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Preparation of micron size copper-silver bimetallic powders

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Abstract

Spherical silver-rich copper-silver bimetallic powders having a uniform size of 0.6 ~ 0.8 μm have been synthesized with the two-stage reduction method. Ascorbic acid was first applied as reducing agent to control the formation rate of nuclei and growth rate of particles effectively, and then hydrazine hydrate was used to reduce metal completely. When pH value of reductive solution was stably controlled in the range of 7 ~ 8, non-agglomerated mono-dispersed silver-rich Cu-Ag bimetallic particles with smooth surface and uniform size were synthesized. With increasing silver content in powders, the particle size and dispersibility of bimetallic powders decreased and increased, respectively. The XRD and thermal analyzer were employed to analyze as-prepared bimetallic powders.

Key words: copper-silver bimetallic powders, chemical reduction, ascorbic acid, hydrazine hydrate

1. Introduction

Fine metal particles with controlled shape and size find extensive application in various fields (ferromagnetic metal particles for high density recording material, silver or copper particles for conductive inks and pastes used in the electronic industry [1–4]). Some of these applications require non-agglomerated metal particles in the micrometer or submicron size range with a narrow size distribution.

When a metal is associated with another metal in bimetallic or alloy form, the properties of the resulting material can be enhanced with respect to those of the pure metals [5]. This is the case for copper-silver bimetallic catalysts, which offer improved higher catalytic activity [6] and selectivity [7] compared with silver alone in the direct epoxidation of ethylene. It is well known that ageing of quenched concentrated Ag-Cu alloys leads to large hardness increase [8].

Many methods have been developed to prepare bimetallic powders. Copper and silver ions in aqueous solution were reduced with chemical reduction method to obtain Cu-Ag particles [9]. Deshpande prepared Ag-Pd powder by co-precipitation technique, and investigated its lead-free conductive thick film [10]. Thermally induced chemical reduction of a mixture of Cu (II) and Ni (II) species in ethylene glycol produces bimetallic Ni-Cu powders [11]. Wu reported that, starting from solid solution powder precursors, $Cu_{50}Ag_{50}$ nanocomposites can be synthesized by milling at elevated temperature or by thermal annealing [12]. In our other work, the copper-rich copper-nickel bimetallic particles were synthesized with chemical reduction method, and their application in microelectronics was studied [13]. From the practical point of view, the method of chemical reduction from aqueous solution is most preferable for obtaining ultra fine copper silver bimetallic powder.

In this paper, we present results on the synthesis of Ag-Cu bimetallic powders with co-precipitation technique. Bimetallic Ag-Cu powders were characterized by X-ray diffraction, thermal analysis and scanning electron microscopy coupled with energy dispersion X-ray for microanalysis.

2. Experimental

2.1. Preparation of Cu-Ag bimetallic powders

All chemicals of reagent grade quality were used

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without further purification. Copper-silver powders were obtained by reaction of mixture of $[Cu(NH_3)_4]^{2+}$ complex and $[Ag(NH_3)_2]^{+}$ complex with reducing agent. In a typical preparation of copper-silver bimetallic powders having a composition of $Cu_{42}Ag_{58}$, firstly, 11.2 g $AgNO_3$, 12 g $CuSO_4 \cdot 5H_2O$ and 50 ml aqua ammonia was mixed, and diluted to 400 ml. The solution was added dropwise during 60 min to a stirred 400 ml solution containing 16.8 g ascorbic acid and dispersion agent, and then hydrazine hydrate was added in solution so that the reduction of metallic ion was completely achieved. The temperature was kept 60 ∼ 70 ℃, and aqueous ammonia was employed to control pH value. The metallic powders were recovered from the solution, washed and dried.

2.2. Characterization

Direct observations of the powders were analyzed by scanning electron microscopy (SEM) on a XL30δDX-4i (Philips). The aggregate size (D_{50}) and the standard deviations were estimated by image analysis of laser size distribution analyzer (LS230). The crystal structure was characterized by X-ray diffraction. Thermogravimetry (TG) and differential thermal analysis (DTA) were carried out at scanning rates of 5 ℃/min in a flowing air atmosphere. The purity of powder was determined with inductively-coupled plasma spectrometer (ICP) (PE Optima 3000).

