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Preparation of pure nickel, cobalt, nickel–cobalt and nickel–copper alloys by hydrothermal reduction

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Reduction of aqueous $NiSO_4$, $CoSO_4$ and $CuSO_4$ with hydrazine has been investigated systematically to obtain ultrafine powders of pure nickel and cobalt, and of nickel–cobalt and nickel–copper alloys. The results show that the pH value and the temperature are the key factors to influence the reactions. When $pH \geqslant 10.0$ and the temperature is higher than 85 °C, pure nickel particles are obtained. Pure cobalt, and nickel–cobalt and nickel–copper alloy powders can be formed only when $pH \geqslant 13$ and the temperature is above 120 °C. The mechanism for the formation of powders of nickel and cobalt, and of nickel–cobalt and nickel–copper alloys is discussed. The XRD patterns reveal that the as-synthesized pure cobalt is the hexagonal phase (h.c.p.), the pure nickel is the cubic phase (f.c.c.) and the $Co_{1-x}Ni_x$ and $Cu_{1-x}Ni_x$ alloys are the f.c.c. phase only when the ratio of Ni to Co is above 1 : 1 and Ni : Cu is below 1 : 9, respectively.

Introduction

Much attention has been paid to fine powder materials due to their unique mechanical, physical and chemical properties compared with conventional polycrystalline materials. It has been shown that many kinds of nanocrystalline metals, intermetallic compounds and alloys exhibit a relatively large increase (4–5 times) in strength and/or hardness with reduction of the grain size to the nanoscale.[1] They have been widely used in metallurgical and ceramic processing and electronics applications. It has been reported that nickel and cobalt nanometer materials and their alloys have some applications in hydrogen evolution reactions as coating electrodes, catalysts for N_2O decomposition and organic synthesis.[2–4] Cu–Ni bimetallic film displays composition-modulated[5,6] and giant magnetoresistance effects.[7] Recently, increasing interest has been shown in preparing and processing metals and alloys. Many methods exist for their preparation, including vapor deposition, solid state milling and solution chemistry. Unfortunately however, straightforward syntheses leading to nanostructured powders of nickel, cobalt, nickel–cobalt and nickel–copper alloys are rare. Gibson *et al.*[8] reported that anisometric cobalt nanoclusters were obtained by sonication of aqueous Co^{2+} and hydrazine. A polyol process has been developed to synthesize finely dispersed bimetallic Co–Cu nanocomposite powders.[9] Ni–Cu alloys have been prepared by vapor deposition.[10]

Experimental

10 M aqueous hydrazine solution (10 ml) was added to 200 ml of a 0.05 M aqueous MSO_4 (M = Co, Ni) solution. In order to investigate the influence of temperature on the reaction, the pH value was adjusted and kept in the ranges 10.0–12.0 for Ni^{2+} and 13.0–14.0 for Co^{2+}. The temperature was kept constant in order to obtain information about the effect of the pH of the reaction mixture.

To obtain alloys, 10 M aqueous hydrazine solution (10 ml) was mixed with 200 ml of a 0.05 M ($[Ni^{2+}]+[M^{2+}]=0.05$, M = Co or Cu) aqueous solution of $NiSO_4$ and $CoSO_4$ (or $CuSO_4$) with the molar ratio of $NiSO_4$ to $CoSO_4$ varying from 1 : 2 to 4 : 1 and that of $NiSO_4$ to $CuSO_4$ from 1 : 4 to 1 : 9. The resulting mixture was poured into a Teflon-lined autoclave which was kept at 150 °C for 3 h.

All reagents were analytically pure. The pH value of the solution was adjusted with Na_2CO_3 and NaOH. All products were washed with distilled water and then absolute alcohol. The compositions of the alloys were determined by chemical titration analysis. X-Ray powder diffraction (XRD) patterns were obtained using a Rigaku D/max-rA X-ray diffractometer with graphite monochromatized Cu-Kα radiation ($\lambda = 1.5418$ Å). The accelerating voltage was set at 50 kV with a scanning rate of $0.05^\circ\ s^{-1}$. Transmission electron microscopy (TEM) was performed with a Hitachi Model H-800 transmission electron microscope using an accelerating voltage of 200 kV and a tungsten filament.

