

Study on thermodynamics and oxidation mechanism of ethylene glycol in the preparation of nanometer nickel powders

Jin Shengming^{*}, Yuan Liangsheng, Zhou Ying,
Qiu Guanzhou^{*}, Wan Cuifeng

*Department of Inorganic Materials, School of Resources Processing and Bioengineering,
Peace Building, Central South University, Changsha, Hunan 410083, People's Republic of China*

Received 20 October 2005; received in revised form 21 March 2006; accepted 29 March 2006

Available online 21 April 2006

Abstract

Nanometer nickel powders have been prepared using the polyol method with NaOH, Ni(NO₃)₂·6H₂O, ethylene glycol (EG), and polyvinylpyrrolidone (PVP) as raw materials. The thermodynamics of the reaction system was studied, and the *E*-pH diagram of Ni-EG-H₂O was plotted. The oxidation products of EG were predicted from the *E*-pH diagram, and CO₃²⁻ in alkaline solutions was identified as the product through the IR spectrum and CaCO₃ sediment. Field-emission scanning electron micrograph (FE-SEM) showed that spherical nanometer nickel powders were obtained.

© 2006 Elsevier Ltd. All rights reserved.

Keywords: A. Metals; A. Nanostructures; B. Chemical synthesis

1. Introduction

Recently, attention has been increasingly focused on uniform-shape and high-purity nanometer metal powders with mean particle size ranging from several nanometers to 100 nm. This attention has arisen from their numerous applications in batteries, hard alloys, and catalysts, and in electrical applications [1]. Among the various kinds of nanometer metal powder, those containing Ni, Co, Fe, and Cu are relatively difficult to prepare because they oxidize easily. Many methods of production of such metal powders of various sizes and shapes have been reported such as the sonochemical method [2], the microemulsion technique [3], and the microwave irradiation method [4]. However, these methods are not appropriate for large-scale production of powders because of the difficulty of the technique and the expensive equipment involved. Usually, chemical reduction in solution is suited for the preparation of nanometer powders. Controlling the size and shape of powders presents a challenge to this field [5,6].

A new method of preparation of metal powders, the polyol process, was considered by Fiévet et al. [7] for deoxidizing Co(OH)₂ or Ni(OH)₂ with ethylene glycol (EG). The polyol process enables an accurate control of the size

^{*} Corresponding authors. Tel.: +86 731 88377204; fax: +86 731 8710804.

E-mail address: shmjin@mail.csu.edu.cn (J. Shengming).

distribution and shape of the particles from the micrometer scale to the nanometer scale. Over the past two decades, the polyol process has been studied much and adapted for the preparation of ferromagnetic metal powders [8,9], nanometer noble metal powders [10,11], metallic nanorods and nanowires [12,13], and nanoscale oxide particles [14]. Even though the polyol process has been used widely for the preparation of various metal powders, the polyol reaction mechanisms have been studied little. Blin et al. [15] have studied the production of EG through oxidation, and the diacetyl was detected in the EG–Ni(OH)₂–H₂O system in 1989. However, the redox reaction in solution was related to the reduction potential, which varied with the pH value when H⁺ or OH[−] participated in the formation of metal powders. Consequently, studying the thermodynamics of the preparation of nanometer nickel powders from EG can give rise to a better understanding of the reduction mechanism.

In this work, a process for preparing nanometer nickel powders by the polyol method was described. The *E*–pH diagram of the Ni–EG–H₂O system was studied according to the thermodynamics of the potential reaction between Ni(OH)₂ and EG. The oxidation reaction direction and the oxidation products of EG were investigated and identified through the IR spectrum.

2. Experimental

The reagents used in the experiments, Ni(NO₃)₂·6H₂O, NaOH, ethanol, and EG, were all analytical grade reagents. Typically, a given amount of Ni(NO₃)₂·6H₂O with 1% polyvinylpyrrolidone (PVP, molecular weight 10,000) was dissolved in distilled water, and 1 M NaOH solution was added to adjust the pH to 11. The mixed solution was stirred at 60 °C for 2 h. Then, the Ni(OH)₂ slurry was filtered using a Buchner funnel. The water content of the Ni(OH)₂ was 77.0%.

