# Preparation of nanocrystalline cobalt powders by a γ-irradiation method

**Yunping Liu,*[a] Yingjie Zhu,[b] Yinhan Zhang,[b] Yitai Qian,[b] Manwei Zhang,[b] Li Yang[c] and Changsui Wang[c]**

[a]*Department of Precision Engineering, University of Science and Technology of China, Hefei, Anhui 230026, P.R. China*
[b]*Department of Applied Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P.R. China*
[c]*Structure Research Center, University of Science and Technology of China, Hefei, Anhui 230026, P.R. China*

Nanocrystalline cobalt powders, consisting of a pure hexagonal phase, and a hexagonal phase mixed with a small amount of a cubic phase, have been prepared from aqueous solutions at ambient temperature and pressure by a γ-irradiation method. The influence of the experimental conditions on the composition, the average particle size and the yield of nanocrystalline cobalt powders has been studied in detail. X-Ray powder diffraction patterns show the smallest average particle size of the nanocrystalline cobalt powders to be 14 nm.

There has been considerable interest in the study of nanocrystalline metal materials because of the effects of their particle sizes on structure, physical and chemical properties.[1] In particular, nanoscale 3d transition-metal iron, cobalt and nickel materials are expected to display unique magnetic and catalytic properties, *etc*.[2] Therefore, the preparation of pure nanoscale iron, cobalt and nickel powders is of importance to the theory and application of nanometre-sized materials. Recently, nanoscale particles of cobalt have been prepared by several different methods,[3,4] but the products prepared by the two-phase non-aqueous route were stable only as a colloidal metal dispersion in an organic solvent,[3] while the cobalt powders produced through leaching of mechanically alloyed cobalt–aluminium were not pure products.[4] Colloidal cobalt particles dispersed in aqueous solution were prepared by γ-irradiation and separated by using a magnet on the basis of the magnetism of cobalt particles.[5]

Recently a γ-irradiation method has been developed to prepare nanoscale metals, alloys and metal oxides[6–9] from aqueous solutions. Nanocrystalline nickel powders with narrow particle size distributions and small average particle sizes have also been prepared by this method, which can be operated at ambient temperature and pressure. In this paper, we report the preparation of nanocrystalline cobalt powders consisting of a pure hexagonal phase and a hexagonal phase mixed with a small amount of a cubic phase from aqueous solutions by this method at room temperature and ambient pressure.

## Experimental

Solutions were prepared by adding analytical grade $CoSO_4 \cdot 7H_2O$ or $CoCl_2 \cdot 6H_2O$ to distilled water, followed by the dropwise addition of a 25% aqueous ammonia solution to complex the $Co^{2+}$ ions. The pH values of the solutions were adjusted by the addition of a buffer consisting of $NH_3 \cdot H_2O$ and $NH_4Cl$. Polyvinyl alcohol (PVA) or sodium dodecyl sulfate (SDS) were chosen as surfactants, and isopropyl alcohol as a hydroxyl radical scavenger. All solutions were bubbled with nitrogen for 1 h to remove oxygen, then irradiated with a dose rate of 67 Gy $min^{-1}$ in the field of a 49 000Ci $^{60}Co$ γ-ray source of which the γ-ray energy was $8 \times 10^6$ eV. The sediment was separated from the irradiated systems by direct precipitation for some time, and was then washed with the 25% aqueous ammonia solution and distilled water, then dried in a vacuum drier at 60 °C. Grey–black powders of cobalt were obtained.

X-ray powder diffraction (XRD) patterns were recorded at a scanning rate of 0.05° $s^{-1}$ with a Japan Rigaku Dmax $\gamma_A$ X-ray diffractometer with monochromatic high-intensity Cu-Kα radiation (= 1.5418 Å). The particle sizes of the powders were calculated from the XRD patterns according to the Scherrer formula:

$$L = K\lambda/(\beta \cos \theta)$$

where $L$ is the average particle size, $K$ is the Scherrer constant related to the shape and index ($hkl$) of the crystals,[10] $\lambda$ is the wavelength (1.5418 Å) of the X-rays, and $\beta$ is obtained from the Warren and Biscoe equation.[11]

$$\beta^2 = B^2 - b^2$$

where $B$ and $b$ are the angular halfwidths of the sample under investigation and of a standard sample, respectively. In these experiments, the standard sample consisted of the cobalt powders after annealing at 350 °C for 4 h in vacuum.

The yield rates were calculated according to the formula:

$$\text{yield rate} = (\text{experimental mass/theoretical mass}) \times 100$$

The experimental masses of the samples were measured with a fully automated electron balance.