Results and discussion

It was found that the formation of nickel and cobalt fine powders by the reduction of Ni^{2+} or Co^{2+} with hydrazine needs different conditions. Both metals form complexes with hydrazine at ambient temperature.[11] These complexes, $[Ni(N_2H_4)_3]^{2+}$ and $[Co(N_2H_4)_3]^{2+}$, are very stable in alkaline systems at room temperature, but with increasing temperature the stability of the complexes decreases. When the temperature reaches a critical point, they decompose to form the pure metals.

$$2[Co(N_2H_4)_3]^{2+} + 4OH^- \rightarrow 2Co(s) + N_2(g) + 4H_2O + 5N_2H_4 \qquad (1)$$

$$2[Ni(N_2H_4)_3]^{2+} + 4OH^- \rightarrow 2Ni(s) + N_2(g) + 4H_2O + 5N_2H_4 \qquad (2)$$

It was found that when the pH of the reaction mixture was over 10.0 and the temperature was higher than 85 °C, pure f.c.c. nickel particles could be obtained. Fig. 1(a) shows the XRD pattern of the obtained Ni sample. When the pH was 14 and the temperature was only 90 °C, the resulting product was a mixture of Ni and $Ni(OH)_2$ [Fig. 1(c)]. Pure cobalt particles were obtained when the pH value and temperature were elevated to 13 and 120 °C, respectively, furthermore only h.c.p. cobalt powders were obtained [Fig. 1(b)]. The difference in the formation conditions (pH and temperature) between the two metals might be explained by the fact that the complex $[Co(N_2H_4)_3]^{2+}$ is more stable than $[Ni(N_2H_4)_3]^{2+}$.

For the preparation of nickel–cobalt alloy powders, the

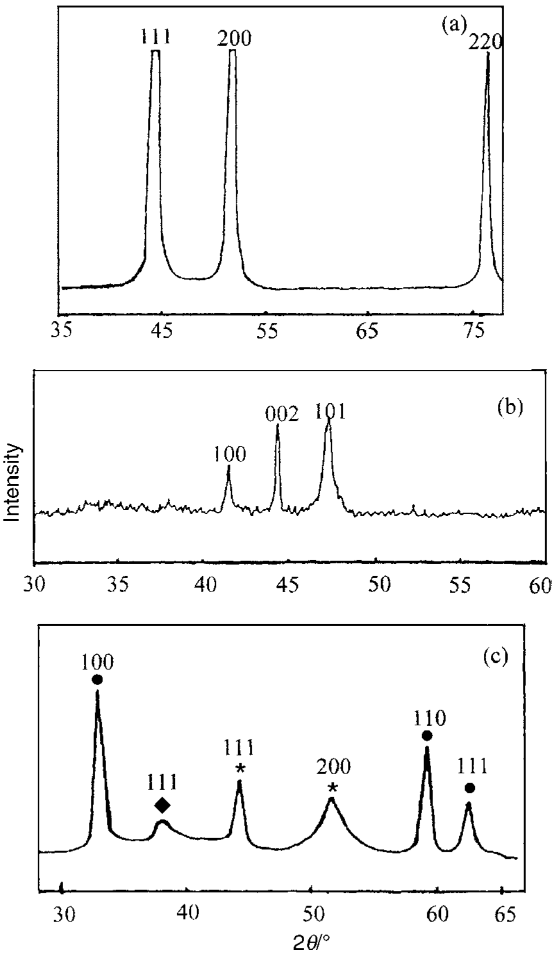

Fig. 1 XRD patterns of nickel and cobalt metal prepared under various conditions. (a) f.c.c. nickel prepared at pH 10.0 with a temperature of about 95 °C. (b) h.c.p. cobalt prepared at pH 14.0 with a temperature of about 180 °C. (c) Nickel and $Ni(OH)_2$ mixture prepared at pH 14.0 with a temperature of about 90 °C. $AgNO_3$ was used to induce nucleation: * Ni, ● $Ni(OH)_2$, ◆ Ag.