The obtained Ni(OH)₂, 3.0 g NaOH, 0.4 g PVP, and 100 mL EG were added to a three-necked flask. The mixture of Ni(OH)₂, NaOH, PVP, and EG was stirred to form Ni(OH)₂ slurry, and then refluxed at 180 °C for 4 h, filtered using a Buchner funnel, washed thrice with distilled water and twice with ethanol, and dried at 45 °C for 24 h. Gray–black nickel powders were obtained. Twenty milliliters CaCl₂ solution was added into filtrate, and the sediments were filtered, dried and then characterized by X-ray diffraction (XRD).

The filtrate was examined using a Nexus 670 IR (Thermo Electron) with a KBr coating, and the nickel powders were characterized by their X-ray diffraction patterns (Rigaku, Dmax/2550) and using a field-emission scanning electron micrograph (FE-SEM) (Sirion200, EDAX).

3. Results and discussion

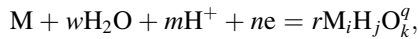
3.1. Thermodynamics of Ni–EG–H₂O system

A redox reaction in solution depends not only on the concentration of the ion but also on the pH of the solution according to the Nernst equation. The free energy of formation of the main substance in the Ni–EG–H₂O system is shown in Table 1. The value of the reduction potential of Ni(OH)₂ in EG is not available in the literature. The order of the potentials of a given electrode reaction as a rule does not significantly differ for different media. Moreover, the half-cell potentials of metal ions in EG are also in agreement with their active order in an aqueous solution [16].

Table 1
The free energy of formation of the major substances in the Ni–EG–H₂O system (*T* = 298 K)

Species	ΔG_f^θ (kJ/mol)
H ₂ O	−238.09
Ni ²⁺	−192.28
Ni(OH) ₂	−448.98
Ni	0
EG	−324.62
Diacetyl	−277.98
CO ₃ ^{2−}	−529.91
OH [−]	−157.89

In an aqueous system, to consider any possible M-bearing species $M_iH_jO_k^q$, the following general reaction can be used [17]:



where $i \neq 0$, $r = 1/i$, $w = ki$, $m = (j - 2k)/i$, $n = (j - 2k - q)/i$.

With $\alpha_{H_2O} = 1$, the Nernst formula can be expressed as,

$$E = -\frac{\Delta G^\circ}{nF} - \frac{RT}{nF} \ln(\alpha_{M_iH_jO_k})^r - \frac{2.303mRT}{nF} \text{pH}$$

The component activity term is then

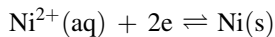
$$\lg(\alpha_{M_iH_jO_k}) = A\text{pH} + BE + C$$

where $A = -m$, $B = (-nF/2.303RT)$, $C = (-\Delta G^\circ/2.303RT)$.

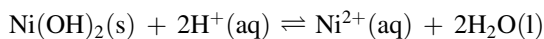
The above formula can be applied to any redox reaction. The potential values in an aqueous solution were used for estimating those in the Ni–EG–H₂O system. The standard potential values could be calculated from the free energies of formation of the substances listed in Table 1. Therefore, the E–pH diagram can be plotted at 298 K when the activities of the related compound, ion and gas fugacity are one during calculation.

In the reaction system of EG and Ni(OH)₂, the potential equilibrium conditions are as follows:

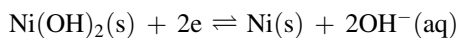
(1) Reactions corresponding to Ni:



$$\varphi_1 = -0.23\text{V} \quad (1)$$

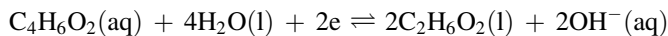


$$\text{pH} = 6.40 \quad (2)$$

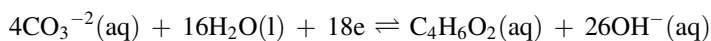


$$\varphi_2 = (0.17 - 0.059\text{pH})\text{V} \quad (3)$$

(2) Reactions corresponding to EG:



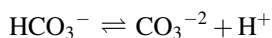
$$\varphi_3 = (-0.95 - 0.059\text{pH})\text{V} \quad (4)$$



$$\varphi_4 = (-0.89 - 0.085\text{pH})\text{V} \quad (5)$$

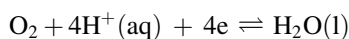


$$\text{pH} = 6.38 \quad (6)$$



$$\text{pH} = 10.25 \quad (7)$$

(3) Water stability:



$$\varphi_{\text{O}_2} = (1.229 - 0.059\text{pH})\text{V} \quad (\text{a})$$



$$\varphi_{\text{H}_2} = (-0.059\text{pH})\text{V} \quad (\text{b})$$

Fig. 1 shows the E–pH diagram (Pourbaix diagram) of the Ni–EG–H₂O system obtained from the above equilibria. In Fig. 1, the dotted lines labelled a and b represent, respectively, the equilibrium reaction of the reduction of water to

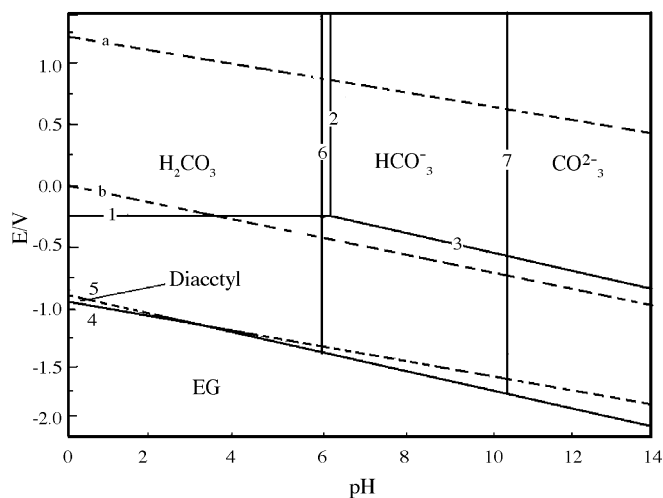


Fig. 1. E-pH diagram of Ni-EG-H₂O system ($T = 298$ K).

gaseous H₂ and of the oxidation of water to O₂ when the partial fugacity of H₂ or O₂ is 1. The lines labelled 4 and 5 denote, respectively, the equilibrium reaction of the oxidation of EG to diacetyl and the oxidation of diacetyl to CO₃²⁻. Lines 6 and 7 represent the dissociation of H₂CO₃ and HCO₃⁻, respectively. The lines labeled 1, 2, and 3 correspond to the equilibrium between Ni, Ni(OH)₂, and Ni²⁺. The E-pH diagram is divided into the regions of stability of diacetyl, EG, H₂CO₃, HCO₃⁻, and CO₃²⁻ by lines 4, 5, 6, and 7.

The E-pH diagram of the Ni-EG-H₂O system can be used to theoretically understand the accumulated sum of experimental findings and predict the oxidation products of EG at different pH values. According to Fig. 1, lines 4 and 5 intersect at pH 2.3, which indicates the variation of the stability of diacetyl and EG. When the pH value is greater than 2.3, the region of diacetyl is below line 4 and thus diacetyl is not thermodynamically stable in the reaction system. Diacetyl tends to be oxidized completely to H₂CO₃, HCO₃⁻, and CO₃²⁻ at different pH values by Ni(OH)₂. In contrast, when the pH value is less than 2.3, the diacetyl region is above line 4, and the thermodynamic stability of diacetyl is greater than that of EG in the reaction system, and an intermediate of diacetyl may form and then be oxidized to form H₂CO₃. It is obvious that through thermodynamic considerations, H₂CO₃ is the product of total oxidation of EG. In addition, when the pH value is less than 2.3, diacetyl can be obtained. Diacetyl has been detected as the main product of EG in acidic solutions in the literature [7,15]. It must be pointed out that Fig. 1 may be invalid practically because of the fact that the reaction temperature is not 298 K but 453 K.

3.2. Characterization of nickel powder

XRD patterns of nickel powder prepared using the polyol process are shown in Fig. 2. Three peaks at $2\theta = 44.5^\circ$, 51.8° , and 76.4° could be indexed to a face-centered cubic system, and the corresponding Miller indices were marked for each diffraction peak. No peaks of nickel hydroxides or other impurities were detected, indicating the complete reduction of nickel hydroxides. The strong and sharp peaks revealed that the nickel particles were well crystalline. Fig. 3 shows field-emission scanning electron micrographs of the same sample. The micrographs show that spherical nanometer nickel powders were obtained.

