

PREPARATION OF Co₅₀Ni₅₀ ULTRAFINES BY CO REDUCTION OF SOLUTION IN PRESENCE OF POLYMER^①

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ABSTRACT The reduction reaction of aqueous Co²⁺-hydrazine, which cannot be conducted under the common condition, is carried out by using both of low-temperature heating and stirring. Metallic ultrafines are prepared by this method. In the presence of polyvinyl alcohol (PVA), it is absorbed on the surface of particles of the product and forms a structure of complex particle, which is favorable to the stability of the powder size distribution. Co₅₀Ni₅₀ magnetic alloy ultrafines with fcc-cubic system can also be prepared from Co²⁺-Ni²⁺ hybrid solution by the same method in the presence of PVA. The effect of PVA amount on the particle size and the stability of Co₅₀Ni₅₀ alloy ultrafines are emphatically discussed.

Key words Co₅₀Ni₅₀ magnetic alloy ultrafines Co-reduction of solution polymer(CRSPP)

1 INTRODUCTION

The metal Co, as one of ferromagnetic transition elements, and its alloys and compounds, especially its ultrafine particles and powders, and granular films and other composites, have been widely applied to permanent magnet, magnetic recording media, magnetic memory and switching devices, catalyst and magnetic fluid^[1-5]. For example, the granular films of Co-Ag or Co-Fe alloy system with a nanometer size have shown a giant magnetoresistance effect which is beneficial to develop some new type magnetic sensors^[2]. CoCrPt/Cr films whose coercivity reaches more than 2 kOe may be used as an important kind of vertical high density magnetic media^[3]. The performances of magnetic fluid or ferrofluid and magnetorheological fluid made of Co-Fe alloy particles are better than those of materials composed of conventional powders. They have emerged as reliable materials capable of

solving many complex engineering problems like searing, damping, bearing and so on^[5,6]. We prepared a magnetorheological suspension containing iron-based complex particles which were decorated by nanometer-sized Co particles on their surface. The experimental results showed that a small amount of Co ultrafine particles as the modifier of the iron particles could lead to a significant enhancement of the yield strengths compared with the suspension without Co particles^[7]. Thus, it is very remarkable to develop new methods for preparation of Co ultrafine particles and powders. Besides gas evaporation^[8,9], polyol process^[10], hydrazine-ultrasound^[1], microemulsion^[11], freeze drying^[12], γ-ray irradiation and ultraviolet radiation^[13,14] are all of characteristic preparing process, and the extending of these methods can be used to prepare Co alloy ultrafines such as Co-Cu, Co-Ni and Co-Fe alloys ultrafines^[9,15-17]. However, it should be pointed out that some of the meth-

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ods above need much expensive equipment, post-treatment of some preparation are lengthy and tedious, and some procedures themselves are complicated. Furthermore, the coalescence of particles in the preparation process is not easy to be controlled. In order to obtain Co alloy ultrafine particles and powders with a well-distribution of particle size in simple steps, it is reported in the present paper that Co50Ni50 magnetic alloy ultrafines are prepared by direct reduction reaction from Co^{2+} - Ni^{2+} mixed aqueous solution using hydrazine in the presence of polymer protectant PVA. The effect of PVA amount on the composition, particle size and stability of product are also discussed.

2 EXPERIMENTAL

All reagents used in the experiment are of analytical grade. The general procedure is as follows. Dissolve cobalt and nickel acetate, or other responsible dissolvable salts in distilled water to prepare Co^{2+} - Ni^{2+} mixing solution with molar ratio 1:1, and drip the mixing solution at 30 drop/min into a solution composed of Na_2CO_3 , hydrazine (50% $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) and polyvinyl-alcohol (PVA, average molecular mass 1750 ± 50) with constant stirring, then keep the temperature of the reaction system in the range of $80 \sim 85^\circ\text{C}$ for 40 min with stirring. The precipitates were separated by a magnet from the parent solution. The wet powder was washed with distilled water and acetone 4~5 times respectively, then dried 2~3 h at about 50°C to obtain the resulting product. Phase analysis of the resulting product was determined with a Japan Rigaku D/Max-VA X-ray diffractometer, and the grain size was estimated by Scherrer formula in XRD patterns obtained by a long scan. Morphology, size and aggregation of the ultrafines were observed with a Japan Hitachi H-800 transmission electron microscope. Infrared spectra (KBr pellets) of the product powder were measured with a 170X FT-IR Infrared spectrometer. The amount of metals remained in the parent solution and in the product powder was determined by spectrophotometry using 2-(5-Bromo-2-pyridyl-

zo)-5-diethylamino-phenol (5-Br-PADAP) as a chromogenic reagent^[18].

