Nanostructured Ni Powder Synthesized from Non-aqueous Bath

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ABSTRACT

Dendritic nickel agglomerates composed of nickel nanoparticles have been synthesized through one-step electro-deposition using $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ as precursor and ethanol as solvent. Analytical results by X-ray diffraction (XRD) and selected area electron diffraction (SEAD) indicate that the as-prepared products belong to face-centered cubic structure of nickel nanoparticles with high purity. Morphological observation reveals that the deposits are mainly dendritic containing nanoparticles. The magnetic properties of deposits have also been measured at room temperature and the results show that the saturation magnetization increases and the coercivity decreases as increasing the $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ concentration.

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1. Introduction

Magnetic nickel nanoparticles are of significant interest to researchers owing to their potential applications as active components in the areas of catalysis, magnetic recording, biomedical and environmental engineering, and nickel-metal hydride batteries^{1–3} etc. Up to now, there are a variety of techniques used to produce Ni nanoparticles, such as chemical reduction,⁴ hydrothermal reduction,^{5,6} thermal decomposition of organometals,^{7,8} emulsion technique^{9,10} and so forth. Generally, most of those wet-chemical methods require the use of highly toxic organometals or reducing agents, which could bring in toxic gases or impurities or a high processes temperature etc., against the development trend of green chemistry and chemical processes. In 1996, Koltypin et al. reported amorphous Ni powder about 10 nm synthesized by sonolysis from nickel tetracarbonyl solution in decane,¹¹ illustrating that nickel powder can be obtained even without reducing agent. Jović et al. prepared nickel powder with cauliflower and spongy shapes by electro-deposition from NiCl_2 aqueous solution.¹² Falong Jia et al. first reported the synthesis of nanoporous Ni particles by ultrasonic electrochemistry in non-aqueous system.¹³ However, few reports can be found about the synthesis of nickel powder from non-aqueous system of inorganic nickel salt (such as NiCl_2). Compared to water, reducing organic solvents can be used as reducing agent and eliminating the electrode reaction and gas evolution as well. They are also preferred due to good chemical stability.¹⁴ Meanwhile, the use of inorganic salt would not bring in toxic gas such as CO and organometallic compounds. In this article, the dendritic nickel particles have been synthesized from non-aqueous system by electrochemical method. Ethanol was used as the solvent because of its non-toxic and NiCl_2 has relatively high solubility in it. The influences of the initial concentration of nickel salt on the crystal texture, morphology and magnetism of powders have been investigated.

2. Experimental

Pure Ti and Pt were used as the cathode and anode respectively because of their strong chemic inertia. Before electro-deposition,

the electrodes were ultrasonically cleaned in acetone, ethanol and deionized water sequentially to remove contamination from the surface. The deposition process was conducted in an additive-free ethanol bath without agitation with a $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ concentration ranging from 6 g/L to 12 g/L due to the fact that pure organic media helps to avoid the formation of nickel oxide or hydroxide or agglomerate.¹⁵ Based on our extensive experiments, the applied pulse potential, duty cycle, and frequency were kept at 40 V, 40%, and 4 kHz, respectively. The electrolyte temperature is $\sim 30^\circ\text{C}$. Because of the poor conductivity of ethanol solution, the pulse dc voltage is much higher than the recovery potential of Ni in aqueous solution. After 6 h, the black precipitates were taken out and washed in pure ethanol for five times before air dry.

The surface morphology of the deposits was observed by employing a scanning electron microscope (SEM, Zeiss Supra55 (VP)). Microstructure was analyzed by X-ray diffraction used a standard XRD θ - 2θ measurement in the range $2\theta = 20^\circ$ – 100° with $\text{CuK}\alpha$ radiation. The size and morphology of the particles were further characterized by transmission electron microscopy (TEM) on Tecnai G220 S-Twin, operating at 200 kV. The nanoparticles were dispersed in ethanol by ultrasonic treatment and then dropped onto a carbon-coated copper grid for TEM analysis. The magnetic property of the particles was measured using a vibrating sample magnetometer (VSM, JDM-13) at room temperature.

3. Results and Discussion

3.1 Results and analysis

Figure 1 shows the XRD patterns of the deposits synthesized at various concentrations of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$. In all diffraction patterns there are five distinctive peaks located at around 44.6° , 51.9° , 76.5° , 93.0° and 98.5° . These peaks are respectively assigned to (111), (200), (220), (311) and (222) reflections of face-centered cubic (FCC) nickel, which is well consistent with the standard card (JCPDS No. 87-712). The XRD diffraction peaks are relatively broad, indicating the nanocrystalline nature of the products. As shown in Table 1, subtle changes can also be observed in the ratios of relative intensity of peaks with the increase of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ concentration from 6 g/L to 12 g/L. The ratio of (111) lattice plane

Figure 1. X-ray diffraction patterns of the samples prepared at various concentrations of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$: (a) 6 g/L, (b) 7.5 g/L, (c) 9 g/L, (d) 10.5 g/L, and (e) 12 g/L.

