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Phase transition and magnetic properties of Mg-doped hexagonal close-packed Ni nanoparticles

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ABSTRACT

Mg-doped Ni nanoparticles with the hexagonal close-packed (hcp) and face-centered cubic (fcc) structure have been synthesized by sol–gel method sintered at different temperatures in argon atmosphere. The sintering temperature played an important role in the control of the crystalline phase and the particle size. The pure hcp Mg-doped Ni nanoparticles with average particle size of 6.0 nm were obtained at 320 °C. The results indicated that the transition from the hcp to the fcc phase occurred in the temperature range between 320 °C and 450 °C. Moreover, the VSM results showed that the hcp Mg-doped Ni nanoparticles had unique ferromagnetic and superparamagnetic behavior. The unsaturation even at 5000 Oe is one of the superparamagnetic characteristics due to the small particle size. From the ZFC and FC curves, the blocking temperature T_B of the hcp sample (6.0 nm) was estimated to be 10 K. The blocking temperature was related to the size of the magnetic particles and the magnetocrystalline anisotropy constant. By theoretical calculation, the deduced particle size was 6.59 nm for hcp Mg-doped Ni nanoparticles which was in agreement with the results of XRD and TEM.

1. Introduction

Due to their small dimensions and large specific surface areas, nanoparticles often exhibit novel material properties that differ considerably from those of the bulk material [1]. In recent years, nanoparticles of ferromagnetic metal such as Fe, Co and Ni attracted more and more interests in terms of their special physical properties and potential applications in catalysts, high-density magnetic recording media, medical diagnostics, ferrofluids, and biomedical fields [2–4]. Among these ferromagnetic metal, Ni nanoparticles were investigated owing to their potential application in magnetic sensors and memory devices [5–7]. Hou et al. developed a facile and chemical reduction route to synthesize size-controlled nickel nanoparticles [8]. Chen et al. prepared nickel nanoparticles from the thermal decomposition of nickel(II) acetylacetonate in alkylamines [9]. Chinnasamy et al. synthesized fcc and hcp Ni nanoparticles in trimethylene glycol by using the fodified polyol process [10]. According to these reports, face-centered cubic (fcc) structure was its equilibrium bulk phase. Another polymorph, the hexagonal close-packed (hcp) structure, was a metastable phase observed mainly in thin films under specific conditions [11,12]. Only a little works was reported on the free-standing hcp nickel because of the difficulties in synthesis, and there were contradicting theoretical reports on the magnetic properties of the hcp Ni nanoparticles obtained by different methods [13].

In this paper, to make the hcp structure more stable and understand the magnetic mechanism of the metastable phase, Mg-doped Ni nanoparticles were synthesized because the equilibrium bulk phase of unalloyed Mg had a hcp structure and the atomic radius of Mg was comparable to that of Ni. By controlling the sintering temperature, we can control the crystalline phase and particle size. Finally, the magnetic properties of the hcp Mg-doped Ni nanoparticles were studied.

2. Experimental details

All chemical reagents in this work were of analytical grade purity. The initial materials included $Ni(NO_3)_2{\cdot}6H_2O$, $Mg(NO_3)_2{\cdot}6H_2O$ and $C_6H_8O_7{\cdot}H_2O$. The appropriate stoichiometric proportions of $Ni(NO_3)_2{\cdot}6H_2O$, $Mg(NO_3)_2{\cdot}6H_2O$ and $C_6H_8O_7{\cdot}H_2O$ were weighed (Ni:Mg = 0.95:0.05, in mol), and their solution were

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mixed, then stirred. The solution was dried at 80 °C to obtain xerogel. After the swelled xerogel was completed at 120 °C, a reticular substance was obtained, and then it was ground to powder in an agate mortar. Sintering the powder at 320 °C, 350 °C, 450 °C, 600 °C and 900 °C, respectively, was carried out under Ar atmosphere for 10 h.

