THE EFFECT OF ULTRASOUND IRRADIATION ON THE MORPHOLOGY OF NI POWDER SYNTHESIZED BY ELECTRODEPOSITION

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ABSTRACT

Nickel powder has found important applications in magnetic materials, hydrogen storage cells, corrosion resistant paints etc., due to its desirable properties. The most conventional method to produce Ni powder is electrodeposition from aqueous solutions. The major disadvantage of this method is its low efficiency due to hydrogen evolution at the cathode. In the first part of this study, nickel powder was synthesized by electrolysis from sulphate solutions and the effect of electrolyte composition was investigated on the current efficiency. In the second part, the influence of ultrasound irradiation on the morphology of electrodeposited nickel powders under optimum conditions was investigated by means X-ray diffraction analysis and scanning electron microscopy. It was shown that applying ultrasound irradiation lead to nano-scale refinement of the grain size. Also, increasing the ultrasound power results in a lower current efficiency, particularly for low-nickel electrolytes.

Keywords: Electrolytic deposition, nickel electrolyte, sonoelectrochemistry, acoustic cavitation, nanostructured powder..

1. INTRODUCTION

Having desirable chemical and metallurgical properties, nickel has found significant applications in various industries including production of alkaline batteries, as catalyst for chemical industries, production of Invar alloy, as pigment for manufacturing corrosion resistant paints, etc. Due to magnetic properties of nickel powder, it has also some applications in the production of magnetic materials. Nickel could be produced by electrolysis of its aqueous solutions at high cathodic polarization conditions such as for Fe and Co. This method leads to deposits of fine crystals which have higher hardness than molten or annealed nickel samples.

According to Căluşaru, in the case of electrodeposition of Ni powder, two general electrolytes, acidic and ammonia electrolytes, have been studied. Fedorova electrodeposited the adhesive dendritic nickel deposits from 20-40% NiSO₄ solution at 80-90 °C temperature and 30-100 A/dm² current density. The grinding of the obtained material was difficult due to its high hardness. Generally, it is revealed that increasing current density and ionic concentration of Ni reduced the powder refinement. Loshkarev et al. obtained 99.5-99.8% purity Ni powder by electrodeposition in the range of limiting current at 30-35 °C temperature range and pH value of 4. Their electrolyte consisted of 10, 20 and 40 g/L of NiSO₄.7H₂O, (NH₄)₂SO₄ and NaCl, respectively [1].

Recently, Jović and his co-workers [2-4] have found that in ammoniacal solutions, pH reduction leads to significant decrease of the current efficiency and more than 3.4% increase in energy consumption due to the elevated H^+ concentration and H_2 evolution. Agrawal et al. [5] obtained electrodeposited Ni powder from sulphate solution which was consisting of ammonium sulfate, boric acid and thio-urea. The current efficiency was relatively low (39-44%).

Sonoelectrochemistry has been found many applications as a new method to obtain fine particles. Jiang et al. [6] has been produced spherical monodisperse silver nanoparticles through a pulsed sonoelectrochemical method. Jia et al. [7] investigated the effect of ultrasound radiation on the production of Ni and Zn nanopowders from chloride solutions. They showed that ultrasound irradiation could lead to the formation of nanoporous particles and suggested a possible mechanism for that. Other researchers have been applied this new method to production of metallic nanoparticles [8-12]. However, there is a lack of information about the effect of ultrasound parameters on the morphology and size of the produced metallic powders.

In this paper, the optimum condition for electrodeposition of Ni powder from sulfate solution was investigated and the effect of ultrasound power was examined on the characteristics of the Ni powder.

2. EXPERIMENTAL

2.1. Materials

The starting electrolyte was prepared by dissolving the required amounts of a commercial $NiSO_4.7H_2O$ (97% purity) and pure $(NH_4)_2SO_4$ and H_3BO_3 powders (both from Merck, Germany) in distilled water.