experimental conditions should satisfy the common requirements for the formation of Co and Ni metal ($pH > 13$; $T > 120$ °C). The results show that raising the reaction temperature can not only improve the solubility of $Ni(OH)_2$ but also accelerate the rates of the reactions, until the reaction rates of nickel and cobalt are comparable. The temperature of 180 °C and the pH value of 14 were favored in our experiments to prepare the alloy powders.

Fig. 2 shows the XRD patterns of the Ni–Co alloys. It is significant to note that when the nickel : cobalt ratio is above 1 : 1, the products are pure f.c.c. phase alloys [Fig. 2(c)]. As we discovered, samples with different Ni : Co ratios all have the same diffraction peaks, which were used for the calculation of lattice parameters by a computer program.[12] The calculation results are shown in Table 1. The mean value of lattice parameter (1) is a little smaller (0.4%) than the literature value for f.c.c. cobalt (3.5447 Å). Similarly, the mean value of lattice parameter (2) shows only a 0.02% deviation from the literature value of f.c.c. nickel (3.5238 Å), which seems to provide evidence for the existence of pure f.c.c. alloy.

Thus it can be inferred that the whole reaction proceeds through two steps: mono-reduction of Co^{2+} and co-reduction of Ni^{2+} and Co^{2+}. As the reduction of Ni^{2+} is easier than Co^{2+}, nickel nucleates first when the reaction begins, then cobalt is reduced and precipitates with nickel on the preformed nickel nuclei. The f.c.c. nickel dopant stabilizes the f.c.c. phase of cobalt and the cobalt–nickel alloy is produced. Such speculation is further supported by the observation that when the nickel–cobalt ratio is 1 : 2, h.c.p. cobalt appears with the f.c.c. alloy (Fig. 3). A possible explanation is that when all the Ni^{2+} has been consumed to form alloy, some amount of Co^{2+} remains which forms h.c.p. cobalt, the more stable phase without the stabilization of nickel at the reaction temperature. The phase transition temperature of cobalt (from f.c.c. to h.c.p.) is about 420 °C,[13] which is greatly lowered to 180 °C in our experiment. The h.c.p. phase stabilization in the cobalt samples may be related to the hydrothermal conditions. The reason for the occurrence of h.c.p. phase cobalt in this system is not clear, further studies are needed to investigate this question.