Structural characterization was performed by XRD on D/max-2500 copper rotating-anode X-ray diffractometer by using Cu Kα radiation (40 kV, 200 mA). In situ experiments on the hcp Mg-doped Ni nanoparticles were carried out with a high temperature X-ray diffractometer, and assisted by vacuum extraction. The sample was heated at a rate of 10 °C/min, held at 320 °C, 350 °C, 400 °C, 600 °C and 900 °C for 1 h. The morphology and size distribution were investigated by TEM (200 keV, JEM-2100HR, Japan). The magnetic properties were measured by Magnetic Property Measurement System (Quantum Design MPMS XL-7) and a Lake Shore 7407 vibrating sample magnetometer.

3. Results and discussion

3.1. Structural characterization

Fig. 1 is the XRD pattern of the hcp Mg-doped Ni nanoparticles obtained at 320 °C. It indicates that the pure hcp Mg-doped Ni nanoparticles crystalline phase is formed and no other impurity peaks is observed. Particle size is 6.0 nm estimated by Scherrer formula. Fig. 2 is the HT-XRD patterns for the hcp Mg-doped Ni nanoparticles at Pt underlay, which cannot be completely covered. The patterns are obtained at 320 °C, 350 °C, 450 °C, 600 °C and 900 °C, respectively. The average particle size of the samples obtained at 450 °C, 600 °C and 900 °C are 10 nm, 41.3 nm and 46.2 nm, respectively. When the temperature is 350 °C (Fig. 2b), the diffraction peaks at $2\theta = 44.6°$, 51.8° and 76.3° (attributed to fcc Ni) appear, it indicates that there are both hcp structure and fcc structure in the samples. When the temperature increases to 450 °C (Fig. 2c), the peaks indexing to the hcp structure disappear and only fcc Ni phase is found at this temperature. That is, the phase transition from hcp to fcc is completed when the temperature increases from 320 °C to 450 °C and it is also the transformation from metastable phase to equilibrium bulk phase, and it is higher than the phase transition temperature of Ni [14]. The hcp structure changes into the fcc structure upon the application of sintering, which confirms the metastability of the hcp structure at room temperature. Moreover, note that the metastable hcp structure does not spontaneously decay into the stable fcc structure at room temperature unless the hcp Mg-doped Ni nanoparticles are heated. And then further increase the temperature, the peaks become sharper and the intensity becomes stronger because of the growth of the crystal particles.

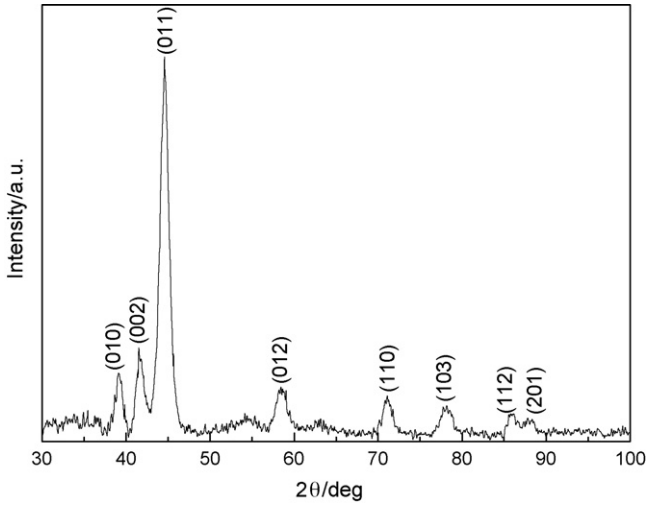

Fig. 1. XRD pattern for the sample synthesized at 320 °C.