3.3. Analysis of the oxidation product of EG

The IR spectrum of the filtrate is shown in Fig. 4. The peaks may be assigned to three kinds of substance: the vibration peaks of all kinds of functional groups of EG, the solvent and reactants, the vibration peaks of C=O of PVP, surfactant, and the vibration peaks of the resultant carbonate. The main vibration peaks are assigned as follows: (1) the experimental bands shown in Fig. 4 have the greatest similarity to the standard IR spectrum of EG; (2) the band at 1641 cm^{-1} corresponds to the stretching -C=O vibration of PVP and the other bands of PVP are overlapped by that of EG; (3) typical vibration peaks assigned to CO₃²⁻ with the structure of a symmetric triangle in a plane (D_{3h}) at 1413

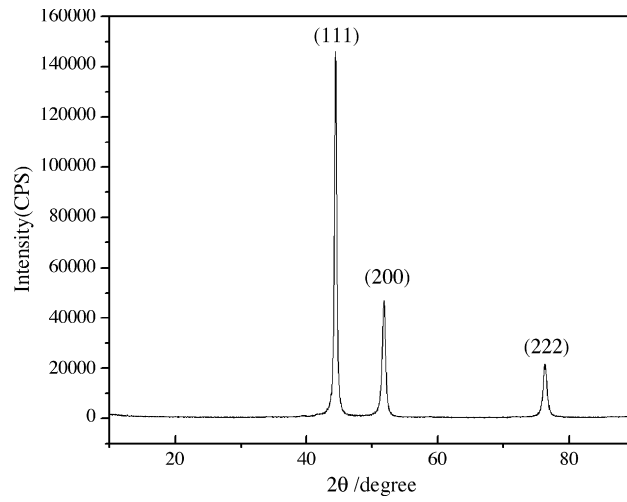


Fig. 2. XRD patterns of nickel powders prepared using the polyol process.

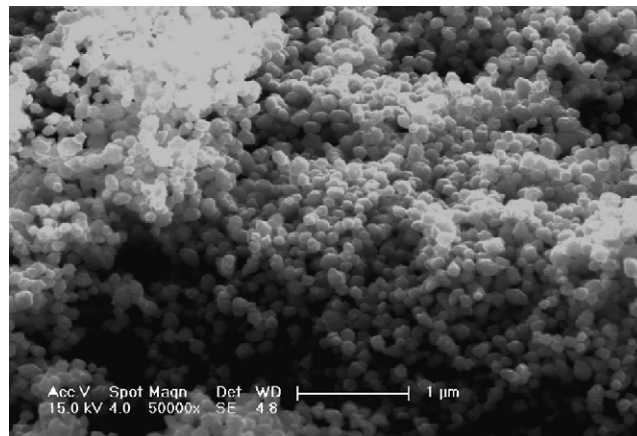


Fig. 3. FE-SEM micrographs of the samples in Fig. 2.

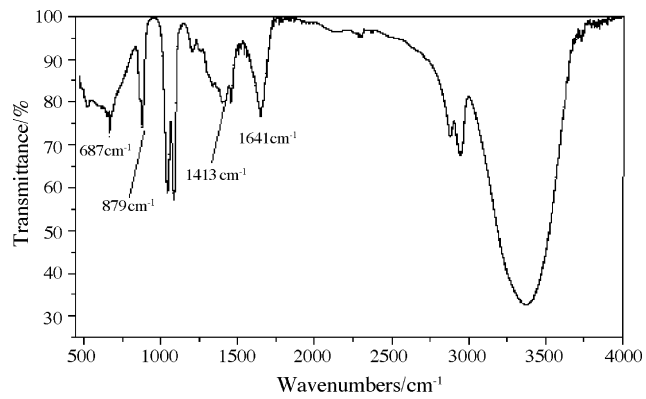


Fig. 4. The IR spectrum of the filtrate.

