ELSEVIER

Journal of Alloys and Compounds 466 (2008) 387–390

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Synthesis and characterization of ultrafine Ni–Co composite powder by freeze-drying

Xi Xiaoli, Nie Zuoren*, Jiang Yabao, Tong Peiyun, Song Shunlin, Xu Jie, Zuo Tieyong

College of Material Science and Engineering, Beijing University of Technology, Beijing 100022, China

Received 23 July 2007; received in revised form 13 November 2007; accepted 13 November 2007
Available online 4 December 2007

Abstract

This research focused on the synthesis of ultrafine Ni–Co composite powder prepared using a freeze-drying technique. In the process of freeze-drying, the Ni–Co powder was prepared by freeze-drying the precursor from simple NiC_2O_4 and CoC_2O_4 powders. Thermal decomposition of the amorphous freeze-dried precursor powder produced the ultrafine Ni–Co composite powder. To assure process control and product characterization, the freeze-dried precursor and the final products were analyzed by means of XRD, SEM, TEM, and IR. The results showed that the freeze-dried powder existed in a non-hygroscopic and non-crystalline state. The final product of the experiments was a Ni–Co composite powder, which existed in the form of a single crystalline state and represented fine, homogeneous, spherical particles, reaching a size range of approximately 40–70 nm. The freeze-dried powder was composed of $[Ni(NH_3)_6]^{2+}$ and $[Co(NH_3)_6]^{3+}$.

Keywords: Nanostructured materials; Amorphisation; X-ray diffraction; Scanning electron microscopy

1. Introduction

With technological advances, materials have often become a limiting factor. Therefore, the need for new materials having better characteristics has increased, and alloying is one of the promising techniques for developing such new materials. Compared with simple Ni/Co metal-powder, ultrafine Ni–Co composite powder exhibits some unique characteristics, thus ultrafine Ni–Co composite powder shows significant promise for future development in some fields, such as hard materials [1,2], magnetic materials [3,4], catalyzing electroplates [5,6], and hydrogen-absorbing alloy anodes [7]. Currently, Ni–Co composite powder is prepared by mechanical alloying [8], sono-chemically [9], hydrothermal reduction [10], multi-mellow reduction [11,12], co-precipitation [13], and gas reduction [14,15].

Recently, as an advanced and eco-friendly method of powder preparation, the freeze-drying technique has been developed. In the freeze-drying technique, a solution of the metal salt is spray-quench-frozen and dried in a vacuum, the solvent is sublimated directly, and the freeze-dried powders are calcined/reduced to obtain the ultrafine powder. The freeze-drying technique has the ability to generate a fine, homogeneous powder with excellent control over impurity levels and lower environmental consumption. The current research focused on the synthesis Ni–Co composite ultrafine powder prepared by the freeze-drying technique.

2. Experimental procedure

The NiC_2O_4 and the CoC_2O_4 powders were dissolved in ammonia separately to prepare their respective aqueous solutions. The reaction equations are as follows:

$$NiC_2O_4 + (6 - X)NH_3 \cdot H_2O + (2X - 6)H_2O \rightarrow [Ni(NH_3)_{6-X}(H_2O)_X]C_2O_4$$

$$CoC_2O_4 + (6 - X)NH_3 \cdot H_2O + (2X - 6)H_2O \rightarrow [Co(NH_3)_{6-X}(H_2O)_X]C_2O_4$$

The two solutions were mixed when each solution was stable and the mixed aqueous solution was stable for a long time. The mixed solution was composed of 0.03 mol/L Ni and 0.07 mol/L Co. The solution was then sprayed into a liquid nitrogen bath cooled to −196 °C, resulting in frozen droplets. These frozen droplets were transferred to the chamber of the freeze-dryer. The frozen droplets were dried at −12 °C at 300 Pa for 25 h. In a hydrogen furnace, reduction of the freeze-dried precursor powder produced the ultrafine Ni–Co composite powder.

* Corresponding author. Tel.: +86 10 67391536; fax: +86 10 67391536.
E-mail address: zrnie@bjut.edu.cn (N. Zuoren).

0925-8388/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2007.11.111

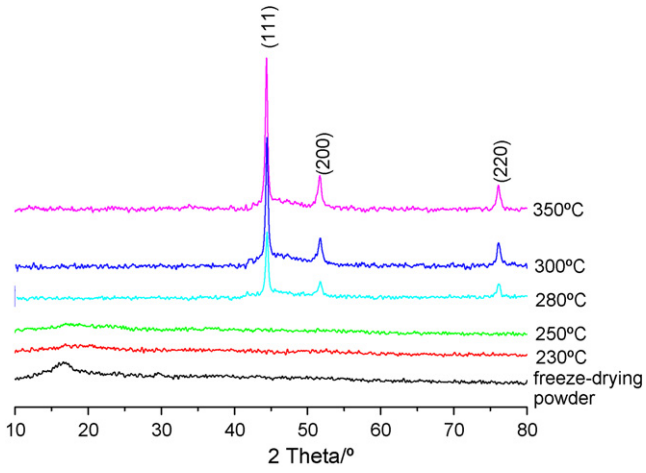

Fig. 1. XRD patterns of the powders.