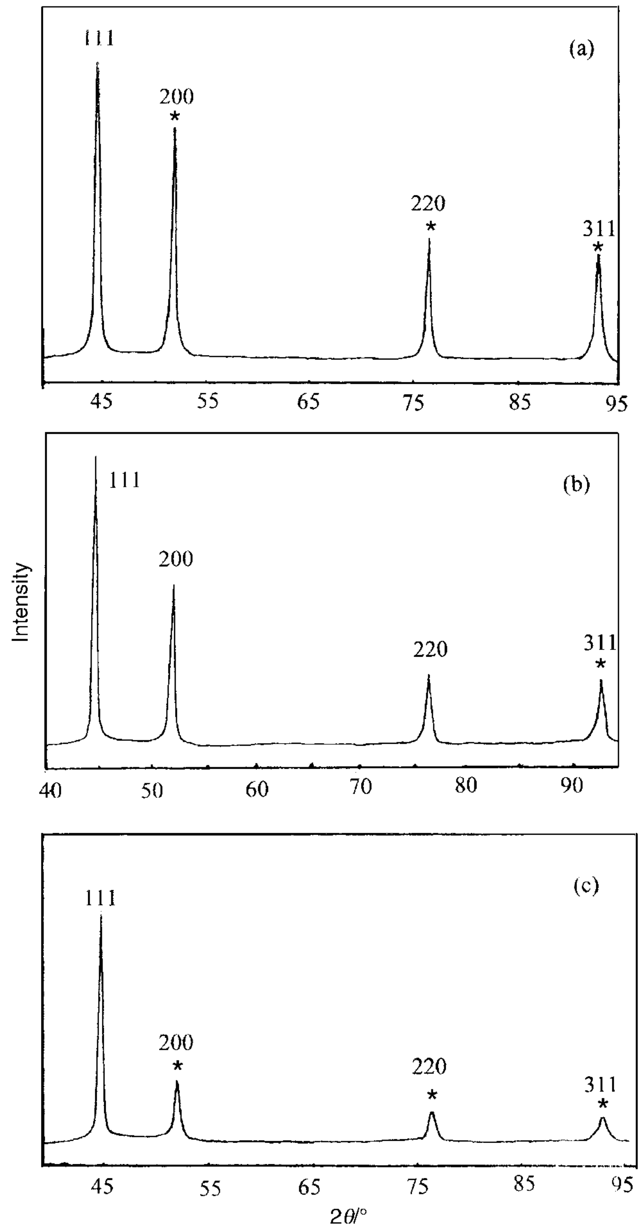

Fig. 2 XRD patterns of synthesized alloys with different initial Ni : Co ratios. (a) Initial Ni : Co ratio 4 : 1. (b) Initial Ni : Co ratio 2 : 1. (c) Initial Ni : Co ratio 1 : 1 (* split peak).

Table 1 Lattice parameters calculated from XRD peak splitting

	Initial Ni : Co ratio		
	2 : 1	4 : 1	Mean value
Lattice parameter (1)/Å	3.5305	3.5307	3.5306
Standard deviation (1)	1.1×10^{-4}	4.1×10^{-4}	—
Lattice parameter (2)/Å	3.5242	3.5218	3.5230
Standard deviation (2)	1.4×10^{-4}	7.0×10^{-5}	—

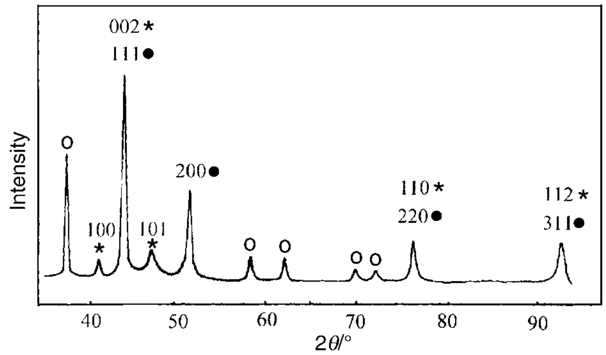

Fig. 3 XRD pattern for the mixture of products prepared with an initial Ni : Co ratio of 1 : 2. * h.c.p. cobalt, ● f.c.c. Co–Ni alloy, ○ $Ni(OH)_2$.

TEM images (Fig. 4) of the Ni–Co alloy show that the particle size distribution varies over a wide range, from tens of nanometers to several hundreds.

For the Ni–Cu alloy, XRD data show that when the starting Ni : Cu ratio was 1 : 9, only copper–nickel alloys were formed [Fig. 5(a)], but when the starting ratio of nickel to copper was raised to 1 : 4, the product was a mixture of a small amount of pure Ni and the alloys [Fig. 5(b)]. Since the lattice parameter mismatch between copper and nickel is about 2.3%, the alloy diffraction peaks can be distinguished from the pure metals. The lattice parameter of the alloys is 3.613 Å, calculated from the XRD patterns, which is close to that of pure Cu (3.615 Å), this shows there is little nickel in the alloy.