Table 1. The relative intensity of corresponding peak.

Initial concentration of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (g/L)	(111)	(200)	(220)	(311)	(222)
6.0	0.6227	0.1831	0.0859	0.0890	0.0193
7.5	0.6146	0.1770	0.0916	0.0922	0.0246
9.0	0.6124	0.1849	0.0974	0.0753	0.0300
10.5	0.5811	0.2069	0.0994	0.0918	0.0209
12.0	0.5734	0.2058	0.1061	0.0894	0.0252

Figure 2. Average grain size of deposits from different concentration ranges of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$.

decreases about 7.9%, while that of (200) and (220) lattice planes increase about 12.4% and 23.5%, respectively. Since intensity of peak is related to the degree of orientation, therefore, it can be concluded that the orientation degree of (111) lattice plane decreases while that of (200) and (220) lattice planes increase with the increase of the nickel ion concentration. No other peaks of impurities such as nickel oxide could be detected, proving the feasibility and reliability of preparation for the single-phased Ni crystallite with a high purity by the new method with a simple one-step electro-deposition.

In addition, it is found that the average grain sizes calculated according to the Scherrer equation increase from ~ 15 nm to ~ 50 nm with the increase of the initial concentration of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ from 6 g/L to 12 g/L, as shown in Fig. 2. This result could be explained by the nucleation rate, the growth speed and Ostwald ripening

Figure 3. SEM images of deposits prepared at $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ concentrations of (a) 6 g/L, (b) 7.5 g/L, (c) 9 g/L, and (d) 10.5 g/L.

Figure 4. (a) Low-magnification TEM image of Ni dendrite, inset shows the corresponding selected-area electron diffraction (SAED) pattern; (b) HRTEM image.

theory.¹⁶ Both nucleation and growth speed increase at higher $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ concentration. Compared to aqueous bath, it is harder for Ni ions to diffuse under a certain voltage in ethanol due to its dielectric constant and higher viscosity than water. Plus the concentration of Ni salt is quite low (for aqueous electro-deposition, Ni salt concentration is usually ~ 250 g/L). The growth speed of nuclei, determined by Ni ions diffusion, would be more sensitive to concentration than nucleation speed. Moreover, for pulsed electrochemical deposition, an Ostwald-like ripening process is likely to occur during the pauses, leading to small crystal dissolution and re-deposition on larger crystals. All of these make the grain size larger at higher concentration.

Typical SEM images are shown in Fig. 3. Irregular nanoparticle aggregations coexisted with some undeveloped dendrite-like structures are observed at low concentration (6 g/L). As the content of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in the electrolyte increases, the irregular aggregations gradually develop into separate dendrite microstructures. When the $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ concentration is 10.5 g/L, nickel dendrites become the dominant product. Dendritic fractals similar to pine-trees are a type of hyperbranched structure, various parts of which generally possess different size distributions in each specimen. This multi-scale dendritic structure might make the nanomaterials exhibit superior performance to other nanomaterials in many fields such as microelectronics, catalysis, medicine and electromagnetism.^{17–19}

Ultra-fine structure of the sample (gained from solution with a concentration of 7.5 g/L) was further investigated by TEM and selected area electron diffraction (SAED). It is clear that the branch of a single dendrite consists of many nano-grains ranging from about 20 nm to 80 nm (Fig. 4a). The concentric ring structure in the SAED pattern could be indexed to the (111), (200), (220) and (311) planes of FCC Ni, which clearly verifies the polycrystalline characteristics. Further structural information can be obtained from

Figure 5. FT-IR spectra of the samples synthesized from $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ solution in ethanol and water system.

the high resolution TEM (HRTEM) image shown in Fig. 4b. The spacing of 2.059 Å between adjacent lattice planes corresponds to interplanar (111) distance of FCC Ni (2.03 Å).

3.2 Reaction mechanism

To the best of our knowledge, the synthesis and the corresponding reaction mechanism of Ni powder by electro-deposition from non-aqueous baths are rarely reported. To understand the difference of reaction mechanism between the synthesis of Ni powder from traditional aqueous and this non-aqueous bath, infrared measurements were performed on dry Ni powder samples synthesized with the same condition except for solution system. The sample A was obtained from ethanol solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and B from aqueous solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$. In the infrared spectra in Fig. 5a, O-H stretching vibration absorption broad peak locates at the wavenumber of 3400–3000 cm^{-1} , and a broadened peak between 3000 and 2940 cm^{-1} is attributed to the stretching vibration peak of C-H. The peak centered at 1456 cm^{-1} and 1352 cm^{-1} attributes to symmetric and asymmetric bending vibration of methyl, respectively. Hence we deduced that C and H in Ni particles came from alcohol solvent. It can be also seen from Fig. 5a that there are three weak absorption peaks at 1608 cm^{-1} , 1456 cm^{-1} and 1352 cm^{-1} . They are in good agreement with the standard peaks of NiCl_2 , which indicates that the synthesized Ni particles may also adsorb a small amount of NiCl_2 molecular. In Fig. 5b, a broad and strong absorption peak of 3650–3000 cm^{-1} is caused by stretching vibration of water molecules. The absorption peaks located at 1633 cm^{-1} , 1446 cm^{-1} and 1383 cm^{-1} match with the standard spectrum of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ molecular well. This suggests that the Ni particles synthesized from aqueous solution contain $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and H_2O molecular.

