Front. Chem. China 2008, 3(2): 157–160
DOI 10.1007/s11458-008-0030-3

RESEARCH ARTICLE

Jie GONG, Yang LIU, Lili WANG, Jinghai YANG, Zhanguo ZONG

Preparation and characterization of hexagonal close-packed Ni nanoparticles

Abstract Hexagonal close-packed Ni nanoparticles were synthesized using a heat-treating technique with the precursors prepared by the sol-gel method. The synthesis condition, structure, and morphology of the samples were characterized and analysed by thermogravimetric analysis (TG), differential thermal analysis (DTA), X-ray diffraction (XRD) and transmission electron microscopy (TEM). Results indicate that the hexagonal close packed Ni nanoparticles were synthesized at a heat-treating temperature of 300°C. The cell constants are calculated at $a = 0.2652$ nm and $c = 0.4334$ nm. The average grain size of the hexagonal close-packed Ni particles evaluated by Scherrer equation is about 12 nm. The phase transformation from a hexagonal close-packed Ni to a face-centered cubic Ni structure occurred when the heat-treating temperature was increased.

Keywords sol-gel, Ni nanoparticles, hexagonal close packed (hcp), phase transformation

1 Introduction

Nanostructured Ni particles have received much attention over the past decades because of their excellent magnetic properties, which make them suitable for applications ranging from magnetic sensors and memory devices to biomolecular separations [1–7]. Natural Ni crystallizes into a face-centered cubic (fcc) structure with ferromagnetic properties [8–13]. Studies of the magnetic properties of hexagonal close-packed (hcp) Ni nanoparticles, however, are rare due to the difficulties in synthesizing hcp Ni. Recently, the synthesis and characterization of nanocrystalline hcp Ni have been attracting widespread attention because of their unique magnetic properties and improved performances by their particle sizes, crystal structures and inter-particle interaction [14–16]. Nanosized Ni can be fabricated by a variety of physical and chemical methods including pyrolysis, sputtering, reversed micelles, aqueous and nonaqueous chemical reduction, sonochemical deposition, and polyol [17–20]. Mi et al. [14], Chinnasamy et al. [17], and Jeon et al. [18] successfully synthesized pure fcc Ni nanoparticles, hcp Ni nanoparticles and a mixture of fcc and hcp Ni nanoparticles in different organic solvents using a chemical reduction method under free-standing conditions. But the conditions for synthesizing single-phase hcp Ni are rigorous and difficult to control. Meanwhile, the magnetic properties are different with different synthetic methods. There exists continuing debate on the magnetic properties of hcp Ni nanoparticles. Also, there are only a few detailed reports on the preparation of hcp Ni nanoparticles using sol-gel method with citrate.

In this study, pure fcc and hcp Ni nanoparticles with Ni $(NO_3)_2$ and citrate ($C_6H_8O_6$) were synthesized by the sol-gel method and the heat-treating technique. This method is rather simple and it is easy to obtain high-quality metal and alloy powders of controlled structure, morphology, size and size distribution. The phase transition and the relationship between the structures for the obtained nanocrystalline Ni particles were explored.

2 Experimental

2.1 Reagents and instruments

$Ni(NO_3)_2$ and citrate ($C_6H_8O_6$) were A.R. reagents, and ultrapure water was used. The thermal behavior of the samples was measured by thermogravimetric analysis and differential thermal analysis (PE TG-DTA 6300, 5°C/min, A.R., USA). The crystal structure of the synthesized particles was characterized by X-ray diffraction

Translated from *Chemical Journal of Chinese Universities*, 2007, 28(7): 1232–1234 [译自: 高等学校化学学报]

Jie GONG (✉), Lili WANG, Jinghai YANG
Institute of Applied Physics, Changchun University, Changchun 130022, China
E-mail: ccdxgj@163.com

Jie GONG, Yang LIU, Zhanguo ZONG
Physical College, Jilin Normal University, Siping 136000, China

(XRD) with Cu Kα radiation using a current of 200 mA and voltage of 40 kV, step length of 0.02° and residence time of 0.2 s (D/max-2500/PC, Japan). The morphology of the grains decomposed ultrasonically, which was supported by Cu grids, was analyzed by a transmission electron microscope with voltage of 200 keV (TEM, JEM-2100HR, Japan).

2.2 Experimental process

Firstly, the solutions of $Ni(NO_3)_2$ and citrate ($C_6H_8O_6$) with a certain ratio were mixed at 50°C to prepare the sol. Then the sol was heated to form a gel at 80°C. With a further heating at 120°C, the precursors of dry gel was obtained. Finally, the Ni nanoparticles were successfully synthesized with the precursors heat-treated in argon atmosphere for 5 h at different temperatures.

