

Preparation of Ultrafine Cobalt Powder by Chemical Reduction in Aqueous Solution

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Abstract: Nanocrystalline cobalt powders have been prepared from aqueous solution by reducing their corresponding metal salts under suitable conditions. The experimental conditions have been studied in detail. X-ray powder diffraction patterns show that the cobalt powder is hexagonal crystallite. The average particle size of the ultrafine cobalt powder is 55 nm.

Keywords: Nanocrystalline, cobalt powder, preparation.

Introduction

The preparation of ultrafine metal powders has been extensively studied in past years due to their scientific interests and potential applications¹. Ultrafine particles exhibit novel material properties that differ from those of the bulk solid state because of the size effect²⁻⁴. In particular, ultrafine cobalt powders have many important industrial applications. They are commonly used in alkaline rechargeable batteries, magnetic recording media, heterogeneous catalysis, and especially, as a pigment in the manufacture of hard metal tools, and grinding or polishing compounds⁵.

It is well known that the powder characteristics (particle size, particle size distribution and shape) are strongly influenced by preparation procedures. Various methods have been reported to synthesize ultrafine powders of cobalt, such as γ -irradiation method⁶, reactive deposition⁷, microwave-hydrothermal method⁸, metal evaporation method⁹ *etc.*, but these methods need expensive equipments and the technique is complex. Usually chemical reduction in aqueous solution is particularly well suited to prepare ultrafine powders, so it is widely used to prepare many kinds of metal powders. However, there has been little work on magnetic ultrafine powders obtained by this procedure¹⁰⁻¹¹. In this paper, the preparation of nanocrystalline cobalt powders from aqueous solution by chemical reduction was reported, and the factors affecting the average size of particle was studied in order to establish the optimum operating condition and to explore practical applications of the technique. X-ray diffraction (XRD) and transmission electron microscope (TEM) were used to characterize the products.

Experimental

Solution of cobalt ion was prepared by dissolving an analytical grade $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in distilled water. Sodium citrate or sodium tartrate was used as complexant. The pH values of the solutions were adjusted by sodium carbonate solution or sodium hydroxide solution. Polyvinylpyrrolidone (PVP), sodium lauryl sulfate (SLS) or cetyltrimethyl ammonium bromide (CTMAB) are chosen as surfactant, and sodium hypophosphite or hydrazine hydrate was used as reducing agent. The mixture was heated to $75 \sim 85^\circ\text{C}$, and then added a small amount of AgNO_3 solution as nucleating agent at which a rapid reaction occurred. All the experiments were performed under the mechanical stirring. The metal powder was separated from the solution by precipitation for some time, and washed with distilled water followed by ethanol and acetone. The powder was finally dried in vacuum at 50°C . Gray-black powder of cobalt was obtained.

X-ray powder diffraction (XRD) patterns were recorded at a scanning rate of 0.1 s^{-1} with a Japan Rigaku DMA-IIIIC X-ray diffractometer using monochromatic high-intensity $\text{CoK}\alpha$ radiation ($= 1.7889\text{\AA}$), size and shape of particles were determined by JEM-100SX transmission electron microscopy (TEM). The average particle size of the powders were calculated from the XRD patterns according to the Scherrer formula.

Results and Discussion

Effects of pH values and complexants

The experiment results show that pH 9 ~ 10 is suitable for the preparation of ultrafine powders. No gray-black powders were produced if the pH < 8. But the pH values of solution decrease from 9.5 to 8 in the reduction procedure, so Na_2CO_3 was employed to keep pH values at 9.5 instead of NaOH solution because it can form the Na_2CO_3 - NaHCO_3 buffer during the reduction process. Pure hexagonal-crystallite cobalt powders from the CoCl_2 solution were obtained at pH 9 ~ 10 in the presence of complex agent (**Figure 1a**).

If the pH of the solution was adjusted to 9.5 by the dropwise addition of NaOH or Na_2CO_3 without complexant, the reduction product was a mixture of cobalt and a small amount of $\text{Co}(\text{OH})_2$ (**Figure 1b**). Thus sodium citrate or tartrate was used as complexant to prevent formation of $\text{Co}(\text{OH})_2$. Sodium citrate can form complex with Co^{2+} more effectively.

The effect of the concentration of cobalt ion, surfactant and nucleating agent

The experimental conditions including the concentration of cobalt ion, the types and concentration of surfactants and nucleating agent were investigated. A detailed correlation between these factors and the average size of particles was given in **Table 1**. The average size of particles listed was calculated from the XRD data of the samples according to the Scherrer formula. From **Table 1**, it can be concluded that the lower

Co²⁺ ion concentration and higher concentration of surfactant are the smaller average size of cobalt particles is. The formation of nanocrystalline cobalt particles comes from aggregation of cobalt atoms in aqueous. In this process, the surfactant molecules coat the cobalt particles to prevent growth of the single particles and adhesion of particles⁶. In addition, nanoscale particles are metastable owing to their large surface area. It is quite reactive and tends to oxidize in air. For obtaining pure nanoparticles of cobalt nitrogen should be bubbled into the solution.

