Phys. Status Solidi A **207**, No. 2, 360–363 (2010) / **DOI** 10.1002/pssa.200925175

physica status solidi a
www.pss-a.com
applications and materials science

Research on nickel morphology of dependence on the microwave-assisted polyol method

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Received 9 April 2009, revised 15 September 2009, accepted 16 September 2009

PACS 75.20.En, 75.50.Cc, 75.60.–d, 75.75.+a, 81.07.Bc

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The structures, morphology and magnetic properties of the ultrafine Ni nanoparticles prepared by microwave-assisted polyol method was investigated, using X-ray diffraction (XRD), transmission electron microscopy (TEM) and vibrating sample magnetometer (VSM), respectively. The XRD results suggested that Ni nanoparticles with an fcc structure were successfully synthesized. It was interesting to note that the Ni nanoparticles are ideally spherical, which were examined by the TEM. As immersed in different solutions, we can get different shape nickel particles with different conditions. Especially, the experimental results indicated that nanohair nickel particles were ferromagnetic.

1 Introduction Nanoscale particles of ferromagnetic metals, such as Fe, Co and Ni has gained wide-spread interests in recent years, due to their unique physical properties and potential applications in diverse areas, such as magnetic recording media, sensors and catalysts. A considerable amount of work has been done in the last decade on various nanoparticles systems [1], such as metal particles, transition metal oxides, Ni ferrite [2] and transition metal-boron alloys, such as Fe–Ni–B and Co–Ni–B [3]. The transition metal oxide systems Fe–FeO, Co–CoO and transition metal insulator systems [4] were studied as well, such as Fe, Co, or Ni dispersed in SiO_2 or Al_2O_3 [5]. Ni nanoparticles addressed much attention over the past decades because of their excellent magnetic properties, which enable them to be applied in the magnetic sensors, memory devices and biomolecular separations [6]. Nickel was widely used in many fields such as catalysis [7], fuel cell electrodes [8] and magnetic storage media [9]. Recently, many researches on core–shell nanostructures of nickel particles, nanoparticles of carbon and palladium encapsulated with Ni nanoparticles used in catalysis [10] and nickel–nickel oxide complex structures used for high density magnetic recording due to the magnetic exchange coupling between the ferromagnetic material (Ni) with the antiferromagnetic material (NiO) [11].

Till now, nickel nanoparticles can be fabricated by a variety of physical and chemical methods including ultrasound irradiation, evaporation technique [12], ultrasonic spray pyrolysis, chemical reduction [13–16], electrochemical technique and polyol method [17, 18]. It was demonstrated that the size, morphology and crystallinity of the nickel particles were critical for their properties and applications. Therefore, shape-controlled synthesis of metallic structures has been a subject of intensive research in recent years. In this paper, the microwave-assisted polyol method was employed to fabricate the monodispersed nickel particles with different shapes including cube, microspheres and nanohairs under different reaction conditions. The effects of surfactant concentration, the temperature and reaction time were discussed. The magnetism of the nickel powders with different morphologies was also investigated.

2 Experimental The starting material was a solution of nickel (II) acetate tetrahydrate (99.998%, Aldrich Chemical Co.) in ethylene glycol (>99%, Bio Lab Ltd.) or triethylene glycol (TREG) (>99%, Bio Lab Ltd.). Following the previously described process [19], a 100 ml glass flask was placed in a microwave oven (Spectra, 900W) and connected to a condenser. In view of nanoscale nickel agglomeration [20], so-called surfactants or dispersants with polyvinylpyrrolidone (PVP, average molecular weight 40 000, Sigma Chemicals) had to be added. Before the reaction, 50 ml of a solution of 0.100–0.250 M $Ni(Ac)_2$ in ethylene glycol (or TREG) was purged by argon for 30 min, then the microwave oven was turned on at the power level of 50–100% with a continued flow of the gas. The reaction was stopped as soon as the black suspension appeared, and immediately cooled in ice water. The resulting solid product was washed thoroughly with ethanol and centrifuged. All these processes were repeated six times. The nickel particles were dried under vacuum and kept in a glove box.

The powder X-ray diffraction (XRD) patterns were collected on a Bruker AXSD* Advanced Powder X-ray diffractometer (using Cu Kα radiation $\lambda = 0.15418$ nm). The particle morphology and nature of Ni were studied by transmission electron microscopy (TEM) employing a JEOL-JEM 100 SX microscope working at 100 kV. After a sonication bath for 20 min in absolute ethanol, samples for TEM were prepared by placing a drop of the sample suspension on a copper grid (400 meshes, Electron Microscopy Sciences) coated with carbon film. Magnetic measurements at room temperature were conducted using an Oxford Instrument, vibrating sample magnetometer (VSM).

