

Synthesis and Soft Magnetic Properties of Mg-doped Ni Nanoparticles

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Abstract Mg-doped Ni nanoparticles with good soft magnetic properties were prepared with the sol-gel method and were sintered at 400, 500, 600, and 900 °C in argon atmosphere, respectively. The structure and magnetic properties of the samples were studied by means of X-ray diffraction, TEM, and VSM magnetometers. X-Ray powder diffraction results show that Ni-Mg solid solution was formed with the single phase of face-centered cubic(fcc) structure. The particle size became larger with the increase of temperature. When the sintering temperature was 400 °C, the particle size was 6.3 nm, whereas it was 46.2 nm at 900 °C. Both the saturation magnetization(M_s) and the coercivity were enhanced with the increase of the particle size. The M_s values of the samples ranged from 18.965 to 46.766 emu/g and the coercivity ranged from 1051.3568 to 9145.0848 A/m.

Keywords Mg; Ni; Nanoparticles; Soft magnetic property; Sol-gel method

1 Introduction

Nanocrystalline materials have become the focus subject of a large number of studies in recent years from the viewpoint of basic researches and applications. Transition metallic materials such as the ferromagnetic metals Ni, Fe, and Co have been extensively studied because of their applications in catalysis, magnetic fluids, magnetic recording media, biomedical field, and solar energy absorption^[1–4]. In particular, nanostructured Ni particles have important applications in magnetic sensors, memory devices, and biomolecular separation^[5,6]. Owing to these potential applications, nanostructured Ni has attracted considerable attention^[7]. Different nanostructures of Ni nanoparticles have been successfully synthesized *via* various methods, such as pyrolysis, sputtering, reversed micelle, aqueous and nonaqueous chemical reduction, and sonochemical deposition^[8–11]. To further discuss the magnetism of Ni and adjust its magnetic properties, Ni is frequently doped with other elements(e.g., Fe, Co, B). However, Mg has rarely been doped in Ni nanoparticles. Since the ion diameter of Mg is comparable with that of Ni, they form solid

solution easily. The results indicate that compared to Ni nanoparticles, the coercivity of Mg-doped Ni nanoparticles decreased, and the saturation magnetization(M_s) increased. It is expected that the soft magnetic nanoparticles will have several practical applications owing to the low coercivity, such as magnetic fluids^[12] and memory device^[5,12]. Therefore, further investigations are important. In this study, the soft magnetic Mg-doped Ni nanoparticles were fabricated by the sol-gel method and the magnetic properties were also analyzed.

2 Experimental

All the chemical reagents in this study were of analytical grade purity. The initial materials included $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$. $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ with appropriate stoichiometric proportions [$n(\text{Ni}):n(\text{Mg})=0.95:0.05$] were weighed and their solutions were mixed; the mixture was homogenized with stirring for 2 h to form a sol. The mixture was subsequently polymerized to form a gel at 80 °C. The gel was prepyrolyzed to become an amorphous

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composite precursor at 120 °C. In argon atmosphere, the precursor was heated up to 400, 500, 600, and 900 °C, respectively, and then kept at the temperatures for 5 h. After being cooled to room temperature, the samples were obtained.

Structural characterization was performed by XRD on a D/max-2500 copper rotating-anode X-ray diffractometer under Cu $K\alpha$ radiation (40 kV, 200 mA). A transmission electron microscope (TEM, 200 keV, JEM-2100HR, Japan) was used to investigate the morphology. The magnetic properties of the samples were measured at room temperature with a Lake Shore 7407 vibrating sample magnetometer.

3 Results and Discussion

3.1 XRD Characterization

Fig.1 shows the XRD patterns of the samples synthesized at 400, 500, 600, and 900 °C. The peaks are assigned to diffraction from the (111), (200), (220), (311), and (222) planes of *fcc* Ni, respectively, which are completely consistent with the PDF card (No. 87-0712). The analysis results show that all samples

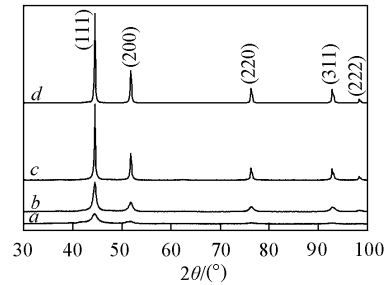


Fig.1 XRD patterns of the samples synthesized at different temperatures

a. 400 °C; b. 500 °C; c. 600 °C; d. 900 °C.

have cubic structure and their space group is $Fm\bar{3}m$. From Fig.1, no characteristic peak of Mg is observed. Thus, we can draw a conclusion that all samples are homogenous solid solutions. The apparent peak broadening shows the continuous reduction of the particle size with the decrease of the synthesis temperature. The grain size is obtained *via* Scherrer formula^[13] (Table 1). The cell constant (a) and the volume of lattice (V_0) are also shown in Table 1. The cracks of peaks occur because the K_α is composed of $K_{\alpha 1}$ and $K_{\alpha 2}$. At wide angle diffraction, the crack becomes clear.