According to the infrared spectra analysis, we can infer that the reaction mechanism in aqueous and ethanol solution is quite different. In ethanol bath, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ is firstly dehydrated before the redox, then NiCl_2 is ionized and Ni ions are adhered to Ni nuclei, which is surrounded by ethanol molecules:

Combined with the reaction product (Ni powder and air bubbles), H_2O discharges on the anode while Ni^{2+} and 2H^+ gain electrons to be reduced on the cathode. The reaction during the electro-deposition could be formulated as:

Figure 6. Magnetic properties of the deposits. a) M-H hysteresis loops of deposits and b) the relationship between the remanence ratio (M_r/M_s) and the initial concentration of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$.

We also think $\text{CH}_3\text{CH}_2\text{OH}$ involves in the discharging process due to the fact that the amount of H_2O is quite small while $\text{CH}_3\text{CH}_2\text{OH}$ molecules are all around and there is few difference between their O-H band dissociation energy. However, there is no absorption peak around 1715 cm^{-1} indicating the existence of C=O, which may produce in electrolysis of ethanol as reported by Zhang.²⁰ Therefore, ethanol may involve in the electrochemical reaction without forming C=O and other new bonds. It can be described as:

Ethanol atmosphere and its involvement in the reaction hinder the discharge of H_2O and OH, protecting Ni particles from oxidation to some extent.

3.3 Magnetism

The magnetic behavior of deposits is examined on a Vibrating Sample Magnetometer. Figure 6a presents the M-H hysteresis loops measured at room temperature and Fig. 6b shows the relationship between the remanence ratio (M_r/M_s) and the initial concentration of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$. As can be seen in Fig. 6a, the saturation magnetization (M_s) values of all the samples are lower than that of the pure FCC Ni in bulk form ($\sim 55 \text{ emu/g}$, 300 K), and gradually increase with the increasing of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ initial concentration. It is well known that both number and size of domains play a major role in magnetic properties. Nano Ni has much smaller particle size and then larger surface area. Surface spin disorder would markedly reduce the total magnetic moment, resulting in the decline of the M_s values in comparison with bulk counterparts.^{21,22} This can also be validated indirectly by the variation trend of the average grain diameter and the M_s with the initial concentration of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, as shown in Fig. 3 and Fig. 6a, respectively. In addition, as the FT-IR data shows, the solution adsorbed on the surface of the Ni

nanoparticles could not be removed completely in post treatment process. The exchange coupling effect among the Ni nanoparticles will be reduced due to the isolation effect of the nonmagnetic matter. Meanwhile, the sample exhibits an enhanced coercivity (ie: H_c) value (239 Oe) compared to that of bulk Ni (0.7 Oe)²³ or that of hollow nickel sub-micro spheres (32.3 Oe),⁹ hollow Ni nanospheres (102 Oe)¹⁰ and dandelion-like Ni nanostructures (130.3 Oe)²⁴ at room temperature. Earlier studies in the magnetic nanosystems have shown that the effective anisotropy re-ins the coercivity,^{25,26} which might explain why dendrite Ni possesses much higher coercivity. However, it should be also noticed that the measured value is still lower than that of one-dimensional Ni nanorods (ca. 332 Oe)²⁷ or nanobelts (ca. 640 Oe)²² which has extremely high anisotropy. Generally speaking, the remanent magnetization (M_r) and coercivity value decrease slightly while M_s value increases a little when the concentration of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ increased from 6 g/L to 12 g/L. This change may be related to grain size, degree of orientation of lattice planes and surface morphology. The remanence ratio (M_r/M_s) can reflect the quality of the soft magnetic properties. A rapidly decrease in remanence ratio, as can be seen in Fig. 6b, indicates that the deposits possess good soft magnetic properties with the increase of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ concentration.

4. Conclusions

In summary, we have developed a simple and environmentally benign method for nickel nanoparticle synthesis. The experiments were conducted in a non-aqueous medium and pure FCC nickel particles have been obtained. The products are mainly dendritic shape and each dendrite consists of fine nanograins. The deposit is ferromagnetic and possesses a high coercivity value. The average grain size, degree of orientation of lattice planes, the surface morphology and magnetic properties of synthesized Ni powders are strongly affected by the concentration of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$.

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