2.2. Experiments

In the first stage of this study, various electrolyte solutions having different concentrations of NiSO₄.7H₂O (5-20 g/L), H₃BO₃ (5-15 g/L) and $(NH_4)_2SO_4$ (10-30 g/L) were used for production of Ni powder by the ordinary electrochemical manner. The volume of the solution was 250 mL. The cathode was cylindrical titanium (20 mm in diameter) which was sealed from its side by an insulator material and the anode was a lead sheet fixed in parallel to the end of the cathode . The cathodic current density and time duration were 0.5 A/cm² and 15 min for all tests, respectively. The precipitated powder was filtered after each test, rinsed by distilled water and dried in the air. The electric energy was supplied by a rectifier which provided direct current in the range of 0-20 A.

In the second stage, ultrasound irradiation was applied to produce Ni powder from two types of solutions which contained 5 and 20 g/L Ni, 10 g/L H_3BO_3 and 30 g/L $(NH_4)_2SO_4$ under different powers of 75, 100 and 150 W. The ultrasound power supply equipment was MPI-Power Ultrasonic (20 kHz, 600 W).

A schematic of the experimental setup is shown in Figure 1.



Figure 1. Schematic desing of experimental setup.

The obtained Ni powders were characterized by JOEL JDX-8030 X-ray diffractometere and VEGA II TESCAN scanning electron microscope.

3. RESULTS AND DISCUSSION

3.1. Evalution of current efficiency (CE)

Figures 2-4 show the effect of concentration of various electrolyte components on the current efficiency (CE) of the Ni electrodeposition. According to Figure 2, by increasing Ni concentration in the electrolyte, current efficiency is increased. Generally, two parallel cathodic reactions as follow could be happened during nickel electrodeposition from acidic solutions:

$$Ni^{2+} + 2e^{-} \rightarrow Ni$$

$$(1)$$

$$2H^{+} + 2e^{-} \rightarrow H_{2}$$

$$(2)$$

Increasing Ni^{2+} concentration, enhances the kinetics of reaction (1). As a result, nickel reduction precedes the competing hydrogen reduction and the current efficiency would be increased. However, by increasing the Ni concentration from 10 to 20 g/L, the obtained nickel particles tend to be coarse and flake like.

Figure 3 shows the current efficiency as a function of boric acid concentration. As it could be seen, increasing the acid boric concentration from 5 to 10 g/L, slightly increases the current efficiency. However, a further increase of boric acid to 15 g/L diminishes the current efficiency, probabely due to encouraging hydrogen evolution at the cathode supported by the increased H+ ions in the electrolyte.



Figure 2. The effect of Ni concentration on the current efficiency of Ni powder electrodeposited from the 10 g/L H₃BO₃ and 30 g/L (NH₄)₂SO₄ electrolytes.



Figure 3. The effect of H₃BO₃ concentration on the current efficiency of Ni powder electrodeposited from the 5 g/L Ni and 30 g/L (NH₄)₂SO₄ electrolytes.

Figure 4 illustrates the effect of the $(NH_4)_2SO_4$ content on the CE of the electrodepostion process. The ammonium sulfate acting as a buffer, maintains the pH of solution in the slightly acidic range and enhances the current efficiency. On the other hand, high concentrations of ammonium sulphate increases the possibility of formation of brownish lead sulphate at the anode surface due to the increased generation of SO_4^{2-} ions in the electrolyte, and consequently a reduced current efficiency. The CE value tend to be almost unchanged at higher concentrations of $(NH_4)_2SO_4$ as a result of acting of these two opposing effects.



Figure 4. The effect of $(NH_4)_2SO_4$ concentration on the current efficiency of Ni powders electrodeposited from the 5 g/L Ni and 10 g/L H₃BO₃ electrolytes.

The effect of ultrasound power on the sonoelectrodeposition of nickel powder is exhibited in Figure 5. As shown, ultrasound irradiation leads to a significant current efficiency enhancement, particularly at lower nickel concentrations and moderate power. The increase is likely due to the agitation of the solution under sonication, which may lead to a better mass transfer of ions. However, a powerful ultrasound reduces the CE value, probably as a result of declining the chance for nickel ions to be reduced on the cathode surface.



Figure 5. The effect of ultrasound power on the current efficiency of Ni powder electrodeposited from the 5 and 20 g/L Ni, 10 g/L H₃BO₃ and 30 g/L (NH₄)₂SO₄ electrolytes.

3.2. Microstructural analysis

Figure 6 shows the X-ray diffraction pattern of a typical electrodeposited powder. Three major peaks is clearly distinguished on this pattern, which belong to Ni.