## Results and Discussion

### Basic chemical reaction

The solutions were pink before being irradiated, and became colourless afterwards. In this process, some chemical reactions occurred, which may be understood[5] as follows:

$$H_2O \xrightarrow{\gamma\text{-rays}} OH,\ H_2O_2,\ H,\ H_3O^+,\ H_2,\ e_{aq}^-$$

where $e_{aq}^-$ can effectively reduce $Co^{2+}$ metal ions,

$$e_{aq}^- + Co^{2+} \rightarrow Co^+$$

$$e_{aq}^- + Co^+ \rightarrow Co$$

The formed metallic cobalt atoms aggregate to form nanoscale particles and precipitate from the aqueous solutions.

### XRD study of nanocrystalline cobalt powders

Fig. 1 shows the XRD patterns of several cobalt powders. Fig. 1(*a*) (sample 2 in Table 1) indicates that the product is a pure hexagonal phase with lattice constants $a = 2.506$, $c = 4.067$ Å, close to the literature values.[12] According to the Scherrer formula, the average particle size of the product is 30 nm.

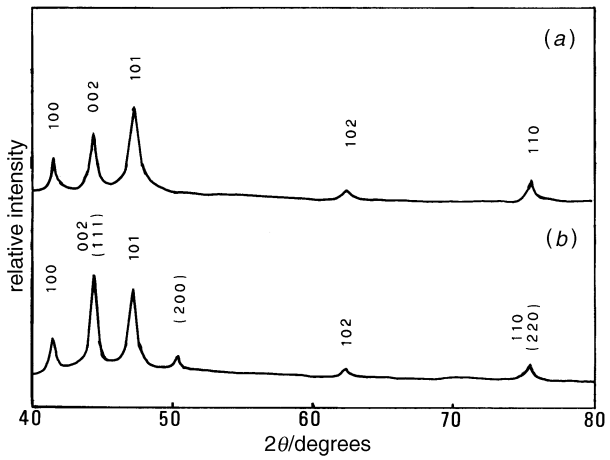


**Fig. 1** XRD patterns of nanocrystalline cobalt powders: (*a*) sample 2 in Table 1, (*b*) sample 6 in Table 1

Fig. 1(*b*) (sample 6 in Table 1) shows the coexistence of a hexagonal phase and a cubic phase (index data in parentheses) of the cobalt powders, of which the hexagonal phase is the major product.

Pure hexagonal-phase cobalt powders were prepared only from the solution consisting of $CoSO_4$ and $NH_4Cl$–$NH_3{\cdot}H_2O$ buffer. If the pH of the solution is kept at 9.5 by the dropwise addition of NaOH solution instead of the $NH_4Cl$–$NH_3{\cdot}H_2O$ buffer, the cobalt powders contain a small amount of the cubic phase. The same products were obtained from the solution consisting of $CoCl_2$ and $NH_4Cl$–$NH_3{\cdot}H_2O$ buffer. The $NH_4Cl$–$NH_3{\cdot}H_2O$ buffer may keep the pH values of the solutions in the range 9.0–9.6, but the solution pH values change from 9.5 before irradiation to 8 after irradiation if the solutions are adjusted with NaOH solution. So the compositions of the nanocrystalline cobalt powders are related not only to the type of cobalt salt but also to the pH of the solutions. The reason for this result is not clear; further research work will be carried out in the near future.

### Average particle size of nanocrystalline cobalt powders

The experimental conditions, including the type of cobalt salt, the concentration of cobalt ions, the type and concentration of surfactant, the radiation dose, the pH of the solution and the concentration of OH radical scavenger, may influence the average particle size of cobalt powders. A detailed correlation between the experimental conditions and the average particle sizes of the hexagonal phase is given in Table 1. The average particle sizes listed in Table 1 were calculated from the XRD data of the samples according to the Scherrer formula.

The experimental results show that the type of cobalt salt, the concentration of cobalt ions, the type and concentration of surfactant and the radiation dose influence the average particle size of the cobalt powders, while the solution pH and the concentration of OH radical scavenger have no influence on the particle size. The data given in Table 1 reveal that a low $Co^{2+}$ ion concentration and radiation dose and a high concentration of surfactant result in a smaller average cobalt particle size; the surfactant concentration has the largest influence.

These experimental results can be explained readily. The formation of nanocrystalline cobalt particles comes from aggregation of cobalt atoms in aqueous solutions. In this process, the surfactant molecules coat the cobalt particles to prevent a single particle from growing and several particles from coming together, so the surfactant concentration can control and adjust the particle size of the cobalt powder, and a higher concentration results in a smaller particle size. A high $Co^{2+}$ concentration increases the probability of aggregation of cobalt atoms and particles, and as a result the average cobalt particle size increases. In addition, nanoscale particles are metastable owing to their large surface area. When they are irradiated with high-energy $\gamma$-rays, they may gather or grow to reduce the surface energy, so that a high radiation dose causes an increase of the average particle size.

Because a decrease in the $Co^{2+}$ ion concentration and a lower radiation dose yield less powder, and a high concentration of surfactant is difficult to wash out from the products, the ideal experimental conditions are as follows: 0.01–0.1 mol $dm^{-3}$ $Co^{2+}$, $>2\times10^4$ Gy radiation dose and 0.1–0.2% PVA surfactant.