3 Results and discussion

Figure 1 shows the TG-DTA curve for precursor samples in argon atmosphere. The endothermic process with about 30% weight loss appears from 80°C to 130°C, which corresponds with the release process of adsorbed gas and water. Weight loss along with a longer exothermic process appears from 160°C to 265°C, which corresponds with the decomposition of the nitrate radical based on the experimental phenomenon of the release of brown gas in the heat-treatment process. In the course of the exothermic process corresponding to the weight loss from 305°C to 375°C, the curve includes two exothermic parts centering on 325°C and 355°C, respectively. Based on the weight loss and heat exchange, it can be deduced that the exothermic process corresponds to that of the citric nickel decomposition to Ni, H_2O, CO and CO_2. The exothermic part centering on 325°C corresponds with the formation of hcp Ni because of the decomposition of citrate and the exothermic part centering on 355°C corresponds with the decomposition of residual citrate. This is because the decomposition of the precursor in the vicinity of 355°C is efficient to generate a lot of heat and heighten the local temperature. It indicates the phase transformation from the metastable hcp Ni obtained in the vicinity of 325°C to fcc Ni and the release of a certain amount of heat at the same time. This process is confirmed with the analysis of XRD. Owing to the influence of the heating rate of the thermal process, the previous process has a certain degree of temperature lag. Therefore, to obtain single-phase hcp Ni, a more prolonged heat treatment is necessary below 325°C. In the decomposition process, the precursor can generate a lot of CO and CO_2, which can prevent Ni from oxidation. Thus, it is unnecessary to use a shield gas with this method to obtain a great deal of nickel or other metal nanoparticles.

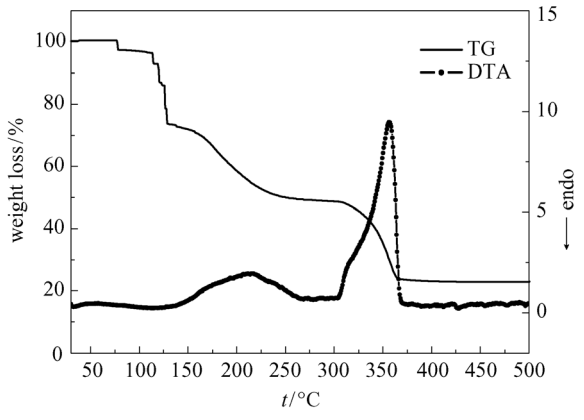

Fig. 1 TG-DTA curves for precursors

Figure 2 shows the XRD pattern of the sample heat-treated for 5 h at 300°C in argon (99.999%) atmosphere. In Fig. 2, all the peaks at different angles are from hcp Ni (010), (002), (011), (012), (110), (103), (112) and (201). This indicates that the single-phase hcp Ni is successfully synthesized at a heat-treating temperature of 300°C, which is further confirmed by TEM analysis. This result corresponds with the XRD patterns of hcp Ni reported by Jeon et al. [18]. No other phase was observed. The calculated cell parameters are $a = 0.2652$ nm and $c = 0.4334$ nm. The average grain size of the hcp Ni particles is evaluated to be 12 nm by Scherrer equation. This implies that the hcp Ni particles obtained are nanocrystalline.

In order to further reveal the morphology and structure of Ni nanoparticles, TEM observation was carried out for the sample heat-treated at 300°C. The typical bright-field (BF) TEM image and ED patterns of the Ni sample prepared with citrate at a heat-treating temperature of 300°C are shown in Fig. 3. Figure 3(a) shows Ni grains of spheric shape with an average grain size of 12 nm. This indicates that the Ni particles synthesized are nanocrystalline. The detailed analysis of the diffraction rings of ED

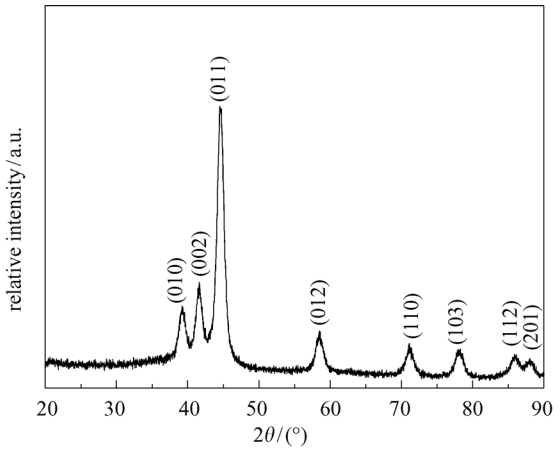

Fig. 2 XRD pattern for the samples heat-treated for 5 h at 300°C with precursor in Ar atmosphere