3. Results and discussion

3.1. Basic chemical reaction and choice of reducing agent

To obtain ultra fine copper-silver bimetallic powders, two-stage reducing process was employed. $[Cu(NH_3)_4]^{2+}$ complex and $[Ag(NH_3)_2]^{+}$ complex were reduced by ascorbic acid, which has a mild reduction power, to obtain mixture of silver, copper and cuprous oxide in the first step, and then the mixture was processed with a powerful reducing agent such as hydrazine hydrate to obtain bimetallic copper-silver powder particles in the second step. In this process, the following chemical reaction occurred:

$$2[Ag(NH_3)_2]^{+} + C_6H_8O_6 \rightarrow \rightarrow 2Ag + C_6H_6O_6 + 2NH_4^{+} + 2NH_3, \quad (1)$$

$$2Cu(OH)_2 + [Cu(NH_3)_4]^{2+} + 2C_6H_8O_6 \rightarrow \rightarrow Cu + Cu_2O + 2C_6H_6O_6 + 3H_2O + 2NH_3 + 2NH_4^{+}, (2)$$

$$Cu_2O + N_2H_4 \cdot H_2O \rightarrow \rightarrow 2Cu + N_2 + H_2 + 2H_2O. \quad (3)$$

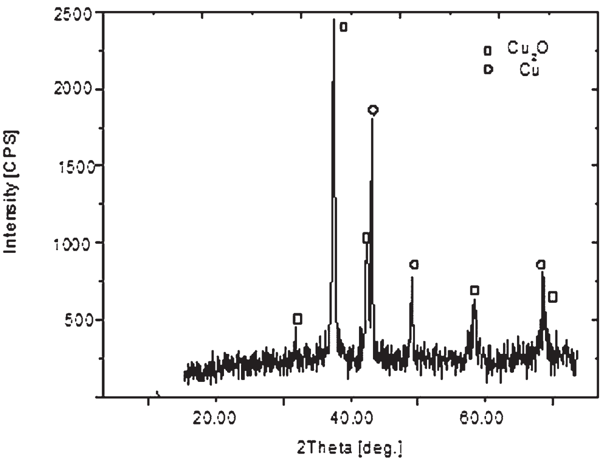

Fig. 1. XRD spectrum of powders prepared by $[Cu(NH_3)_4]^{2+}$ complex and ascorbic acid.

$CuSO_4 \cdot 5H_2O$ solution and aqueous ammonia were mixed to obtain stable $[Cu(NH_3)_4]^{2+}$ complex prior to reacting with ascorbic acid, and then the solution containing stable $[Cu(NH_3)_4]^{2+}$ complex was added into reductive solution with pH 6.5. The reaction occurred after 30 minutes in the higher temperature range from 80 ℃ to 90 ℃ and the blood-red powders were obtained, whose XRD spectrum is given in Fig. 1. From Fig. 1 it is obvious that the diffractogram exhibits the characteristic peaks of crystalline metallic copper (fcc) $\cdot$ d (Å) = 2.0891, 1.8091, 1.2787 (respectively) and the characteristic peaks of cuprous oxide d (Å) = 2.4623, 2.1291, 1.5074, which are very close to those given by JCPDS (d (Å) = 2.465, 2.135, 1.510). The XRD pattern indicated that the powders prepared by reaction of $[Cu(NH_3)_4]^{2+}$ complex and ascorbic acid were a mixture containing pure copper and cuprous oxide. The reasonable explanation for it is that $[Cu(NH_3)_4]^{2+}$ complex is more difficult to be reduced than $CuSO_4$ in this system. It is very necessary to apply hydrazine hydrate for reducing metallic copper-silver powders completely.

XRD spectrum of as-prepared copper-silver bimetallic powders of $Cu_{41}Ag_{59}$ is given in Fig. 2. The XRD pattern shows the characteristic reflection of copper at 43.28° and 50.36° related to the (111) and (200) planes, respectively, which are very close to those of pure copper powders prepared by the same method and standard pattern (JCPDS file 4-0836).

However, the XRD pattern shows the characteristic reflection of silver at 38.22, 45.36, 64.80 and 77.56, respectively, corresponding to the (111), (200), (220) and (311) planes. They all are shifted to high 2θ comparing with those of the pure silver powders prepared by as-method, whose characteristic reflections were at 38.14, 44.30, 64.46, and 77.44, respectively (JCPDS file 4-0783). The diffraction lines of Cu-Ag bimetallic powders became relatively broader than those of

