Two-Step Hydrometallurgical Preparation of Ultrafine Cobalt Powders

Peng Qu,* Shengquan Yang, Chao’an Wang, and Houkun Han

ABSTRACT: A two-step hydrometallurgical method was carried out to prepare ultrafine cobalt powders for the first time. The products were characterized by scanning electron microscopy coupled with energy-dispersive spectrometry, X-ray diffraction, laser particle size analyzer, and inductive coupled plasma. The cobalt powders contained the hcp-cobalt phase and fcc-cobalt phase. The proportion of hydrazine hydrate used in the two steps was found to be essential for the size of cobalt powders. As the proportion of hydrazine hydrate changed from 1:4 to 4:1, an obvious mean size evolution was observed from 1000 to 300 nm. A transition state \([\text{Co(NH}_3\text{)}_6\text{(OH)}_x]^{(x-2)-}\) was proposed to explain the preparation process of ultrafine cobalt powders.

INTRODUCTION

Cobalt, known as “industrial vitamin”, is widely used in cemented carbides, demand tools, magnetic materials, lithium-ion batteries, and high-temperature alloys due to the great hardness, high melting point, stable chemical performance, and strong magnetism.\(^1\)\(^-\)\(^2\) In particular, ultrafine cobalt powders are of deep interest over a long period of time for researchers from a wide range of fields.\(^3\)\(^-\)\(^4\) For instance, spherical cobalt powders are mostly needed in the progressive cutting tool industries.\(^5\)\(^-\)\(^6\) One-dimensional cobalt nanorods have applications in magnetic sensors and drug delivery.\(^7\)\(^-\)\(^8\)

It has been reported that nanosize cobalt powders could be prepared by hydrometallurgical methods.\(^9\)\(^-\)\(^13\) Liquid-phase hydrogen reduction is one of the most typical processes for cobalt synthesis due to the economic and environmental consideration.\(^5\)\(^,\)\(^10\)\(^,\)\(^14\) However, this process requires high pressure and temperature. Kunda and Hitesman prepared CoSO\(_4\) solution with the NH\(_3\)/Co molar ratio ranging from 2.3 to 4.0 and reduced the solution at 200 °C with hydrogen, which was controlled under 3 MPa.\(^9\) The cobalt powders obtained possessed a large specific surface area of 12.4 m\(^2\)/g. Other hydrometallurgical methods include reduction of cobalt salts by strong reductants, such as hydrazine hydrate, sodium borohydride, and potassium borohydrate.\(^11\)\(^-\)\(^13\) Liu et al. added Co(NO\(_3\))\(_2\)/ethanol solution into the sodium hydroxide/hydrazine hydrate mixture at 50 °C and got cobalt powders with a size distribution between 500 nm and 4 \(\mu\)m.\(^12\) It is obvious that such a simple method is valuable for producing nanosize cobalt powders as a consequence of the moderate reaction conditions.

In this paper, a two-step hydrometallurgical route was developed to prepare ultrafine cobalt powders based on the previous report.

RESULTS AND DISCUSSION

Figure 1 shows characterization results of cobalt powders of sample 4. In Figure 1a,b, detailed scanning electron microscopy (SEM) pictures are given at a large and small scale, respectively. It is obvious that the size of ultrafine cobalt powders ranges from 200 to 800 nm, as shown in Figure 1a. In Figure 1b, ultrafine cobalt powders are homogeneously distributed in the whole picture. In Figure 1c, the average particle size of cobalt powders is 300 nm and diameters of over 90% of cobalt powders are less than 650 nm based on laser particle size analyzer (LPSA) analysis. Figure 1d demonstrates the X-ray powder diffraction (XRD) pattern of ultrafine cobalt powders prepared. According to the reported data JCPDS no.: 05-0727 and 15-0806, phase compositions of cobalt powders include the hcp-cobalt phase and fcc-cobalt phase. In Table 1, similar phase percentages could be found between different cobalt samples. The average percentages of fcc-cobalt and hcp-cobalt phases are 85 and 15%, respectively. Figure 1e presents the energy-dispersive spectrometry (EDS) spectrum of cobalt...
The sample mainly consists of cobalt with a small amount of oxygen species. The small content of oxygen in cobalt powders may be due to reoxidation during the reaction. The proportion of hydrazine hydrate used in the two steps plays an important role in the size of cobalt powders. An obvious mean size evolution from 1000 to 300 nm is observed. Cobalt powders with the size distribution of 500−1400 nm are obtained when the amount of hydrazine hydrate used in the

![Figure 1. Cobalt powders of sample 4: (a) SEM image at a large scale; (b) SEM image at a small scale; (c) particle size distribution; (d) XRD pattern; and (e) EDS spectrum.](image)

| samples | fcc-cobalt (%) | hcp-cobalt (%) |
|---------|----------------|----------------|
| 1       | 83.1           | 16.9           |
| 2       | 87.5           | 12.5           |
| 3       | 84.7           | 15.3           |
| 4       | 85.7           | 14.3           |