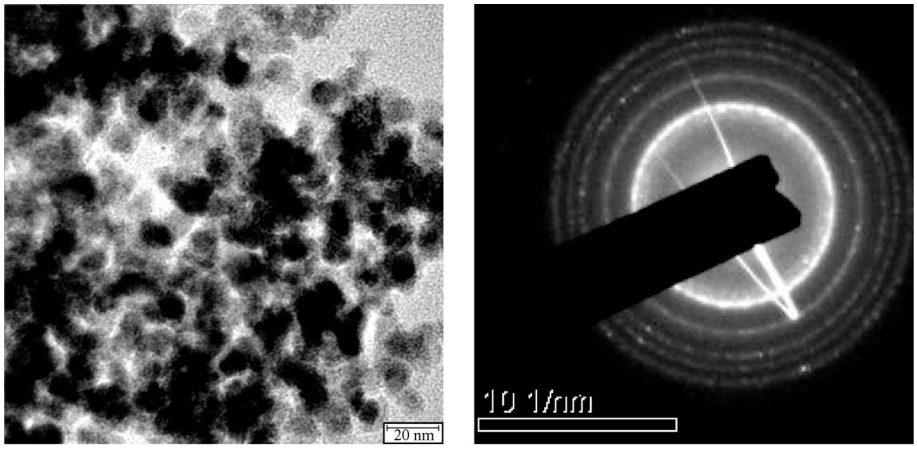

Fig. 3 TEM images and electron diffraction patterns of nanocrystalline Ni synthesized at 300°C

patterns in Fig. 3(b) reveals that the sample indeed has a hexagonal close-packed structure.

Figure 4 shows the XRD patterns of the sample with precursors heat-treated for 5 h at different temperatures of 350°C and 400°C, respectively, in argon (99.999%) atmosphere. When the heat-treating temperature further increases to 350°C, the diffraction peaks in Fig. 4 appear at $2\theta = 44.6°$, 51.8° and 76.3°, which are attributable to fcc Ni (111), (200) and (220), suggesting a mixture of hcp and fcc Ni in the samples. The average grain sizes are about 14 nm and 15 nm, respectively. When the heat-treating temperature increases to 400°C, the intensity of fcc Ni (111) peak increases significantly. Only one fcc Ni phase is found at this temperature. The average grain size of the fcc Ni particles is calculated to be 19 nm by Scherrer equation. The calculated cell parameters are $a = 0.3528$ nm.

The synthesis condition, structure and morphology of the samples were characterized and analyzed by thermogravimetric analysis (TG), differential thermal analysis (DTA), X-ray diffraction (XRD) and transmission electron microscopy (TEM). Results indicated that single-phase hcp Ni nanoparticles of good dispersion and uniform distribution were successfully synthesized by sol-get method at a heat-treating temperature of 300°C. At a heat-treating temperature of 400°C, single-phase fcc Ni nanoparticles can be obtained.

This method is rather simple and feasible. It is unnecessary to add the protection of gas in preparing a large number of metal nanoparticles, because CO gas with reducing power will be given off during the process of sintering the precursors and the oxidation problem could be effectively solved. This method can not only be used to prepare Ni nanoparticles, but can also be used to prepare other metal nanoparticles, such as those of Fe and Co. By adjusting the heat-treating time and temperature, the size of nanoparticles can be controlled in a certain range.

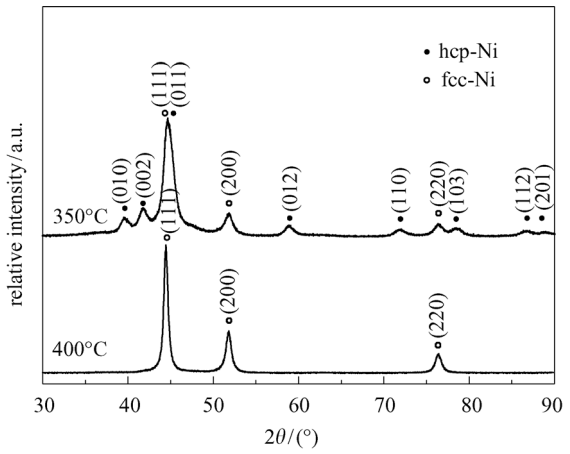

Fig. 4 XRD patterns for the samples heat-treated at 350°C and 400°C with precursors

Acknowledgements The authors gratefully appreciated the financial support given by the Technology Programming Foundation of Jilin Province (Grant No.20050415).