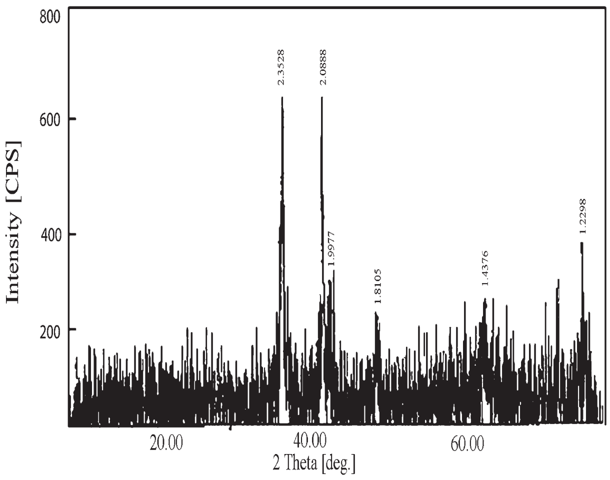

Fig. 2. XRD spectrum of Cu-Ag bimetallic powders.

single metal. This line broadening suggests that there is a little variation in composition within a particle or among particles. The peaks are shifted to higher 2θ values indicating a contraction in the Ag lattice as a result of the substitution of Ag by Cu. Alloying of silver-copper particles proceeds in the case of the sample. It was reported that the most intense Ag-Pd diffraction peak was located at a 2θ position between the positions where the most intense peak occurred for pure Ag and Pd metal in the literature for alloy [10].

In the course of reaction, addition of dispersed mixtures of $[Cu(NH_3)_4]^{2+}$ and $[Ag(NH_3)_2]^+$ complex droplet into the dispersed ascorbic acid is important. The aforehand experiment showed that $[Ag(NH_3)_2]^+$ complex was more easily reduced than $[Cu(NH_3)_4]^{2+}$ complex in this reaction system. It can be generally accepted that, firstly, silver nuclei appeared, secondly, copper was reduced and deposited on the silver nuclei to form silver-rich primary particles, thirdly, primary particles aggregated to larger final products. The dispersibility of powder can be expressed in the following Eq. (4):

$$R = D_{50}/d. \tag{4}$$

In Eq. (4), D_{50} is the aggregate size of powders by laser size distribution analyzer (LS230), and d is an average particle diameter by SEM analysis. Generally speaking, the smaller the R value is, the better is the dispersibility.

When hydrazine hydrate was directly employed to reduce the mixture of $[Cu(NH_3)_4]^{2+}$ and $[Ag(NH_3)_2]^+$ complex, particle size of the copper-silver bimetallic powders was small to 0.1 ~ 0.3 μm as given in Fig. 3a. However, the aggregate size (D_{50}) of powders was up to 1.04 μm. The high R value of 5 shows that the dispersibility of powders is terrible. Because of the high reductive power of hydrazine hydrate in aqueous ammonia media, the reductive reaction occurs at a quite rapid speed so that it is very difficult to prevent the powders from coming together. In the two-stage reduction process, ascorbic acid was first applied to control the formation rate of nuclei and growth rate of particles effectively. Figure 3b shows that spherical non-agglomerated monodispersed copper-silver powder particles were synthesized. The particle size was uniform in the range of 0.7 ± 0.1 μm, and the shape of particles was spherical. The aggregate size (D_{50}) of powders was 1.7 μm. The low R value of 2.5 shows that the dispersibility of powders is excellent.

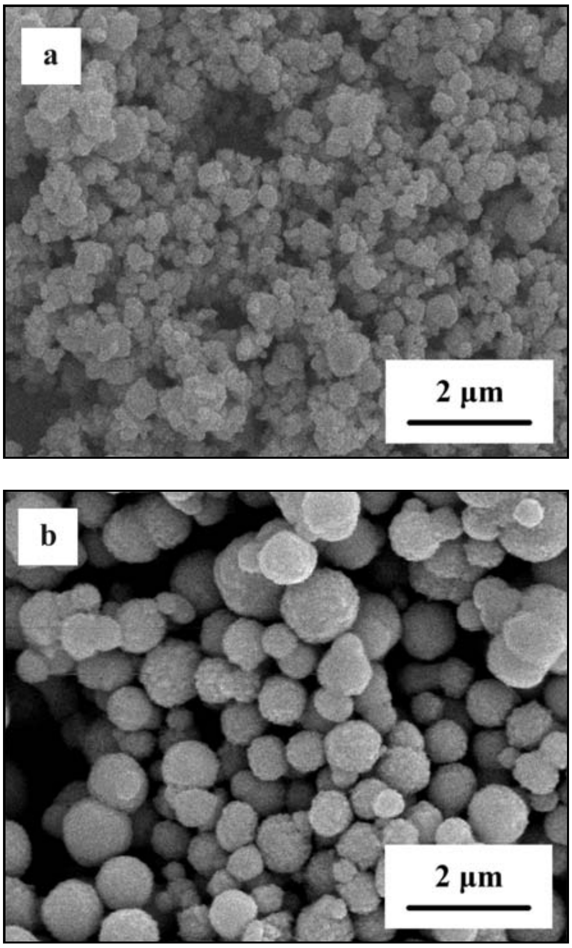

Fig. 3. SEM photographs of copper-silver bimetallic powder using (a) hydrazine hydrate, and (b) ascorbic acid in the first stage and hydrazine hydrate in the final stage, as reducing agent.