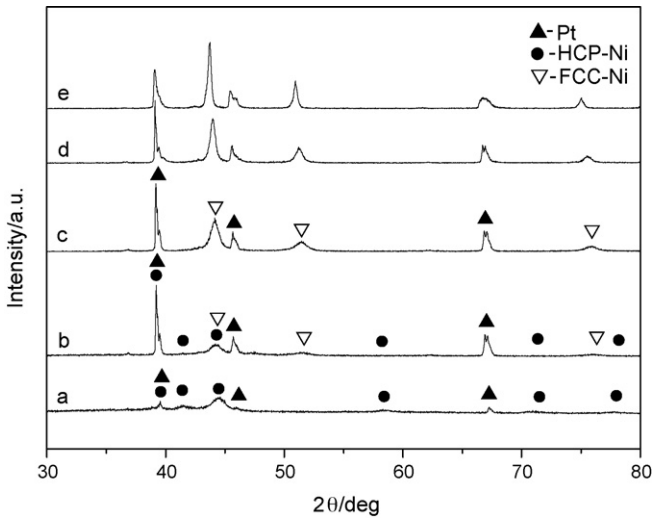

Fig. 2. HT-XRD patterns of hcp Mg-doped Ni nanoparticles 320 °C (a), 350 °C (b), 450 °C (c), 600 °C (d) and 900 °C (e).

Fig. 3 shows the TEM image of the samples synthesized at 320 °C, 450 °C, 600 °C and 900 °C. It can be seen that the sample has spherical shape and narrow size distribution. The average particle size is about 6.0 nm for Fig. 3a, about 10 nm for Fig. 3b, about 41 nm for Fig. 3c and about 46 nm for Fig. 3d, in agreement with the calculated values by Scherrer formula.

3.2. Magnetic characterization

Fig. 4 is the hysteresis loops of the hcp Mg-doped Ni nanoparticles obtained at 320 °C and measured at room temperature. The hcp Mg-doped Ni nanoparticles have a coercivity of 32.906 Oe and are not saturated in the maximum field of 5000 Oe. This results show that the hcp Mg-doped Ni nanoparticles have unique ferromagnetic and superparamagnetic behavior. The magnetic properties can be understood in terms of the particle size distribution. It is known that the samples have ferromagnetic behavior when the particle size is bigger than the critical size, while superparamagnetic behavior occurs when the particle size is smaller than it. The unsaturation even at 5000 Oe is one of the superparamagnetic characteristics due to the small particle size. The magnetization of the particles may become unstable due to thermally activated fluctuations when the particle size is reduced to several nanometres. In this case, superparamagnetic behavior occurs. The hcp Mg-doped Ni nanoparticles with larger particle size show ferromagnetic behavior. This ferromagnetic behavior is similar to Mi et al. [12]. However, the magnetization and coercivity of our sample are smaller than the results reported by Mi et al. [12]. Such behaviour is most likely the outcome of surface effects. Because from the TEM, we know that the sample is spherical shape, to make the energy reach the minimum, the spin is in vortex state, which results in the decrease of both magnetization and coercivity. Similar situation has already been observed in the $CoFe_2O_4$ system in the same size range [15].

The temperature-dependent magnetization (M–T) of the hcp Mg-doped Ni nanoparticles was measured under zero-field-cooled (ZFC) and 100 Oe field-cooled (FC) conditions (Fig. 5). The ZFC curve agrees with FC curve very well along the high temperature side, and