### Yield of nanocrystalline cobalt powders

The influence of the experimental conditions on the yield of nanocrystalline cobalt powders has been studied in detail. The experimental data are listed in Table 2.

From Table 2, we can conclude that the type of cobalt salt, the cobalt ion concentration, the radiation dose, the solution pH and the concentration of OH radical scavenger influence the yield of cobalt powders. $CoSO_4$ solutions give larger yields than $CoCl_2$ solutions. Higher radiation doses result in greater yields. The pH range 9–9.5 is suitable for the preparation of nanocrystalline powders. The concentration of OH radical scavenger should be 2 mol $dm^{-3}$ in the solutions.

There may be two main reasons for the relatively low yields: one is that some of the $Co^{2+}$ ions in solution cannot be reduced; the other is that some of the reduced metal cobalt atoms redissolve before the sediment can be separated from the irradiated system because the clusters and nanoscale particles of metal cobalt atoms are very reactive towards oxygen.

**Table 1** Correlation between the experimental conditions and the average particle size of cobalt powders (buffer pH = 9.5)

| sample | $C_{Co^{2+}}$ mol $dm^{-3}$ | $Co^{2+}$ source | surfactant | radiation dose/Gy | average particle size/nm |
|---|---|---|---|---|---|
| 1 | 0.005 | $CoSO_4$ | 0.1% PVA | $2.56\times10^4$ | 29 |
| 2 | 0.01 | $CoSO_4$ | | | 30 |
| 3 | 0.02 | $CoSO_4$ | | | 30 |
| 4 | 0.05 | $CoSO_4$ | | | 32 |
| 5 | 0.1 | $CoSO_4$ | | | 38 |
| 6 | 0.01 | $CoCl_2$ | | | 22 |
| 7 | 0.05 | $CoCl_2$ | | | 25 |
| 8 | 0.01 | $CoSO_4$ | 0.01% PVA | | 42 |
| 9 | 0.01 | $CoSO_4$ | 0.05% PVA | | 33 |
| 10 | 0.01 | $CoSO_4$ | 0.2% PVA | | 17 |
| 11 | 0.01 | $CoSO_4$ | 0.01 mol $dm^{-3}$ | | 25 |
| 12 | 0.01 | $CoSO_4$ | 0.04 mol $dm^{-3}$ | | 14 |
| 13 | 0.01 | $CoSO_4$ | 0.1% PVA | $4.76\times10^4$ | 34 |
| 14 | 0.01 | $CoSO_4$ | 0.1% PVA | $6.50\times10^2$ | 38 |

**Table 2** Correlation between the experimental conditions and the yield of cobalt powders

| sample | $C_{Co^{2+}}$/ mol dm$^{-3}$ | $Co^{2+}$ source | pH | $Pr^iOH$/mol dm$^{-3}$ | ratiation dose/Gy | yield (%) |
|---|---|---|---|---|---|---|
| 1 | 0.005 | $CoSO_4$ | 9.5[a] | 3 | $2.56 \times 10^4$ | 87 |
| 2 | 0.01 | $CoSO_4$ | | | | 87 |
| 3 | 0.05 | $CoSO_4$ | | | | 82 |
| 4 | 0.1 | $CoSO_4$ | | | | 75 |
| 5 | 0.01 | $CoCl_2$ | | | | 74 |
| 6 | 0.05 | $CoCl_2$ | | | | 62 |
| 7 | 0.01 | $CoSO_4$ | 8 | | | 17 |
| 8 | | | 9 | | | 85 |
| 9 | | | 10.5 | | | 78 |
| 10 | | | 10[a] | 1 | | 84 |
| 11 | | | | 2 | | 85 |
| 12 | | | | 4 | | 87 |
| 13 | | | | 3 | $4.76 \times 10^4$ | 91 |
| 14 | | | | | $6.50 \times 10^4$ | 92 |

[a]Buffer.

## Conclusions

Experimental results show that the γ-irradiation method is a good method for the preparation of nanocrystalline cobalt powders. This method can be operated at ambient pressure and temperature. The type of cobalt salt and the solution pH influence the composition of the nanocrystalline cobalt powders. A pure hexagonal phase of cobalt powders was prepared only from the solution consisting of $CoSO_4$ and $NH_4Cl$–$NH_3 \cdot H_2O$ buffer. The cobalt ion concentration, the type and concentration of surfactant and the radiation dose affect the average particle size of the nanocrystalline cobalt powders. A low $Co^{2+}$ ion concentration, a high surfactant concentration and a small radiation dose favour a small average particle size. The most favourable conditions are: a low $Co^{2+}$ ion concentration, a high radiation dose, pH 9–9.5 and $>2$ mol dm$^{-3}$ OH radical scavenger.

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