For preparing fine powder with chemical reduction method, it is very important to choose an appropriate dispersion agent. In our other works, a polymer surfactant was employed to prepare micron size, monodispersed nonagglomerated silver powder particles with a uniform size of 1 ~ 2 μm [1]. Inor-

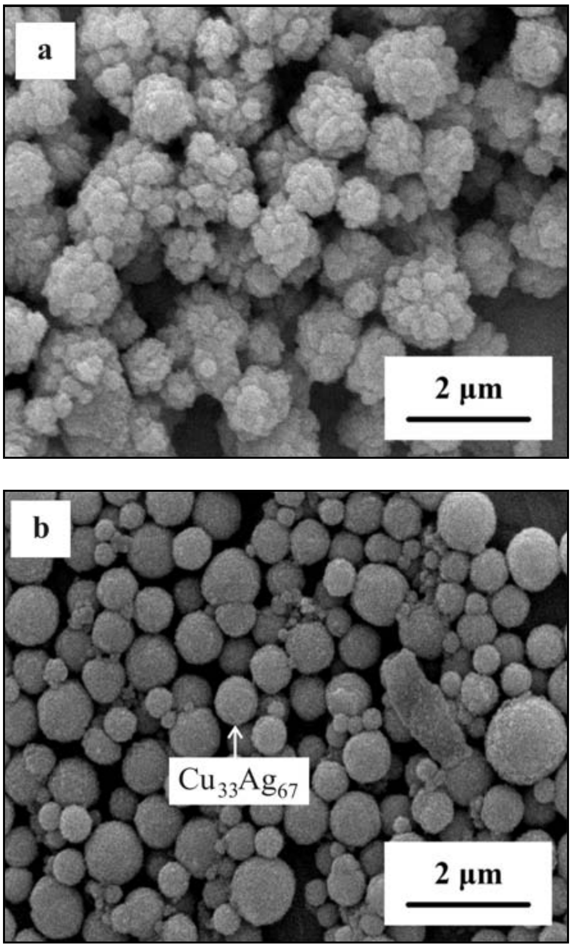

Fig. 4. Influences of pH value on copper silver bimetallic powders: (a) pH 3, (b) pH 7.

ganic surfactant was used to make micron size copper powders having a particle size of 2.5 ± 0.3 μm [2]. Nature polymer surfactant, for example gelatin, was also applied to synthesize the ultra fine silver coated $BaTiO_3$ composite powders [14]. In this work, we choose the modified starch as a protective agent.

3.2. Influence of pH value on powder particles

Influence of pH value on the reduction power of ascorbic acid was obvious. According to Eq. (5), the potential decreased with an increasing pH value. It showed the increase in reduction power of ascorbic acid.

$$C_6H_6O_6 + 2H^+ + 2e = C_6H_8O_6,$$

$$E^\theta = 0.08V \ (\mathrm{pH} = 6.4),$$

$$E = E^\theta - 0.059\mathrm{pH}. \qquad (5)$$

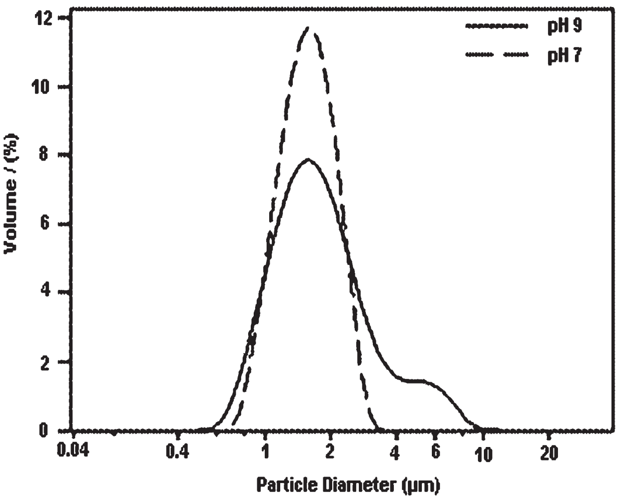

Fig. 5. Size distribution pattern of bimetallic powders prepared with different pH value.