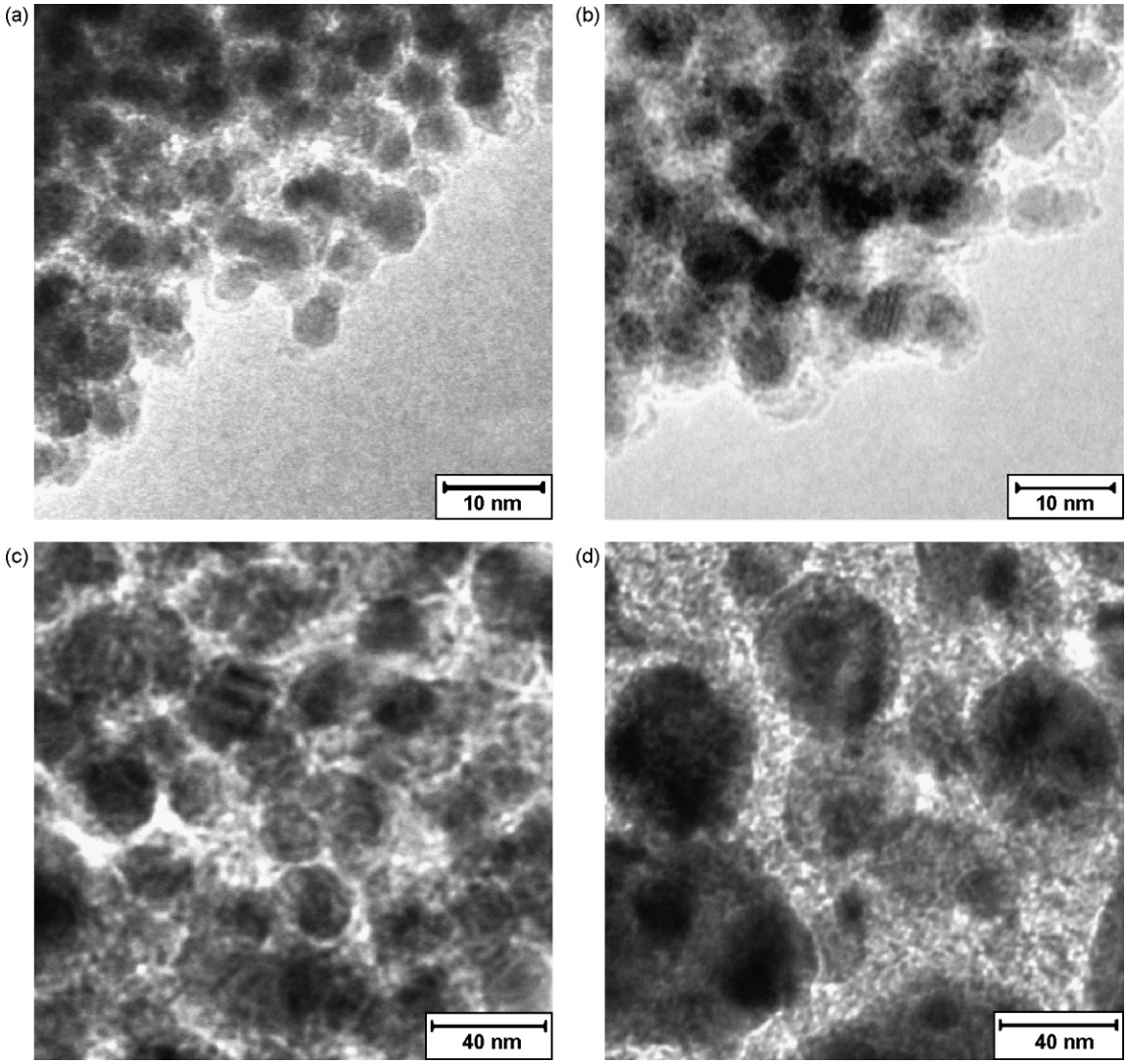

Fig. 3. TEM image of samples synthesized at 320 °C (a), 450 °C (b), 600 °C (c) and 900 °C (d).