Figure 6. X-ray diffraction pattern of obtained Ni powder.

Furthermore, the grain size of the obtained Ni powders were estimated by using XRD profile analysis and the Scherrer formula:

(3)

$$D = \frac{0.9\lambda}{B\cos\theta}$$

where D is the grain size (nm), λ is the Cu_{Ka} wavelength (0.1541 nm), B is the full width of the maximum intensity peak (radian) and θ is the Bragg's angle. The results are summarized in Table 1. As it could be seen, the average grain size which was calculated through this manner is about 50 and 20 nm for electrodepisited and sonoelechtrodeposited samples, respectively. The result confirms that, ultrasound irradiation could lead to a significant refining of the microstructure compared to the ordinary electrodeposition.

Table 1. Average grain size of the electrodeposited Ni powders

Type of electrodeposition	Average grain size (nm)
Ordinary	50
Ultrasound assisted	20

SEM images of the synthesized powders are also shown in Figure 7. It is illustrated that the ordinary electrodeposited powders without sonication have primarily denritic and cauliflower shapes, while those obtained under ultrasonic irradiation are mainly irregular. Moreover, SEM images confirm the refined nanostructure of the ultrasonically electrodeposited samples, which was suggested by the Scherrer equation.



Figure 7. SEM images of the Ni powder which is electrodeposited under non-irradiatied (*a* and *b*) and ultrasound irradiation condition (*c* and *d*).

4. CONCLUSIONS

In the present paper, production of Ni powders by electrolytic deposition from sulphate solutions both with and without ultrasonic irradiation was investigated. The main findings of the research can be concluded as follows:

1. Increasing Ni content in the electrolyte leads to a significant increased current efficiency of the process, while H_3BO_3 and $(NH_4)_2SO_4$ concentrations would have a moderate effect on the current efficiency.

2. The morphology of the ultrasonic-assited electrodeposited powder was found to be irregular compared to the denritic- and cauliflower-shaped particles obtained by ordinary electrodeposition.

3. Ultrasonic irradiation has a considerable refining effect on the microstructure of the electrodeposited powders; it was possible to produce powders having an average grain size of about 20 nm.

REFERENCES

- 1. A. Călușaru, "Electrodeposition of Metal Powders", Elsevier, New York, 1979.
- V.D. Jović, B.M. Jović, V. Maksimović, M.G. Pavlović, Electrochimica Acta, Vol. 52, 2007, pp. 4254-4263.
- V.D. Jović, V. Maksimović, M.G. Pavlović, K.I. Popov, Journal of Solid State Electrochemistry, Vol. 10, 2006, pp. 373-379.
- 4. V.D. Jović, B.M. Jović, M.G. Pavlović, Electrochimica Acta, Vol. 51, 2006, pp. 5468-5477.
- A. Agrawal, D. Bagchi, S. Kumari, V. Kumar, B.D. Pandey, Powder Technology, Vol. 177, 2007, pp. 133-139.
- 6. L.P. Jiang, A.N. Wang, Y. Zhao, J.R. Zhang, J.J. Zhu, Inorganic Chemistry Communications, Vol. 7, 2004, pp. 506-509.
- 7. F. Jia, Y. Hu, Y. Tang, L. Zhang, Powder Technology, Vol. 176, 2007, pp. 130-136.
- 8. J. Zhu, S. Liu, O. Palchik, Y. Koltypin, A. Gedanken, Lamguir, Vol. 16, 2000, pp. 6396-6399.
- 9. I. Haas, S. Shanmugam, A. Gedanken, Chemistry a European Journal, Vol. 14, 2008, pp. 4696-4703.
- J.J. Zhe, Q.F, Qiu, H. Wang, J.R. Zhang, J.M. Zhu, Z.Q. Chen, Inorganic Chemistry Communications, Vol. 5, 2002, pp. 242-244.
- 11. H. Lei, Y.J. Tang, J.J. Wei, J. Li, X.B. Li, H.L. Shi, Ultrasonics Sonochemistry, Vol. 14, 2007, pp. 81-83.
- 12. A. Aqil, H. Serwas, J.L. Delplancke, R. Jerome, C. Jerome, L. Canet, Ultrasonics Sonochemistry, Vol. 15, 2008, pp. 1055-1061.