In addition, the existing states of silver ion and copper ion depend on the pH value in aqueous ammonia media. Influences of the two above-mentioned factors on powder particles having a composition of $Cu_{30}Ag_{70}$ were investigated.

In order to obtain monodispersed particles, a general condition must be fulfilled: nucleation and growth must be two completely separated steps [15]. To obtain a definite separation between the nucleation and growth steps, the homogeneous nucleation can be replaced by heterogeneous nucleation by seeding the reactive medium with foreign nuclei.

When pH value of reductive solution was less than 5, the metallic ions existed in the form of Cu^{2+} and Ag^+, which could be directly reduced to metallic copper and silver by ascorbic acid as given in Fig. 4a. From this photograph, one can see that the surface of powder particles was fairy rough. Because the difference of potential between copper and silver was large when the pH value was 3, formation of nuclei and growth proceeded simultaneously, as a result, junior nuclei were adsorbed on the particles to form the rough surface. It is very difficult to prevent particles from agglomerating according to the same reason. However, when pH was stable at 7, the potential of copper was very close to that of silver because of complexing effect. Formation of nuclei and growth of particles occurred in completely separated stage, as a result, the non-agglomerated monodispersed spherical silver particles were synthesized as shown in Fig. 4b. The majority of particles have a diameter of 0.7 ± 0.1 μm. The aggregate size (D_{50}) of powders was 1.5 μm as exhibited in Fig. 5, which shows a normal and narrow size distribution. The low R value of 2 indicates very good dispersibility of powders. The microstructure of particle signed in Fig. 4b was analyzed by EDX.

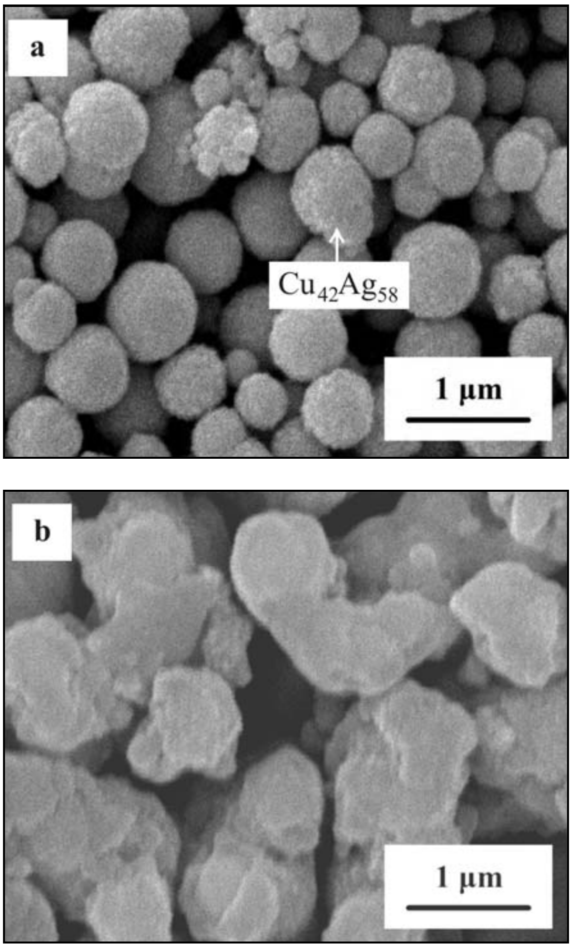

Fig. 6. Influence of copper content on copper-silver bimetallic powder particles. Copper content (mol %) = 42 (a), 80 (b).

The results show that the composition of particle was $Cu_{33}Ag_{67}$, which is very close to that by XRD analysis. When pH value increased to 9, the reductive power of ascorbic acid increased so that the dispersibility of powders decreased. Figure 5 shows that the size distribution of bimetallic powders prepared at pH 9 was broader than that synthesized at pH 7, and had a distinct tailed peak, which implied a degree of agglomeration.