References

1. Wang Z K, Kuok M H, Ng S C, Lockwood D, Cottam M G, Nielsch K, Wehrspohn R B, Gösele U. Spin-wave quantization in ferromagnetic Nickel nanowires. Phys Rev Lett. 2002, 89(2): 027201-1–027206-3
2. Sun L, Searson P C, Chien C L. Magnetic anisotropy in prismatic nickel nanowires. Appl Phys Lett. 2001, 79(26): 4429–4431
3. S Pignard, G Goglio, A Radulescu, L Piraux, S Dubois, A Declémy, J L Duvail. Study of the magnetization reversal in individual nickel nanowires. J Appl Phys, 2000, 87(2): 824–829
4. Hinotsu T, Jeyadevan B, Chinnasamy C N, Shinoda K, Tohji K. Size and structure control of magnetic nanoparticles by using a modified polyol process. J Appl Phys. 2004, 95(11): 7477–7479
5. Guo G Y, Wang H H. Gradient-corrected density functional calculation of elastic constants of Fe, Co and Ni in bcc, fcc and hcp Structures. Chin J Phys. 2000, 38(5): 949–961
6. Tzitzios V, Basina G, Gjoka M, Alexandrakis V, Georgakilas V, Niarchos D, Boukos N, Petridis D. Chemical synthesis and

characterization of hcp Ni nanoparticles. Nanotechnology. 2006, 17(15): 3750–3755
7. Bonder M J, Kirkpatric E M K, Martin T, Kim S J, Rieke R D, Diandra L. Leslie-Pelecky. Grain size effects on the magnetic properties of chemically synthesized Ni:Ni_3C nanocomposites. J Mag Mag Mater. 2000, 222(1–2): 70–78
8. Papaconstantopoulos D A, Fry J L, Brener N E. Ferromagnetism in hexagonal-close-packed elements. Phys Rev B. 1989, 39(4): 2526–2528
9. Zach M P, Penner R M. Nanocrystalline Nickel Nanoparticles. Adv Mater. 2000, 12(12): 878–883
10. Host J J, Block J A, Parvin K, Dravid V P, Alpers J L, Sezen T, LaDuca R. Effect of annealing on the structure and magnetic properties of graphite encapsulated nickel and cobalt nanocrystals, 1998, 83(2): 793–801
11. Rakhimov R R, Jackson E M, Hwang J S, Prokof'ev A I, Alexandrov I A, Karmilov A Y, Aleksandrov A I. Mechanochemical synthesis of Co, Ni, Fe nanoparticles in polymer matrices. J Appl Phys, 2004, 95(11): 7133–7135
12. Jiao Jun, Seraphin Supapan, Wang Xikun, Withers James C. Preparation and properties of ferromagnetic carbon-coated Fe, Co, and Ni nanoparticles. J Appl Phys, 1996, 80(1): 103–108
13. Estournés C, Lutz T, Happich J, Quaranta T, Wissler P, Guille J L. Nickel nanoparticles in silica gel: Preparation and magnetic properties. J Mag Mag Mater, 1997, 173(1–2): 83–92
14. Mi Yuanzhu, Yuan Dingsheng, Liu Yingliang, Zhang Jingxian, Xiao Yong. Synthesis of hexagonal close-packed nanocrystalline nickel by a thermal reduction process. Mater Chem Phys, 2005, 89(2–3): 359–361
15. Sun L, Searson P C, Chien C L. Magnetic anisotropy in prismatic nickel nanowires. Appl Phys Lett, 2001, 79(26): 4429–4431
16. Pignard S, Goglio G, Radulescu A, Pirau L X, Dubois S, Declémy A, Duvail J L. Study of the magnetization reversal in individual nickel nanowires. J Appl Phys, 2000, 87(2): 824–829
17. Chinnasamy C N, Jeyadevan B, Shinoda K, Tohji K, Narayanasamy A, Sato K, Hisano S. Synthesis and magnetic properties of face-centered-cubic and hexagonal-close-packed Ni nanoparticles through polyol process. J Appl Phys, 2005, 97(10): 309 1–3
18. Jeon Yoon Tae, Moon Je Yong, Lee Gang Ho, Park Jeunghee, Chang Yongmin. Comparison of the magnetic properties of metastable hexagonal close-packed Ni nanoparticles with those of the stable face-centered cubic Ni nanoparticles. J Phys Chem B, 2006, 110(3): 1187–1191
19. Chow G M, Ding J, Zhang J, Lee K Y, Surani D, Lawrence S H. Magnetic and hardness properties of nanostructured Ni–Co films deposited by a nonaqueous electroless method. Appl Phys Lett, 1999, 74(13): 1889–1891
20. Laidani N, Calliari L, Speranza G, Micheli V, Galvanetto E. Mechanical and structural properties of Ni–C films obtained by RF sputtering. Surf Coat Tech, 1998, 100–101: 116–124