3 Results and discussion

3.1 Morphology and structural characterization by TEM

In order to reveal the morphology and structure of Ni nanoparticles, the TEM experiment was performed for the sample prepared under a solution of 0.250 M $Ni(Ac)_2$ in TREG. A typical TEM image of the Ni sample is shown in Fig. 1a, which shows Ni grains of a polygon structure with the grain sizes in the range of 500–800 nm. The particle morphology is very similar to that given in literature [18]. Its growth process was usually attributed to the Ostwald ripening. The formation of quasi-spherical clusters in the TREG solution must result from an even quicker aggregation during both nucleating and growing stage at the boiling temperature (285 °C).

The conventional polyol method was previously used to prepare metallic nickel particles, but the particles of the corresponding reaction under microwave radiation were slightly large and rather uniform. During the current experiments in a solution of 0.100 M $Ni(Ac)_2$ in ethylene glycol, some PVP were added (4 g PVP). It is found that the nickel particles have roughly particles about 10 nm in diameter and a few particles are connected together. It is clear to see that the size and morphology of nickel particles in Fig. 1b are different from that in Fig. 1a. We found that a suitable amount of PVP is needed to stabilize the nanoscale cluster produced during the microwave-assisted reaction and prevent the agglomeration. It indicates that the average particle size of the sample obtained with the addition of the surfactant is relatively smaller than that without the addition of the surfactant. It can be thought that the surfactant has two essential effects: the absorption and the decrease of surface tension, and the colloid effect. Therefore, the surfactant molecules coat the nickel particles to prevent the single particle from growing and several particles from coming together in ethylene glycol solution added adequate PVP.

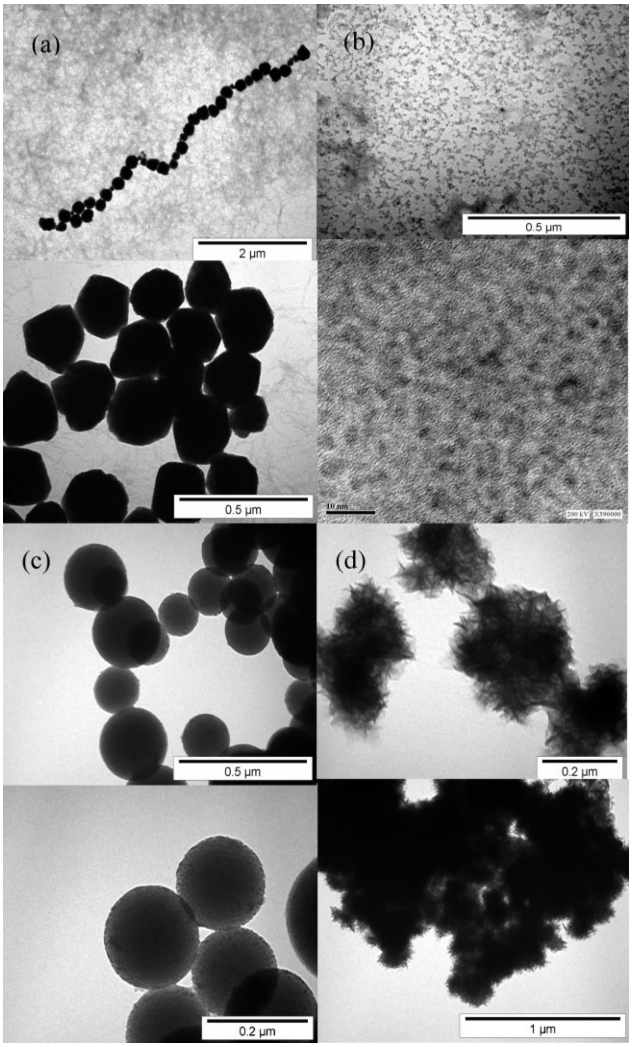

Figure 1 TEM images of samples with two photos for each sample: (a) Ni particles (800 nm) in TREG at the power level of 100% of the microwave oven; (b) Ni particles (10 nm) in ethylene glycol with 4 g PVP, HRTEM is given at the bottom; (c) Ni (spherical) in TREG at the power level of 70% of the microwave oven; and (d) Ni (nanohairs) in ethylene glycol at the power level of 75% of the microwave oven.