3.3. Influence of copper content on powders

In the process of alloying, copper enters silver lattice and substitutes silver. According to phase diagram of Cu-Ag alloy, silver-rich bimetallic solid solution or copper-rich bimetallic solid solution is easily formed with chemical reduction method. Influence of copper content on Cu-Ag bimetallic powder particles was investigated. Non-agglomerated monodispersed silver-rich Cu-Ag bimetallic powder particles have a spherical shape and uniform size of 0.7 μm as being observed in Fig. 6a. The size distribution pattern of as-powder shows excellent symmetry. The aggregate size (D_{50}) of powders is low to 1.1 μm. The very low R value of 1.5 indicates excellent dispersibility. The bimetallic powders have a specific area of 1.5 m^2 g^1 and tap density of 3.8 g cm^{-3}. With an increasing copper content in Cu-Ag bimetallic powders, the particle size increased, however, agglomeration of particles became serious simultaneously, i.e. the dispersibility of powder decreased. Surface of particles was rough due to large amount of small particles adsorbed on the large particles surface as the copper mol content varied in the range from 50 to 70 %. When the copper content was up to mol % 80, the surface of copper-rich Cu-Ag bimetallic powder particles became smooth, and several particles agglomerated to form irregular larger particles as shown in Fig. 6b. It seems that several copper particles were soldered by silver, and produced a larger aggregate particle. Deshpande [10] reported that particle size of Ag-Pd alloy powder increased with increasing palladium content. It is very similar with our work.

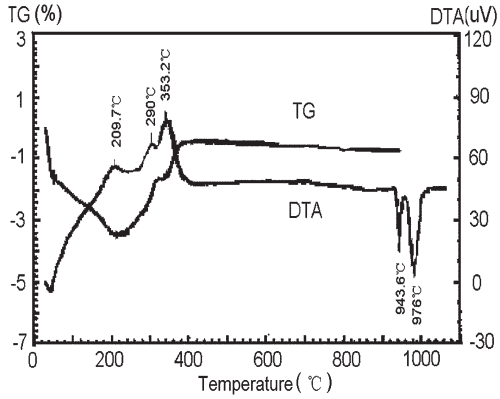

Fig. 7. Thermal analysis pattern of bimetallic powders.

3.4. Thermal analysis of Cu-Ag bimetallic powders

Metallic copper-silver bimetallic powders having a composition of $Ag_{58}Cu_{42}$ were analyzed by TG/DTA in an air flowing. Figure 7 shows the TG/DTG/DTA curves with a heating rate of 5 ℃ min^{-1}. According to TG analysis, in the first step, the loss of weight could be attributed to the vaporization of water or organic materials in powders. The oxidation of copper contributed to the peak at 209.7 ℃ and 342 ℃ related to formation of Cu_2O and CuO, and the reactions were exothermal. Above 500 ℃, the TG curve levelled off. Comparing with the exothermal peaks of pure copper powders at 250 ℃ and 410 ℃ [4], the oxidized temperatures decreased due to the grain refining of copper. The oxidation of silver was not obvious, however, there was a clear exothermal peak at 290 ℃ determined by DTA, with a slight weight loss. It could be attributed to exothermic dissociation of silver oxide. Pure silver powder had a strong endothermal peak at 960 ℃, which meant the melting of silver, however, in this pattern, two strident endothermal peaks appeared at 943.6 ℃ and 976 ℃.

Nishiura [16] reported that phase equilibria in the Ag-CuO-Cu_2O system were experimentally determined using thermal analysis, and structural and compositional studies. Three reactions were observed in air: (1) $L_1 = CuO + Ag$, (2) $L_2 = CuO + L_1$, and (3) $Cu_2O = CuO + L_2$. Results from equilibrium phase studies indicate that there are two invariant points in the pseudobinary Ag-CuO_x phase diagram, respectively, corresponding to an eutectic and a monotectic reaction. The eutectic and monotectic temperatures of the Ag-CuO_x system are 942 ℃ and 969 ℃, respectively. It is in agreement with our observation.

4. Conclusions

We have synthesized spherical silver-rich copper-silver bimetallic powders having a uniform size of $0.6 \sim 0.8\ \mu$m with the two-stage reduction method. Ascorbic acid was first applied to control the formative rate of nuclei and growth rate of particles effectively, and then hydrazine hydrate was used to reduce metal completely. When pH value of reductive solution was stably controlled in the range of $7 \sim 8$, non-agglomerated monodispersed silver-rich Cu-Ag bimetallic particles with smooth surface and uniform size were synthesized. With increasing silver content in powders, the particle size and dispersibility of bimetallic powders decreased and increased, respectively. The XRD and thermal analyzer were employed to analyze as-prepared bimetallic powders. The results show that the eutectic and monotectic temperatures of the Ag-CuO_x system were 943.6 ℃ and 976 ℃, respectively.

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