ELSEVIER

Materials Science and Engineering B 137 (2007) 10–19

MATERIALS SCIENCE & ENGINEERING B

www.elsevier.com/locate/mseb

Preparation of solid nickel nanoparticles by large-scale spray pyrolysis of $Ni(NO_3)_2 \cdot 6H_2O$ precursor: Effect of temperature and nickel acetate on the particle morphology

Kyeong Youl Jung [a,*], Jong Ho Lee [b], Hye Young Koo [c], Yun Chan Kang [c], Seung Bin Park [d]

[a] *Department of Chemical Engineering, Kongju National University, 182, Shinkwan-dong, Kongju, Chungnam 314-701, Republic of Korea*
[b] *Materials R&D Group, Electronic Device Division, Samsung Electro-Mechanics Co., Ltd., 314, Maetan3-Dong, Yeongtong-Gu, Gyunggi-Do, Suwon 442-743, Republic of Korea*
[c] *Department of Chemical Engineering, Konkuk University, 1 Hwayang-dong, Gwangjin-gu, Seoul 143-701, Republic of Korea*
[d] *Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, 373-1, Guseong-dong, Yuseong-gu, Daejeon 305-401, Republic of Korea*

Received 14 July 2006; received in revised form 18 September 2006; accepted 30 September 2006

Abstract

Spherical nickel nanoparticles were prepared by a large-scale spray pyrolysis process with two continuous reactors and were investigated in terms of particle-formation mechanism, surface property, particle shape, and size with changing the temperature of two continuous reactors and the type of precursor. When nickel nitrate was used as a precursor and the second reactor temperature was over 1200 °C, solid Ni particles were obtained, but many ultra-fine particles of less than tens nanometer were simultaneously formed via a gas-to-particle conversion mechanism. The formation of such ultra-fine particles was reduced by making hollow particles in the first reactor at 500 °C and thereafter densifying them in the second reactor at 1400 °C, but could not completely prevent. The addition of about 5–10 mol% nickel acetate instead nitrate precursor was found to be very effective to avoid the formation of such ultra-fine particles as well as producing solid particles with clean and smooth surface. On the basis of the results obtained, a mechanism of particle formation in the large-scale spray pyrolysis was proposed. Finally, spherical and solid nickel nanoparticles, which had clean surface and high density (larger than 8.4 g/cm^3), were prepared from the mixed precursor (nitrate/acetate) at a residence time of about 3 s without any chemical additive.

Keywords: Spray pyrolysis; Nanoparticle; Nickel; MLCC; Electrode

1. Introduction

Nickel particles have been used as electrode materials instead of noble metals for multilayer ceramic capacitors (MLCCs) which is a key component of electronic devices [1]. As electronic devices become smaller and more complicated, the MLCCs are required to be smaller and to have larger capacitance. To meet such demands, it is necessary to increase the number of inner electrode and dielectric layers, simultaneously reducing the thickness of each layer [2]. Now, the thickness of one electrode layer goes down to several micrometer or submicron. Accordingly the size of nickel particles should become smaller than several hundred nanometers. The particles with spherical shape and narrow size distribution are also advantageous to prepare ultra-thin electrode of several hundred layers without any delamination.

Spray pyrolysis is considered as a promising process for the preparation of metal or metal oxides with spherical shape and narrow size distribution [3–5]. The particles produced by spray pyrolysis, however, have hollow morphology because droplets are fast evaporated in a hot furnace and consequently precipitation of salts begins at the surface of droplets [6]. Thus, how to make dense-structured particles by spray pyrolysis has been a critical research topic [7,8]. The variables affecting the particle morphology are drying rate of droplets, temperature for pyrolysis or interparticle reactions, solution concentration, residence time, and the property of starting materials. Normally, solid particles can be formed when the drying of droplets proceeds slowly

* Corresponding author. Fax: +82 41 858 2575.
E-mail address: kyjung@kongju.ac.kr (K.Y. Jung).

0921-5107/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.mseb.2006.09.025

enough to induce a volumetric precipitation and the densification occurs at high temperature in a sufficient heating time (a long residence time).

According to previous studies [5,9], in lab-scale spray pyrolysis, the solid nickel particles could be produced from $Ni(NO_3)_2{\cdot}6H_2O$ or $Ni(Cl)_2{\cdot}6H_2O$ aqueous solution at the reactor temperature above 1000 °C with flowing 5–20% H_2/N_2 gas mixture and a sufficient residence time. Nagashima et al. reported that the reactor temperature should be higher than the melting point of metal particles to obtain solid particles [10]. Che et al. prepared dense spherical Ni particles and hollow NiO particles by spray pyrolysis using nickel nitrate aqueous solution [3]. They reported that hollow NiO particles are reduced by H_2 above 300 °C and densified at pyrolysis temperature over 1000 °C with a residence time of 30–150 s. Xia et al. prepared nickel particles from nickel ammine complex by spray pyrolysis [5]. They suggested the use of $NH_3{\cdot}H_2O$, NH_4HCO_3 with $NiCl_2{\cdot}6H_2O$ precursor and reported that dense and spherical Ni particles could be obtained in the aerosol reactor operated at 1000 °C at a residence time of 7–9 s.