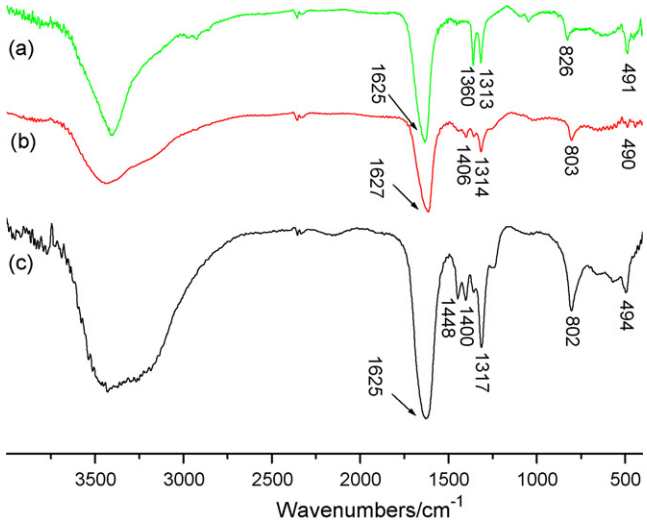

Fig. 2. IR spectrograms of the freeze-dried powders: (a) $[Co(NH_3)_{6-X}(H_2O)_X]C_2O_4$; (b) $[Ni(NH_3)_{6-X}(H_2O)_X]C_2O_4$; (c) $[Ni(NH_3)_{6-X}(H_2O)_X]C_2O_4 + [Co(NH_3)_{6-X}(H_2O)_X]C_2O_4$.

The phase composition (i.e., the freeze-dried powders and the reduced powders) was analyzed by X-ray diffraction (XRD) and infrared (IR) spectroscopy. Particle size and powder morphologies were analyzed by transmission electron micrographs (TEM) and field emission scanning electron micrographs (FESEM).

3. Results and discussion

3.1. X-ray diffraction studies

An important feature of the freeze-drying process is that the composition of the product can be accurately controlled in the initial stage of the liquid solution preparation process. Fig. 1 shows the phase composition of the freeze-dried precursor powder and the reduced product under different temperatures by XRD.

According to Fig. 1, the non-crystalline pack appeared at about $2\theta = 17^\circ$, so the freeze-dried powder was a non-crystalline state substance. This could be explained as a result of sublimation of water during the freeze-drying process, while at the same time, because there were little atomic moves, Ni, Co, and other elements remained as ions in aqueous solutions.

With reducing temperatures of 230 and 250 °C, the reduced powders also displayed the character of a non-crystalline state. However, the color of the powder turned from brown to purple. It was demonstrated that the composition of the powder had changed though it remained the previous form in structure. Additional experiments should be carried out to elucidate this issue.

At a reducing temperature of 280 °C, the reduced powders were found to be crystallized into a Ni–Co phase. Three peaks were indexed to three planes (1 1 1), (2 0 0), and (2 2 0) of the FCC phase. With the temperature increasing from 280 to 350 °C, the intensity of the peaks became stronger. That is to say, the higher the temperature, the easier the crystalline was reduced to a powder.

3.2. IR analysis

Fig. 2 shows the result of IR analysis of the freeze-dried powder. The appearance of the IR peak at 1625 and 1317 cm^{-1} originated from the vibration of the δa(HNH) bond of $[Co(NH_3)_6]^{3+}$ or $[Ni(NH_3)_6]^{2+}$, respectively. The appearance of the IR peak at 1315 cm^{-1} originated from the vibration of the δa(HNH) bond of $[Co(NH_3)_6]^{3+}$. The IR peak at 802 cm^{-1} originated from the vibration of the ρr(NH_3) bond of $[Co(NH_3)_6]^{3+}$ or $[Ni(NH_3)_6]^{2+}$. Finally, the IR peak at 490 cm^{-1} originated from the vibration of the Co–N bond of $[Co(NH_3)_6]^{3+}$. Thus,

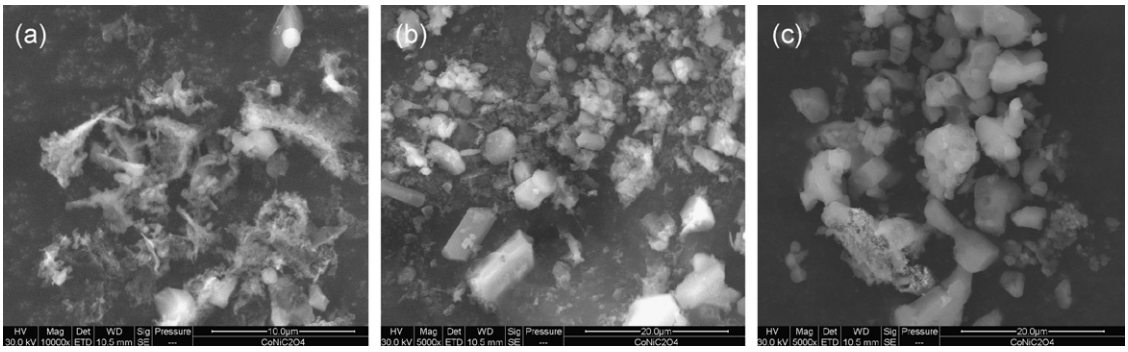

Fig. 3. SEM of freeze-dried powder.