The morphology of the particles was further revealed by TEM measurements. These particles are synthesized in a solution of nickel (II) acetate tetrahydrate (99.998%, Aldrich Chemical Co.) in TREG (>99%, Bio Lab Ltd.). Before the reaction, 50 ml of a solution of 0.100 M $Ni(Ac)_2$ in TREG was purged by argon for 20 min, after which the microwave oven was turned on at a power level of 70% with a continued flow of the gas. The reaction was stopped as soon as a black suspension appeared which was immediately cooled in ice water. The resulting solid product was washed thoroughly with ethanol and centrifuged. TEM demonstrated that the morphology of Ni nanoparticles is predominantly ideally

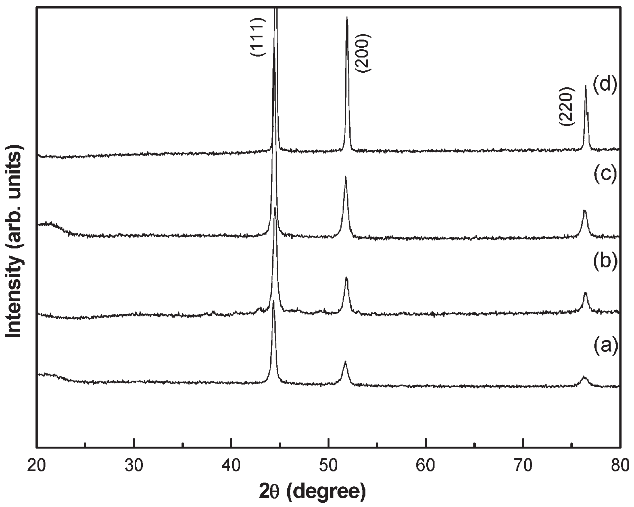

Figure 2 X-ray powder diffraction pattern of the samples: (a) Ni polygon particles (100 nm), (b) Ni particles (10 nm), (c) Ni (spherical), and (d) Ni (nanohairs).

spherical with smooth surfaces and uniform size. Figure 1c presents a magnified TEM image.

Some hairy zones in the Ni nanoparticles, the monomorphic and uniform hair-like Ni nanoparticles, can be detected for a solution of 0.200 M $Ni(Ac)_2$ in ethylene glycol at the power level of 75% of the microwave oven. Furthermore, with increasing the temperature, the addition of a little amount of PVP (1 g) was beneficial to the formation of hair-like Ni nanoparticles with a small diameter and narrower distribution, shown in Fig. 1d. This indicates that the as-synthesized Ni nanohairs were actual monodispersive self-organization by hundreds of smaller primary nanolines, which can be regarded as a secondary nanostructure. This self-organization should be ascribed to the mutual attraction of magnetic forces, and with the synthesis time increased, the collision and coalescence rates of Ni nucleus would get higher.

3.2 Structural characterization by XRD Figure 2 shows the XRD patterns for the precipitated powder at different reaction conditions. The position of the diffraction peaks matches closely the reported JCPDS (4-850) data. In Fig. 2, all the peaks at different angles are from fcc Ni(111), (200) and (220). This indicates that the single phase fcc Ni is successfully synthesized by the microwave-assisted polyol method.

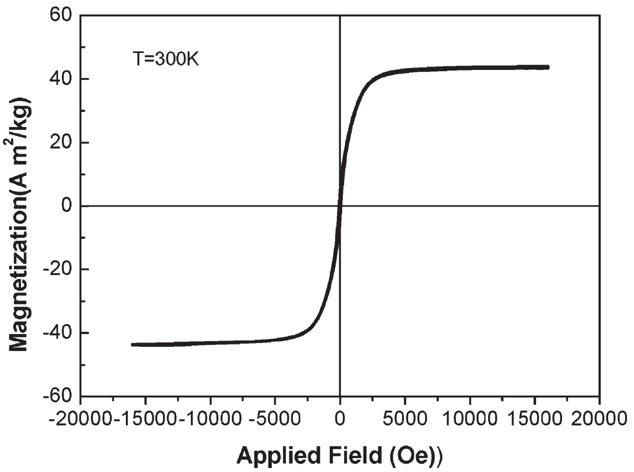

Figure 3 The magnetic hysteresis loops of polygon nickel particles by VSM at room temperature.

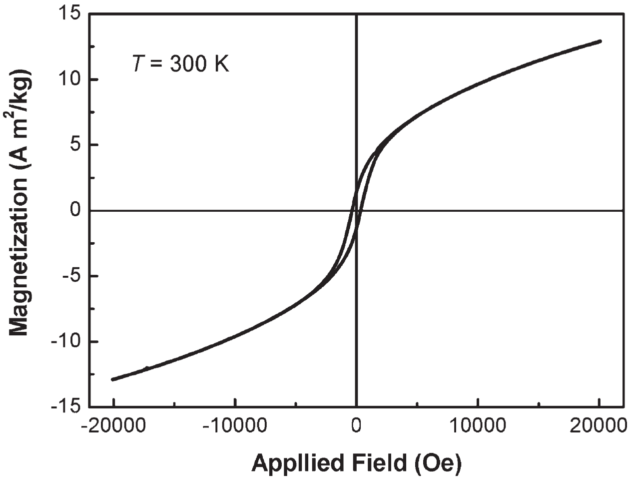

Figure 4 The magnetic hysteresis loops of Ni nanohairs by VSM at room temperature.