When spray pyrolysis is scale-up, the conditions for particle formation become much worse. That is, the droplets are dried much faster and the residence time of precipitates or particles becomes short because a large quantity of droplets should be treated in a short residence time. For high production rate, the concentration of salts is required to be high, but do not obtain nanoparticles because the particle size increases with the salt concentration. Thus, the concentration should be lowered to prepare nickel nanoparticles. Then, more quantity of droplets should be pyrolyzed faster for high production rate. As a result, the produced particles have porous structure, low crystallinity as a consequence of poor densification even at high temperature with a short residence time.

In this work, nickel nanoparticles were prepared from $Ni(NO_3)_2{\cdot}6H_2O$ aqueous solution by a large-scale spray pyrolysis process with two continuous reactors in which the particle formation is achieved in a residence time of less than 3 s. The particle morphology was monitored by changing the temperature of two reactors. According to the results obtained, the densification of hollow nickel nanoparticles was achieved when the reactor temperature was over 1200 °C. Many ultra-fine particles with the size less than tens nanometer, however, were simultaneously formed by the gas-to-particle conversion. The formation of such ultra-fine particles should be suppressed by controlling the preparation condition. Thus, we investigated a simple, but very effective way that makes it possible to prevent the formation of ultra-fine nickel particles with producing solid Ni nanoparticles which have spherical shape, high crystallinity, smooth surface, and high density. The final goal of this work is to provide a preparation strategy by which solid nanoparticles are successfully obtained by a large-scale spray pyrolysis process using $Ni(NO_3)_2{\cdot}6H_2O$ aqueous solution without any chemical additive.

2. Experimental

Fig. 1 shows a schematic diagram showing the large-scale spray pyrolysis process used for preparing Ni nanoparticles. The apparatus was composed of an ultrasonic atomizer, a quartz reactor equipped with two electrical furnaces, and a bag filter. The atomizer has seventeen resonators with the frequency of 1.7 MHz. The length and the inner diameter of the quartz reactor were 2000 mm and 95 mm, respectively. The temperature (T_1) of the first reactor with a length of 500 mm was changed from 300 °C to 900 °C. The temperature (T_2) of the second reactor with a length of 1200 mm and three-zone heaters was varied form 900 °C to 1400 °C.

Nickel nitrate, $Ni(NO_3)_2{\cdot}6H_2O$ (Aldirch, 99+%), was used as a precursor. Nickel acetate, $Ni(CH_3COO)_2{\cdot}4H_2O$ (Aldrich, 98%), was used as a secondary precursor to control the morphology of Ni particles. The content of nickel acetate was varied in molar ratio from 5% to 25% of nickel nitrate. The concentration of $Ni(NO_3)_2{\cdot}6H_2O$ solution was changed from 0.02 M to 0.5 M. The prepared aqueous solution was atomized by the ultrasonic aerosol generator mentioned above and the produced droplets were carried into the tubular reactor by nitrogen gas containing 10% H_2. The flow rate of carrier gas was varied from 50 l/min to 100 l/min. When the carrier gas is 50 l/min, the residence time was summarized in Table 1 for all operating conditions. The residence time in each reactor was less than 2.2 s and the total residence time was about 1.5–3.7 s. The produced nickel particles were collected by a bag filter. Some nickel samples were

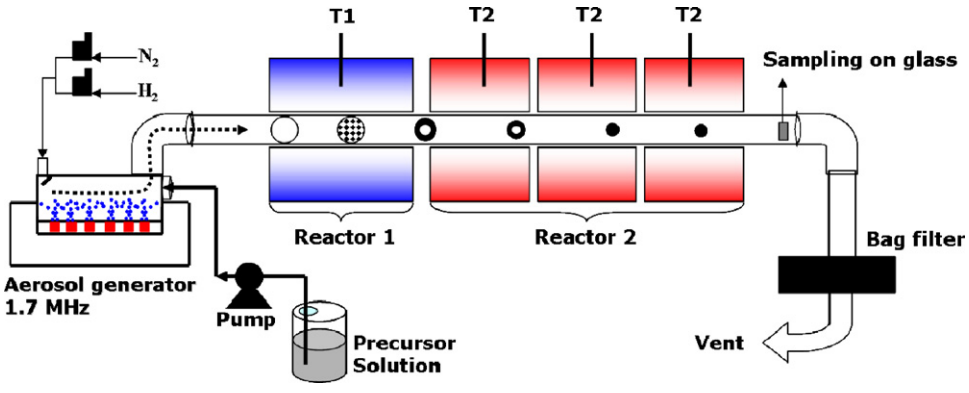

Fig. 1. Schematic of the spray pyrolysis process used for nickel nanoparticles.