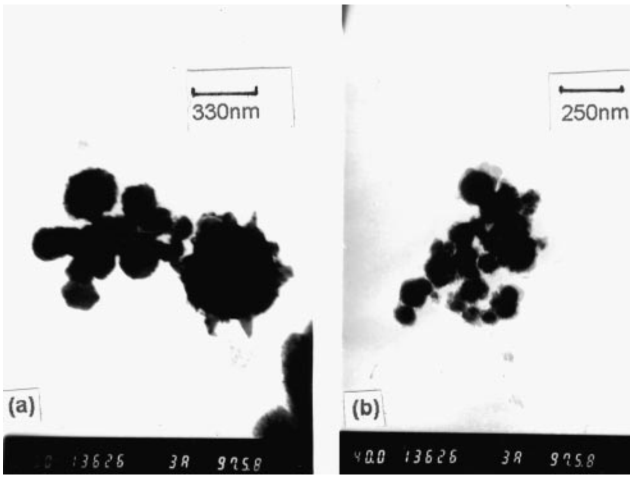

Fig. 4 TEM images of products prepared with different initial Ni : Co ratios. (a) Ni : Co ratio 2 : 1 (mixture of f.c.c nickel and f.c.c. alloy). (b) Ni : Co ratio 1 : 2 (mixture of h.c.p. cobalt and f.c.c. alloy).

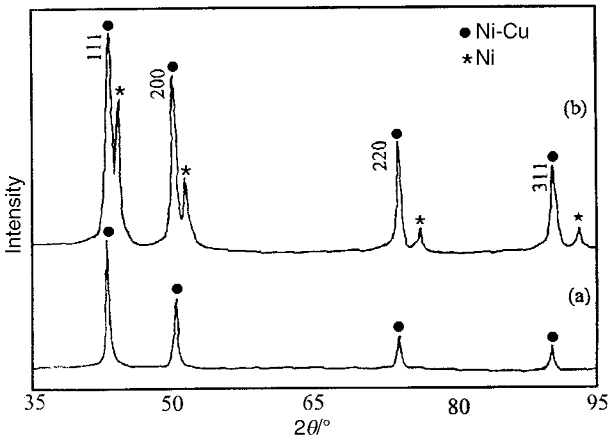

Fig. 5 XRD pattern of Ni–Cu alloy. (a) Ni–Cu alloy prepared from the initial Ni : Cu ratio 1 : 9. (b) Ni–Cu alloy prepared from the initial Ni : Cu ratio 1 : 4.

Since the reduction potential of nickel is higher than that of copper ($E^{\circ}_{\mathrm{Cu(OH)_2/Cu}} = 0.224$ V), the copper(II) ion can be reduced more easily than the nickel(II) ion. In order to obtain nickel–copper alloy, the first problem is to control the experimental conditions such that they are optimal for the reduction of nickel and copper simultaneously. We obtained the co-reduction products by controlling the starting pH value at 12–13 and choosing 150 °C as the reaction temperature. These parameters were employed in order to accelerate the reduction rate of nickel and to force concurrent reduction of nickel and copper.

The second problem is to find the optimal ratio of nickel to copper for the Ni–Cu alloy, since the lattice parameter mismatch between nickel and copper is about 2.3%. Our results show that only when the ratio of Ni to Cu was 1 : 9 or less, was a pure nickel–copper alloy phase produced.

Conclusion

Using hydrothermal reduction to prepare fine powders of nickel and cobalt, and of nickel–cobalt and nickel–copper alloys, we arrive at the following conclusions.

1. Straightforward preparation of these materials at moderate reaction temperatures has been demonstrated.

2. Pure nickel particles can easily be obtained when $\mathrm{pH} \geqslant 10.0$ and $T \geqslant 85$ °C. However, the pure cobalt and nickel–cobalt alloy powders can only form when $\mathrm{pH} \geqslant 13$ and $T \geqslant 120$ °C. This is explained by the proposed mechanism.

3. Reduction of mixtures containing different ratios of nickel to cobalt has been investigated in detail. When the ratio is over 1 : 1 f.c.c. Ni–Co alloy can be obtained, but h.c.p. cobalt fine powders form with the f.c.c. Ni–Co alloy particles if the ratio is below 1 : 1.

4. Reduction of mixtures containing different ratios of nickel to copper has been investigated in detail. Only when the ratio is below 1 : 9 is the Ni–Cu alloy obtained.

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