3 RESULTS AND DISCUSSION

The reduction of Co^{2+} ions in an aqueous solution with hydrazine does not occur in fact under common condition although the attempted reaction is, in theory, thermodynamically allowed and quite exothermic ($\Delta G = -54 \text{ kJ/mol} < 0$). Gibson and his colleagues heated the reaction system to moderate temperature ($\leq 100^\circ\text{C}$), but it was still unsuccessful. At last, the reduction reaction was performed by the application of high-intensity ultrasound^[1]. In our opinion, since the reduction of Co^{2+} (aq)-hydrazine, which is exothermic, is permitted in thermodynamics, it is the matter about kinetic rate-control. The reaction should be completed by using not only high-intensity ultrasound but also other moderate reaction conditions. Our experiments show that metal cobalt ultrafine particles may be reduced from Co^{2+} (aq)-hydrazine system with moderate heating ($< 100^\circ\text{C}$) and stirring simultaneously. It should be pointed out that stirring is essential to reduction reaction process. Though the kinetic rate is relatively low at the beginning of the reaction, it is the situation that helps prepare anisometric cobalt nanoclusters. When PVA is added into the Co^{2+} - Ni^{2+} mixing solution with molar ratio 1:1 where the concentration of hydrazine, Na_2CO_3 , $\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ and $\text{Ni}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ are respectively 0.2, 0.05, 0.01, and 0.01 mol/dm³, fcc-Co-Ni alloy magnetic ultrafines with composition near Co50Ni50 are easily prepared. It is the presence of PVA that makes the stability and dispersion of alloy ultrafines increase, and the particle size does not increase rapidly with the storage life of the ultrafines. In addition, redispersion of the alloy ultrafines is easier than that of the conventional product. Table 1 lists the comparison for ultrafines obtained by co-reduction of solution in the presence of polymer (CR-SPP) and by some of reference methods. It is shown that the characteristics of ultrafines synthesized by this method are compatible with

Table 1 Comparison of ultrafines obtained by co reduction of solution in presence of polymer (CRSPP) and some reference methods

Method for preparation	Solution system	Ultrafines	Range of particle size/ nm	Reference
CRSPP	$\text{Co}^{2+} / \text{Ni}^{2+}$	fcc- Co50 Ni50	20 ~ 100	Present work
Gas evaporation	Co(metal)	fcc- Co	20	[8]
Sputter deposited	Fe/ Co(metal)	bcc- Fe(1 - x) Co x	100	[9]
Hydrazine-ultrasound	Co^{2+}	α Co	100	[1]
Polyol process	$\text{Co}^{2+} / \text{Cu}^{2+}$	fcc- Co xCu(100 - x) + α Co	100	[10]
Microemulsion	Co^{2+}	Co(no structure)	3 ~ 10	[11]
Inversed micelles	Co^{2+}	Co	1.8 ~ 4.4	[11]
Cryochemical synthesis	Co or $\text{Co}^{2+} / \text{Al}_2\text{O}_3$	Co or Co/ Al_2O_3	15	[12]
Ultraviolet radiation	Co^{2+}	Co	5 ~ 30	[13]
γ -ray irradiation	Co^{2+}	Co	20 ~ 30	[14]
Polyol process	$\text{Co}^{2+} / \text{Ni}^{2+}$	fcc- Co20 Ni80	300 ~ 1 400	[15]
Inversed micelles	$\text{Co}^{2+} / \text{Fe}^{2+} / \text{Cu}^{2+}$	Co- Fe- Cu	7 ~ 19	[16]
γ -ray irradiation	$\text{Co}^{2+} / \text{Ni}^{2+}$	fcc- Co x Ni(100 - x)	40 ~ 80	[17]

those of the same ultrafines by other methods both in morphology and distribution of the particle size. The additional advantages of the present way are simple preparation process, high yield and good stability.