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The color of the mixture changes from cherry red to navy blue when hydrazine hydrate is added into cobalt salt solution. In this process, the existence form of cobalt varies from Co²⁺ to a coordination compound \([\text{Co(NH}_3\text{)}_6\text{]}^{2+}\). However, hydrazine molecules could decompose into ammonia as the reaction stops. Hydroxyl ions have more strong interactions with Co³⁺ rather than hydrazine molecules. Therefore, cobalt hydroxide would be formed in priority and the transition state \(\{[\text{Co(NH}_3\text{)}_6\text{](OH)}_x\}\) cannot be obtained.

Table 2 gives the chemical compositions of ultrafine cobalt powders. The content of oxygen in cobalt powders is 0.63%.

### EXPERIMENTAL SECTION

Ultrafine cobalt powders were synthesized through a two-step hydrometallurgical method. CoCl₂·6H₂O was dissolved in deionized water to form 0.25 mol/L cobalt salt solution. Then, 50 wt % hydrazine hydrate was added into cobalt salt solution in two steps with a total amount of 3.0:1 N₂H₄/Co molar ratio. Table 3 gives the amount of hydrazine hydrate used in each step.

### CONCLUSIONS

Ultrafine cobalt powders are prepared by a two-step hydrometallurgical method. It is found that the proportion of hydrazine hydrate used in two steps plays a key role in the size changes of cobalt powders. A transition state \(\{[\text{Co(NH}_3\text{)}_6\text{](OH)}_x\}\) is proposed to explain the preparation process. This work provides a novel perspective on the preparation method of cobalt powders.

### Table 2. Chemical Compositions of Cobalt Powder

| Element | Content (%) | Element | Content (%) |
|---------|-------------|---------|-------------|
| O       | 63.22       | Mg      | 0.0001      |
| S       | 0.010       | Mn      | 0.0001      |
| Al      | 0.010       | Na      | 0.0010      |
| Ca      | 0.0005      | Ni      | 0.0038      |
| Cr      | 0.0002      | Pb      | 0.0025      |
| Cu      | 0.0041      | Zn      | 0.0001      |
| Fe      | 0.0021      |         |             |

Other impurities, such as sulphur, are all less than 0.01%. Therefore, the purity of ultrafine cobalt powders is over 99.9% and could be a future material for the next generation of cutting tools.

### Table 3. Amounts of Hydrazine Hydrate Used in Each Step

| Samples | First Step (N₂H₄/Co molar ratio) | Second Step (N₂H₄/Co molar ratio) |
|---------|----------------------------------|-----------------------------------|
| 1       | 0.6                              | 2.4                               |
| 2       | 1.2                              | 1.8                               |
| 3       | 1.8                              | 1.2                               |
| 4       | 2.4                              | 0.6                               |

In the first step, a certain amount of hydrazine hydrate was added into cobalt salt solution under vigorous stirring at 70 °C. The color of the mixture varied from cherry red to navy blue. In the second step, the pH value of the mixture was adjusted to be 11 with solid NaOH and another amount of hydrazine hydrate was added into the mixture again to obtain a gray black slurry. The slurry was stirred continuously for 1 h until it became transparent. The precipitation was filtered, rinsed with deionized water and ethanol for several times, and dried in a nitrogen atmosphere at 60 °C for 6 h. Finally, ultrafine cobalt powders were obtained. It was essential to add...
a small quantity of sodium borohydride in every step to activate the reaction.

Phase composition of cobalt powders was determined on XRD (AXS D8, Bruker, Germany). Morphology of cobalt powders was characterized by SEM (JEOL 6400, JEOL, Japan). Size distribution of cobalt powders was tested by a LPSA (BIC 90Plus, Brookhaven, USA). Chemical compositions of cobalt powders were measured by inductive coupled plasma (Optima 5300DV, PerkinElmer, USA) and EDS (JEOL 6400, JEOL, Japan).

### AUTHOR INFORMATION

**Corresponding Author**

Peng Qu — Nanjing Hanrui Cobalt Co., Ltd, Nanjing 211100, P.R. China; orcid.org/0000-0003-4437-3522; Email: qupeng@hrcobalt.com

**Authors**

Shengquan Yang — Nanjing Hanrui Cobalt Co., Ltd, Nanjing 211100, P.R. China

Chao’an Wang — Nanjing Hanrui Cobalt Co., Ltd, Nanjing 211100, P.R. China

Houkun Han — Nanjing Hanrui Cobalt Co., Ltd, Nanjing 211100, P.R. China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c07159

**Notes**

The authors declare no competing financial interest.

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