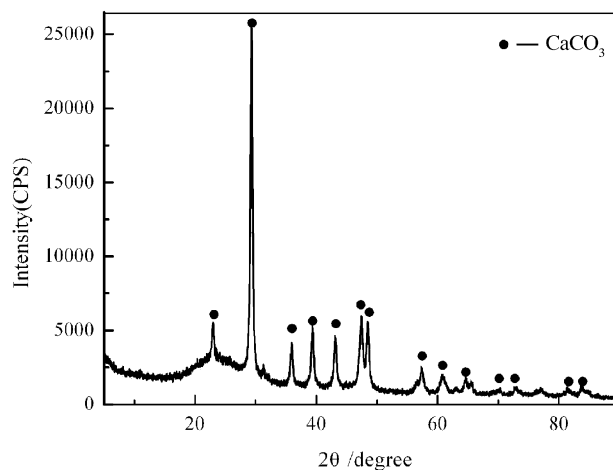
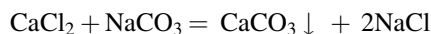


Fig. 5. XRD patterns of sediment from filtrate.

and 687 cm^{-1} correspond to asymmetric stretching and in-plane bending of CO_3^{2-} , respectively, and the out-of-plane bend vibration peak at 879 cm^{-1} is overlapped by the corresponding peak of EG.

However, the band at 1413 and 879 cm^{-1} could be connected with vinyl-group of PVP and band at 879 cm^{-1} with valence vibration of C–N. The characterization of sediment from filtrate was carried out by XRD (shown in Fig. 5).

The results show that the characteristic peaks for CaCO_3 are observed, indicating that the CaCO_3 sediment come into being. The reaction formula was as follows when the CaCl_2 solution was added into filtrate:



It is obvious that the complete oxidation of EG in an alkaline solution yielded CO_3^{2-} because the typical peaks of CaCO_3 shown in Fig. 5 are in accordance with that predicted from Fig. 1.

4. Conclusions

Nanometer nickel powders have been successfully prepared using the polyol method. The thermodynamics of the preparation of nanometer nickel powders using the polyol method have been investigated, and the E -pH diagram of the Ni-EG- H_2O system shows that the pH value of 2.3 is the intersection of the oxidation equilibria of EG and diacetyl. When the pH value is greater than 2.3, diacetyl is not stable thermodynamically in the reaction system, and complete oxidation of EG occurs directly with $\text{Ni}(\text{OH})_2$; when the pH value is less than 2.3, complete oxidation of EG occurs through an intermediate diacetyl. The typical peaks of CaCO_3 shown in the XRD patterns of the sediment from the filtrate confirm the complete oxidation of EG in an alkaline solution, in accordance with the results obtained from the E -pH diagram.

References

- [1] V. Dan, M. Egon, *New J.Chem.* 22 (1998) 1203.
- [2] Y. Kolytyn, G. Katabi, X. Cao, et al. *J. Non-Cryst. Solids* 201 (1996) 159.
- [3] X. Ni, X. Su, Zh. Yang, et al. *J Cryst. Growth* 252 (2003) 612.
- [4] Y. Wada, H. Kuramoto, T. Sakata, et al. *Chem. Lett.* 7 (1999) 607.
- [5] Y.D. Li, C.W. Li, H.R. Wang, et al. *Mater. Chem. Phys.* 59 (1999) 88.
- [6] J. Gao, F. Guan, Y. Zhao, et al. *Mater. Chem. Phys.* 71 (2001) 215.
- [7] F. Fiévet, J.P. Lagier, B. Blin, et al. *Solid State Ionics* 32 (33) (1989) 198.
- [8] G. Viau, F. Fiévet-Vincent, F. Fiévet, *Solid State Ionics* 84 (3–4) (1996) 259.
- [9] H. Yin, G.M. Chow, *J. Electrochem. Soc.* 149 (1) (2002) 68.
- [10] F. Bonet, V. Delmas, S. Grugeon, R. Herrera Urbina, et al. *Nanostruct. Mater.* 11 (8) (1999) 1277.
- [11] T. Masaharu, H. Masayuki, N. Yuki, et al. *Mater. Lett.* 58 (2004) 2326.

- [12] Y.J. Zhu, X.L. Hu, *Mater. Lett.* 58 (2004) 1234.
- [13] Y.J. Zhu, X.L. Hu, *Chem. Lett.* 33 (6) (2004) 760.
- [14] C. Feldmann, H.O. Jungk, *Chem. Int. Ed.* 40 (2001) 359.
- [15] B. Blin, F. Fiévet, D. Beaupere, et al. *New J. Chem.* 13 (1989) 67.
- [16] H. Yin, G.M. Chow, *J. Electrochem. Soc.* 149 (1) (2002) 68.
- [17] H. Liu, C. Zhang, *Calphad* 25 (3) (2001) 363.