However, two important factors should be paid attention to in this process. First, metal nickel has only a cubic system ($a = 0.35328 \text{ nm}$), but metal cobalt has both α Co with hexagonal system ($a = 0.364 \text{ nm}$) and ϵ Co with cubic system ($a = 0.35328 \text{ nm}$). α Co is generally formed by reduction in the aqueous solution containing pure Co^{2+} . However, when Co^{2+} and Ni^{2+} coexist in the same mixing aqueous solution, fcc- Ni, which is at first reduced according to priority of the redox potential of $\text{Co}^{2+} / \text{Co}$ (- 0.277 V) and $\text{Ni}^{2+} / \text{Ni}$ (- 0.246 V), will actually become the center of nucleation for Co particles growth. All these are analogous to what happened in the polyol reduction process of Co^{2+} doped Pd^{2+} or Ag^{+} [19]. Second, even though co reduction reaction above is completed in the optimum conditions, elemental analysis indicates that the composition of the ultrafines obtained in the Co^{2+} - Ni^{2+} mixing solution with 1:1 molar ratio is Co46Ni54 approaching to ideal Co50Ni50, which is attributed to the tiny difference between the redox potential of Co^{2+} and Ni^{2+} .

It should be emphasized that characteristics of product powder is affected by the amount of PVA. Table 2 demonstrates the effect of the PVA amount on the particle size, composition and stability of alloy ultrafines. Fig.1 shows X-ray diffraction patterns of alloy ultrafines with different amounts of PVA. It is noticed that the diffraction peaks are obviously broadened, thus the crystalline grain size estimated by Scherrer formula decreases with increasing PVA concentration in the reaction system. This means that PVA in the powder is capped on the surface of the particles to prevent the ultrafine particles from further aggregation. Fig.2 shows the morphology and selected area ED pattern for the particles obtained by redispersion of sample C in TEM analysis. The latter clearly indicates that Co50Ni50 alloy ultrafine particles show fcc structure, but some of them have a tendency of anisotropic growth. This result agrees with TEM morphology analysis of particles. The size of most of the particles is less than 30 nm, and the size of a few particles relatively large, but not larger than 100 nm. In practice, some larger particles are observed to be composed of many small particles, and the surface of all particles is covered by a layer of PVA which has a relatively weak TEM contrast. This is consistent with the IR spectra analysis. It is also noticed that there

with a composition nearly Co50Ni50 prepared by hydrazine co-reduction in the presence of protectant PVA from Co^{2+} - Ni^{2+} mixed aqueous solution have an excellent stability. Sample C was ever stored at common environment for 30 d, then was thermally treated at 150 °C and 300 °C in the air. The experiment indicates that the XRD patterns of the treated samples are nearly completely similar to Fig.1C, only the particle size of the treated ultrafines increases to some extent.

4 CONCLUSION

Metallic ultrafines were prepared by reduction reaction of Co^{2+} -hydrazine aqueous solution, which does not occur in the ordinary conditions. The magnetic alloy ultrafines with a composition nearly Co50Ni50 were synthesized from Co^{2+} - Ni^{2+} mixed aqueous solution with molar ratio 1:1, and PVA as polymer protectant that coexists in the solution plays an important role in the increasing dispersion of system and stability of alloy ultrafines and decreasing grain size of ultrafines. The morphology by TEM and IR spectra indicate that PVA was absorbed on the surface of alloy ultrafine particles to form a thin PVA layer, and complex particles were constituted.