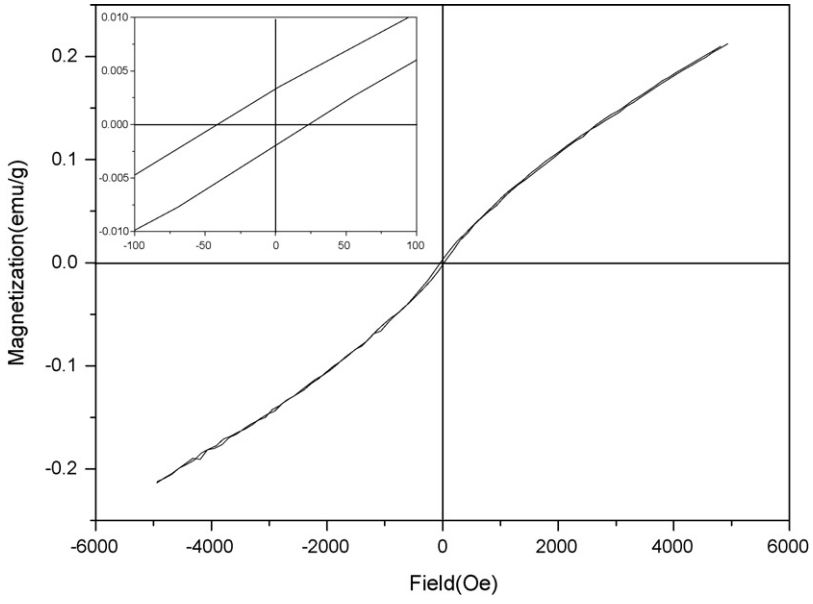

Fig. 4. Hysteresis loops of hcp Mg-doped Ni nanoparticles measured at room temperature.

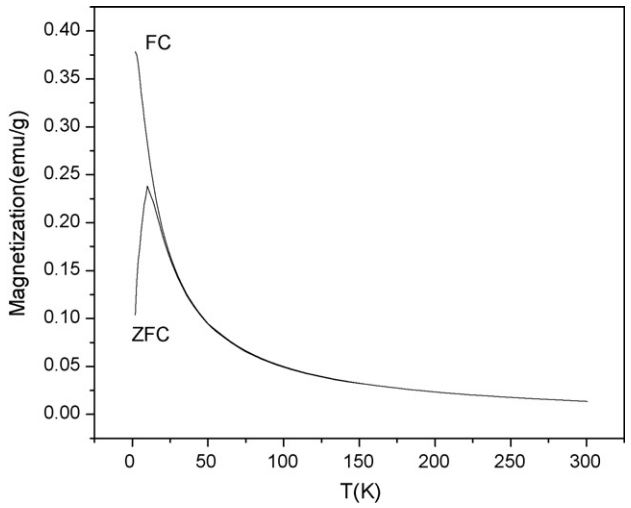

Fig. 5. Zero-field-cooled (ZFC) and field-cooled (FC) curves of hcp Mg-doped Ni Nan particles.

the deviation happens below 25 K. A sharp peak corresponding to the blocking temperature (T_B) is observed at around 10 K. The observed behavior reveals the progressive blocking of the superparamagnetic particle moments, with a distribution of relaxation time to the size and anisotropy axis direction. There is a small dependence of T values on the particle size [16]. That is T_B generally increases with increasing particle size. The T_B value of our sample is 10 K, and others report that the T_B is 12 K for the sample with 13.2 nm, 12.5 K for the sample with 25 nm [17].

In the FC curve, the magnetization continues to increase below the peak temperature T_B without a tendency towards saturation, showing superparamagnetic particles in the hcp Mg-doped Ni nanoparticles, not spin-glass or spin-canting [18]. It leads to the result that the temperature dependence of the low-field magnetization depends on the type of anisotropy energy barrier for an assembly of non-interacting magnetic nanoparticles. Above the blocking temperature, the magnetizations in both of the ZFC and FC curves of the hcp Mg-doped Ni nanoparticles begin to decrease and reach a value close to zero. The blocking temperature is related to the size of the magnetic particles and the magnetocrystalline anisotropy constant (K) by the equation $K = 25k_BT_B/V$, where k_B and V are the Boltzmann constant and the volume of a single particle, respectively, and T_B is the blocking temperature. For hcp Mg-doped Ni nanoparticles with the blocking temperature of 10 K, if K value (2.3×10^5 erg cm^{-3}) is substituted in the equation and the particles are sphere, the deduced particle size is 6.59 nm, which is in agreement with the results of XRD and TEM [19].

4. Conclusion

The synthesis of Mg-doped Ni nanoparticles with hcp and fcc structure by sol–gel method was reported. The transition from the hcp to the fcc phase occurred in the temperature range between 320 °C and 450 °C. The hcp Mg-doped Ni nanoparticles had unique ferromagnetic and superparamagnetic behavior from the M–H curves. The ZFC and FC curves showed the blocking temperature (T_B) was around 10 K for the hcp Mg-doped Ni nanoparticles with particle size 6 nm. The theoretical calculation value for superparamagnetic critical size was in agreement with the results of XRD and TEM.

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