Table 1 Grain sizes, cell constants, volumes of lattice and magnetic properties of heat-treated samples

Sample	Temperature/°C	Grain size/nm	a/nm	V_0/nm^3	$M_s/(\text{emu}\cdot\text{g}^{-1})$	Coercivity/(A·m ⁻¹)
1	400	6.3	0.3498	0.0428	18.965	1051.3568
2	500	10.0	0.3521	0.0436	39.232	2953.3988
3	600	41.3	0.3524	0.0437	44.343	5642.3664
4	900	46.2	0.3526	0.0438	46.766	9145.0848

3.2 TEM Characterization

Fig.2 shows the TEM images of the samples synthesized at 400 and 900 °C, indicating the nano-structured alloy of spherical shape and narrow size distribution. The average particle size was about 6.0 nm for Fig.2(A), and about 40 nm for Fig.2(B), which are in agreement with the results of the XRD.

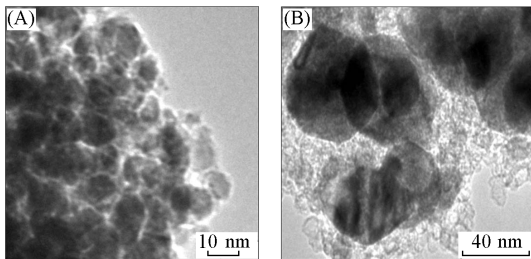


Fig.2 TEM images of the samples synthesized at 400 °C (A) and 900 °C (B)

3.3 Magnetic Properties

Fig.3 shows the hysteresis loops of Mg-doped Ni nanoparticles measured at room temperature for the

samples prepared at 400, 500, 600, and 900 °C. Table 1 shows the coercivity and M_s of our samples synthesized at different temperatures. The values of the coercivity and M_s are 2953.3988 A/m and 39.232 emu/g, respectively, when the grain size is 10 nm; and the values of the coercivity and M_s are 9145.0848 A/m and 46.766 emu/g, respectively, when the grain size is 46.2 nm. The random anisotropy action occurs when the particle size is less than the exchange length^[14], that is, magnetocrystalline anisotropy decreases when the decrease of the particle size is positively proportional to D^6 , where, D is the grain size. When the particle size is similar to the exchange length, the magnetization depends on the magnetocrystalline anisotropy constant K_1 , and the coercivity approaches the maximum. The change of the coercivity is related to the particle size. Du *et al.*^[15] reported that the coercivity decreased with the decrease of particle size when the particle size was smaller than 65 nm; and the samples changed to superparamagnetism under 15 nm. The coercivity of our Mg-doped Ni nanoparticles is

smaller than that of those prepared by Du *et al.*^[15] when the particle sizes are comparable to each other. Aus *et al.*^[16] reported that the coercivity was 3184 A/m when the particle size of Ni was 10 nm. Our result is smaller than 3184 A/m. When the particle size is less than the exchange length, according to the formula, $H_c = P_c K_1^4 D^6 / \mu_0 M_s A^3$, where, P_c is the constant,

K_1 is the anisotropy constant, D is the grain size, μ_0 is the vacuum permeability, and A is the exchange constant, we may probably draw a conclusion that the decrease of coercivity is due to the Mg doping, which may be explained by the decrease of K_1 or by the increase of the exchange constant A ^[15].

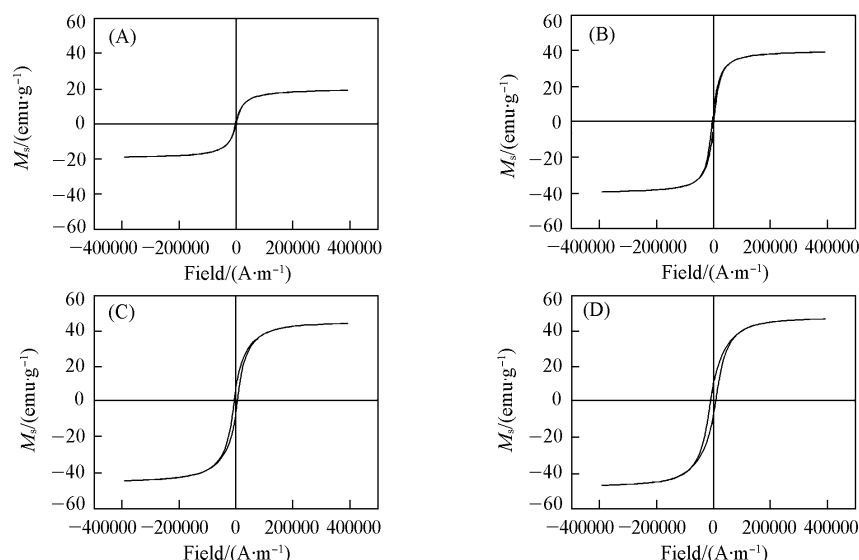


Fig.3 Hysteresis loops of the samples synthesized at different temperatures

(A) 400 °C; (B) 500 °C; (C) 600 °C; (D) 900 °C.

The dependence of the M_s on the particle size is presented in Table 1. It is found that an increase in the particle size is accompanied by an increase in M_s . This is because of the surface effect and the small-scale effect. For nanoparticles, the net magnetic moment decreases because of a high surface-to-volume ratio. Most metallic ions are on the surface. The distortion of lattice on the surface causes the bond distance to change and the bond-angle to deform. Thus, the magnetic moments on the surface of nanoparticles are not colinear; there is spin flip on the surface or the inside. For Mg-doped Ni nanoparticles, the decreased sintering temperature leads to the decrease of the particle size, the increase of the surface-to-volume ratio, and the enhancement of the spin flip on the surface or the inside, and therefore, the M_s decreases. The M_s of all the samples is below that of bulk Ni (54 emu/g). Chen *et al.*^[17] reported that the M_s is 32 emu/g when the particle size is 12 nm for Ni(fcc).

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