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is some difference between the crystalline grain size estimated by Scherrer formula and the particle size measured by TEM. The latter suggests a certain extent coalescence of the particles because supersonic equipment used for dispersion for magnetic materials is not very effective due to magnet interaction. It is very interesting that α Co XRD peaks (marked by * in Fig.1 D) appear when PVA concentration increases too much. Maybe fcc Ni as a cubic crystal nucleation is excessively covered by a relatively high concentration of PVA to prevent Co from crystallizing on the surface of Ni. Fig.3 shows the change of FT-IR spectra of the samples with different PVA concentration. From this figure it can be seen that characteristic absorption bands of PVA are observed at 3 400, 1 400, and 1 100 cm^{-1} , and the first and third bands are assigned to the O-H and C-O stretching vibration of PVA and second to the C-H deformation vibration of PVA. All these intensities of the bands increase

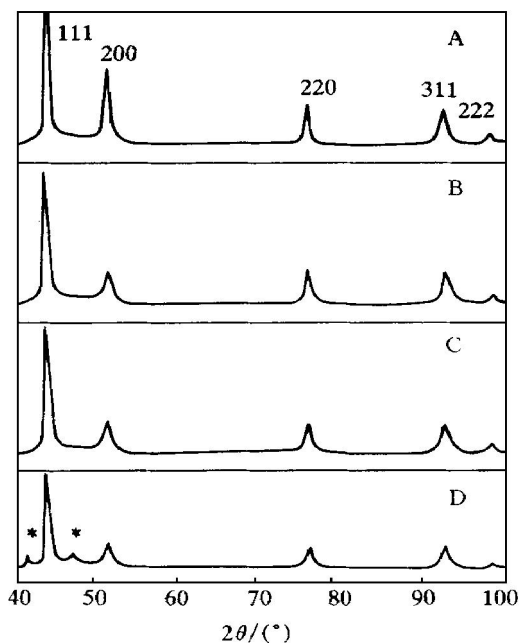


Fig.1 X-ray diffraction patterns of Co50 Ni50 alloy ultrafines obtained by different PVA amounts (Illustration of samples A ~ D are shown in Table 2.)

Table 2 Effect of PVA amount on average grain size and stability of Co50 Ni50 alloy ultrafines

No.	Mole ratio of PVA and ($\text{Co}^{2+} - \text{Ni}^{2+}$)	Average grain size/ nm	PVA in Co50 Ni50 alloy ultrafines / %	Stability
A	0	20	0	Poor
B	0.86	15	8.1	Good
C	1.43	10	12.7	Good
D	1.71	10	11.1	Good

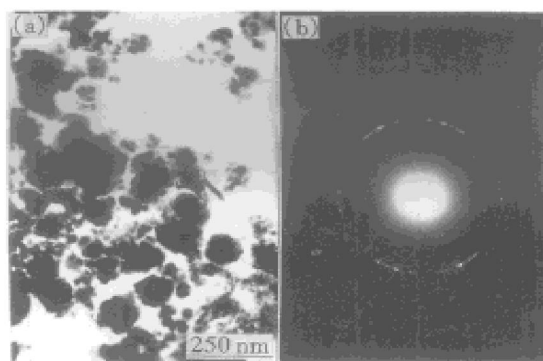


Fig.2 TEM analysis of Co50 Ni50 alloy ultrafines (sample C) protected by PVA (a) — Morphology; (b) — Electron diffraction

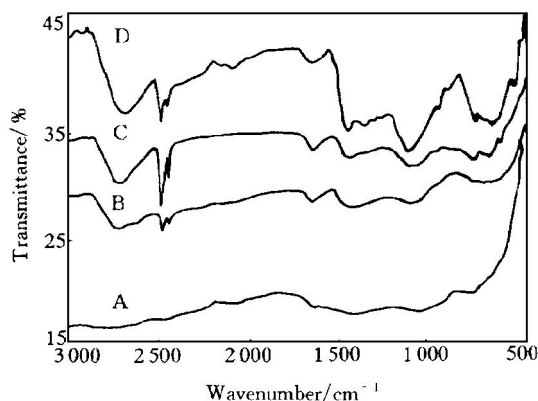


Fig.3 Infrared spectra of Co50 Ni50 alloy ultrafines obtained by different PVA amounts (Illustration of samples A ~ D are shown in Table 2.)

with increasing PVA concentration.

In summary, the magnetic alloy ultrafines