than -20 dB were obtained in the 3.4–6.7 GHz range with absorber thickness of 2.4–4.2 mm. With the increase of Fe content, the wider frequency bands (RL < -20 dB) were achieved with thinner absorber thickness. For the $\text{Fe}_{0.20}(\text{CoNi})_{0.80}$ -paraffin composite, RL values less than -20 dB were observed in the 5.4–18 GHz range with a thin absorber thickness of 1.2–2.9 mm,

FIG. 3. (Color online) Frequency dependence of RL for the $\text{Fe}_x(\text{CoNi})_{1-x}$ -paraffin composites of (a) $\text{Fe}_{0.14}(\text{CoNi})_{0.86}$, (b) $\text{Fe}_{0.20}(\text{CoNi})_{0.80}$, and (c) $\text{Fe}_{0.25}(\text{CoNi})_{0.75}$ ternary alloy nanoparticles.

and in that of the 6.7–18 GHz range with an absorber thickness of 1.4–2.9 mm for $x = 0.25$ sample. The effective absorption band locates at the C band (4–8 GHz) for the $x = 0.14$ sample, X band (8–12.4 GHz) and K_u band (12.4–18 GHz) for $x = 0.20$ and 0.25 samples. In addition, a maximal reflection loss (RL_{max}) of -49.0 dB was obtained at 4.7 GHz with an absorber thickness of 3.2 mm for $\text{Fe}_{0.14}(\text{CoNi})_{0.86}$ sample. RL_{max} is -58.9 dB at 7.1 GHz with thickness of 2.4 mm for the $\text{Fe}_{0.20}(\text{CoNi})_{0.80}$ sample and that of -59.0 dB at 9.5 GHz with thickness of 2.3 mm for the $\text{Fe}_{0.25}(\text{CoNi})_{0.75}$ sample. It is worth noting that another strong absorption peak with intensity of -56.1 dB was also observed at 16.9 GHz with a thin absorber thickness of 1.6 mm for the $\text{Fe}_{0.25}(\text{CoNi})_{0.75}$ sample. It can be seen that the values of RL_{max} are enhanced and the corresponding frequency shifts to higher frequency region with increasing Fe content. In this paper, RL_{max} is significantly higher than most of the reported ferromagnetic metal micro-particles as filler systems.^{8–12} The significant influence of the filler type on the intensity and location of effective EMA band was investigated in this alloy nanoparticles system. In addition, the absorption band shifts to low frequency range with the increase of absorber thickness; however, the absorption peak intensity does not decrease with that.

In conclusion, $\text{Fe}_x(\text{CoNi})_{1-x}$ ($x = 0.14, 0.20, 0.25$) ternary alloy nanoparticles were prepared with the self-catalyzed reduction method. The electromagnetic parameters were adjusted by the changing of Fe content. With the increase of Fe content, the dielectric loss decreases and magnetic loss increases. Furthermore, a significant influence of Fe content on EMA properties was found. Both the location and intensity of the main absorption band can be adjusted remarkably with the variety of Fe content. The enhanced EMA properties mainly result from improved electromagnetic matching, strong natural resonance, as well as the dielectric relaxation.

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