Table 1 Correlation between the experimental conditions and the average particle sizes of cobalt powder (pH = 9.5)

Sample	Conc. Co ²⁺ (mol/L)	Surfactant	particle size of Average (nm)
1	0.1	0.2%SLS	68
2	0.1	0.5%SLS	62
3	0.2	1.5%PVP	83
4	0.1	1.5%PVP	77
5	0.05	1.5%PVP	55
6	0.05	0.5%PVP	90
7	0.05	0.5%CTMAB	112
8	0.05	1.0%CTMAB	104

Because the standard reduction potentials of Co (II) ($E_{Co^{2+}/Co} = -0.277$ v) is very low, it is not easy to be reduced. At the beginning of the reaction, only a few crystal seeds can be produced in solution and then slowly grow into larger particles. But when a small amount of AgNO₃ was added as nucleating agents, a large number of nuclei were produced in solution. According to the Lamer Chart of formation of ultrafine particle¹² and the growth theory of crystals¹³, competition between the nucleation and growth of crystals exists in the solution. The more rapid the nucleating process is, the more the number of nuclei before release of supersaturation is. As a result, the average cobalt particle size decreases when AgNO₃ is used as nucleating agent, and the reaction changes to heterogeneous nucleation from homogeneous nucleation. The increase in nucleation rate result in small particle size.

X-ray diffraction(XRD) and transmission electron microscope analysis of the samples

Under above optimum conditions, we have obtained ultrafine cobalt powder. The XRD patterns (**Figure 1a**) showed that the products were pure Co with hexagonal crystallite, and the average size of particles was 50 nm according to the Scerrer formula.

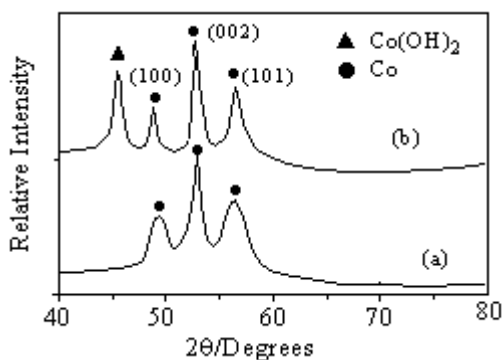
Figure 2 was the TEM images of the sample, the size of particles was 55 nm and this was in accordance with the XRD analysis.

Conclusions

Pure hexagonal ultrafine cobalt powder was obtained by reducing CoCl₂ solution using hydrazinehydrate in an aqueous medium of a NaHCO₃-Na₂CO₃ buffer, pH 9 ~ 10, keeping the temperature at 75 ~ 85°C. The molar ratio of CoCl₂ to sodium citrate is

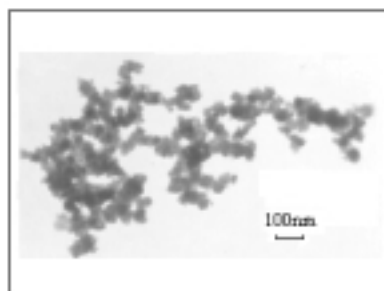
1:1. High concentration of surfactant and low concentration of Co^{2+} were suitable conditions to form nanoscale cobalt powders.

Figure 1 XRD patterns of ultrafine cobalt powders



(a) sodium citrate as complexant in solution,
(b) without complexant in solution.

Figure 2 TEM photograph of ultrafine cobalt powder



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References

1. J. S. Bradley, E. Hill, M. E. Lepmpwocz, H. Witzke, *J. Mol. Cat.*, **1987**, 47, 59.
2. R. E. Cavicchi, R. H. Silsbee, *Phys. Rev. Lett.*, **1984**, 52, 14533.
3. P. Ball, L. Garwin, *Nature*, **1992**, 355, 761.
4. W. P. Halperin, *Rev. Modern Phys.*, **1986**, 58, 532.
5. The Cobalt Development Institute(CDI), *Cobalt news*(London), **1989**, 89 (2), 2.
6. Y. Liu, Y. Zhu, Y. Zhang, Y. Qian, M. Zhang, L. Yang and C. Wang, *J. Mater. Chem.*, **1997**, 7 (5), 787.
7. C. Q. Cui, J. Y. Lee, T. C. Tan, *J. Mater. Sci.*, **1994**, 29, 6495.
8. S. Komarneni, R. Pidugu, Q. H. Li, R. Roy, *J. Mater. Res.*, **1995**, 10 (7), 1687.
9. S. H. Wu, X. Q. Wang, *Chemistry*(in chinese), **1991**, 10, 34.
10. N. G. George, J. K. Keneth, M. S. Christopher, C. H. George, *Langmuir*, **1993**, 9, 162.
11. V. S. Vadim., P. Gvidona, S. Andrei, A. Nahla, *J. Phys. Chem.*, **1996**, 100, 19632.
12. V. K. Lamer, R. H. Dinegar, *J. Am. Chem. Soc.*, **1950**, 72, 4847.
13. A. W. Adamson, *Physical Chemistry of Surfaces*, 3rd ed., Science Press, Beijing, **1985**, 394.

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