3.3 Magnetic properties In order to get more insight into the nature of the as-prepared samples, the magnetic state of the as-prepared samples has been checked at room temperature, measured by VSM in Figs. 3 and 4. It is worth noting that the Ni nanohairs at 300 K are ferromagnetic as shown in Fig. 4. The magnetic hysteresis loops of Ni nanohairs are given with the coercivity $H_c = 335$ Oe and saturation magnetization $\sigma_s = 12.9$ A m^2/kg. By comparison with the results of the coercivity $H_c = 110$ Oe and saturation magnetization $\sigma_s = 44.5$ A m^2/kg in Fig. 3, it is found that the coercivity is higher than that of the polygon structure (110 Oe). It can be thought that the interaction between particles would decrease the coercivity. However, the *M*–*H* hysteresis loop of the nanohair samples shows that it is not a saturation magnetization curve absolutely under the applied field with 20 000 Oe. Our results indicate that the magnetic hysteresis loops of the spherical nickel particles shown in Fig. 1c is very similar to that in Fig. 3 and the coercivity H_c and saturation magnetization σ_s is not obviously different. For the sample in Fig. 1b, we cannot get the magnetic hysteresis loop in exact definition because it is only a superparamagnetic curve.

4 Conclusions Our experiment shows that the single phase fcc Ni by XRD is successfully synthesized by the microwave-assisted polyol method. Under different reaction conditions, we can get different shape nickel particles by TEM such as polygon, microsphere, hair, etc. The concentration of PVP played the key role in the formation of the novel structure in ethylene glycol or TREG solution. Especially, the experimental results indicate that nanohair nickel particles are ferromagnetic.

Acknowledgements This work was supported by the National Natural Science Foundation of China under Grant No. 50672001.

References

[1] J. L. Dorman, D. Fiorani, and E. Tronc, Adv. Chem. Phys. **98**, 283 (1997).

[2] R. H. Kodama, A. E. Berkowitz, E. J. Mcniff, Jr., and S. Foner, Phys. Rev. Lett. **77**, 394 (1996).

[3] E. D. Biasi, C. A. Ramos, R. D. Zysler, and H. Romero, Phys. Rev. B **65**, 144416 (2002).

[4] F. Bodker, S. Morup, S. W. Charles, S. Linderoth, and J. Magn, Magn. Mater. **18**, 196 (1999).

[5] T. Sekino, T. Nakajima, and K. Niihara, Mater. Lett. **29**, 165 (1996).

[6] Y. Mi, D. Yuan, Y. Liu, J. Zhang, and Y. Xiao, Mater. Chem. Phys. **89**, 359 (2005).

[7] S. Sato, A. Kawabata, M. Nihei, and Y. Awano, Chem. Phys. Lett. **382**, 361 (2003).

[8] M. Saitou and R. Hashiguchi, J. Phys. Chem. B **107**, 9404 (2003).

[9] A. G. Boudjahem, S. Monteverdi, M. Mercy, D. Ghanbaja, and M. M. Bettahar, Catal. Lett. **84**, 115 (2002).

[10] X. C. Sun and X. L. Dong, Mater. Res. Bull. **37**, 991 (2002).

[11] H. Meiklejohn and C. P. Bean, Phys. Rev. **102**, 1413 (1956).

[12] Y. D. Yao, Y. Y. Chen, M. F. Tai, D. H. Wang, and H. M. Lin, Mater. Sci. Eng. A **217**, 281 (1996).

[13] Y. L. Hou and S. Gao, J. Mater. Chem. **13**, 1510 (2003).

[14] L. Bai, F. Yuan, and Q. Tang, Mater. Lett. **62**, 2267 (2008).

[15] D. Wang, D. Sun, H. Yu, Z. Qiu, and H. Meng, Mater. Chem. Phys. **113**, 227 (2009).

[16] K. H. Kim, Y. B. Lee, S. G. Lee, H. Park, and S. S. Park, Mater. Sci. Eng. A **381**, 337 (2004).

[17] S. I. Nikitenko, Y. Koltypin, O. Palchik, I. Felner, X. N. Xu, and A. Gedanken, Angew. Chem. Int. Ed. **40**, 4447 (2001).

[18] L. Bai, J. Fan, Y. Cao, F. Yuan, A. Zuo, and Q. Tang, J. Cryst. Growth **311**, 2474 (2009).

[19] B. Vaidhyanathan and K. J. Rao, Chem. Mater. **9**, 11969 (1997).

[20] K. S. Suslick, M. M. Fang, and T. Hyeon, J. Am. Chem. Soc. **118**, 11960 (1996).