Formation of spherical dense nickel particles by pyrolyzing the aerosol of an ammine complex solution in nitrogen atmosphere

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Spray pyrolysis has been applied in the preparation of metal, metal oxide and non-oxide powders [1]. The most important characteristics of the spray pyrolysis technique compared with the other wet chemical processes is that the solution is divided into micron-sized droplets in the process. Chemical and physical reactions are limited within every droplet or particle, and finally one droplet changes to one particle at high temperature. Therefore, it is possible to control the structure of the particles obtained by controlling the intra-droplet/intra-particle reactions [2].

One of the major problems of spray pyrolysis is the formation of hollow particles, especially in the preparations using nitrate as the starting materials. For example, in the preparation of NiO and Ni particles by spray-pyrolyzing a Ni(NO₃)₂ solution, all NiO particles and a fraction of Ni particles were found to be hollow [3]. In this case, the hydrate of Ni(NO₃)₂ dissolves into its own crystalline water and liquefies above 35°C [4]. Therefore, dried particles of nitrate formed in the drying stage liquefy to droplets again and are subsequently easily inflated by the decomposition gases and evaporated water. This is a typical mechanism of the formation of hollow oxide particles by spray pyrolysis using nitrates as the starting materials [1, 5]. To obtain dense particles, a preparation condition of a flat temperature profile and sufficient heating time is considered to be desirable. However, this operating condition often leads to the decrease of powder production.

To prevent the formation of hollow particles, the formation of solid from a droplet in the drying stage should be volume precipitation, not surface precipitation. In the present case, it is desirable that the salt is changed to other types. This can be achieved by introducing reactions into the starting solution or into the droplets before the solvent is completely evaporated [2]. We have reported the formation of dense PdO and Pd particles from a pH-adjusted Pd(NO₃)₂ solution that hydrolyzes below 100°C [6]. In this letter, we added some ammonia into the Ni(NO₃)₂ starting solution to make an ammine complex of nickel, which was found to be effective in preventing the formation of hollow particles.

NiO and Ni powders were prepared from a 1.0 mol dm⁻³ aqueous solution of Ni(NO₃)₂·6H₂O, which was converted into a dark blue solution of nickel ammine complex by mixing it with 28% ammonia solution. The synthesis apparatus [6, 7] was composed of two heating zones, and N₂ was used as the carrier gas at a flow rate of 2.0 or 3.0 cm s⁻¹. The temperatures of the two heating zones of the reaction tube were varied in the ranges of drying temperature \(T₁ = 200–600°C\) and pyrolysis temperature \(T₂ = 400–1400°C\).

X-ray diffraction (XRD) analysis of the powders prepared at different pyrolysis temperatures showed that particles obtained below the pyrolysis temperature of \(T₂ = 600°C\) are single-phase NiO with very broad diffraction peaks. Ni is formed above 600°C and pure Ni powders are obtained above 1000°C at the flow rate of 2.0 cm s⁻¹. The content of Ni in the powders increases with the pyrolysis temperature, as shown in Fig. 1, which has been shown by thermogravimetric analysis (TG) of the powders. A slower carrier gas flow rate gives a higher purity at the same pyrolysis temperature.

Fig. 2 shows scanning electron microscopy (SEM) photographs of the particles prepared at different pyrolysis temperatures and a gas flow rate of 2.0 cm s⁻¹. Spherical NiO particles formed at \(T₂ = 400°C\) have rough surfaces. Some fractured particles were observed that showed the dense interior of the particles. This is very different from the morphology reported for NiFe₂O₄ particles.

![Figure 1](image-url) The purity of Ni powders as a function of pyrolysis temperature and carrier gas flow rate.
prepared by spray-pyrolyzing the nitrate solution between 550–750 °C in an Ar–NH₃ atmosphere [8], in which case the particles were hollow spheres. As the reduction of NiO to Ni occurs, the surfaces of the particles become uneven, and a fraction of irregular particles are observed at T₂ = 600–800 °C. At T₂ = 1000–1400 °C, almost all the Ni particles become ideal spheres with smooth and dense surfaces. The decrease of particle size with the increase of pyrolysis temperature T₂ is attributed to the reduction of the NiO and the densification of the Ni particles.

Transmission electron microscopy (TEM) photographs of the microtomed sections of the same particles shown in Fig. 2 are given in Fig. 3, showing the development of the particle structure. It is clear that all NiO particles formed at 400 °C are dense spheres composed of aggregated primary NiO particles of nanometer sizes. Consistent with the broad XRD peaks, the electron diffraction ring pattern indicates that the NiO particles are nearly amorphous. Ni particles formed at T₂ = 800 °C keep the dense structure shown in Fig. 3b. Ni crystal grains around 100 nm and some pores between the grains can be observed, showing the growth of Ni crystallites within a particle. The diffraction pattern indicates that the particles are polycrystalline and multiphase. Ni particles formed at T₂ = 1200 °C are denser and more fully crystallized. No pores are present. Electron diffraction indicates that most of the Ni particles are nearly single-crystals.

It may be assumed that the structure of a Ni particle is determined by (1) the drying of a droplet, (2) the reduction of NiO to Ni and (3) intragranular sintering [2, 3]. TEM (Fig. 3a) shows that all NiO particles formed from the dried droplets are dense. Considering that all NiO particles formed from a Ni(NO₃)₂ starting solution were hollow [3], this result indicates that the liquefaction of nitrate did not occur in the present preparation. This is attributed to the formation of the ammine complex of Ni in the starting solution. By adding ammonia into the Ni(NO₃)₂ starting solution, Ni²⁺ and NH₃ make a hexammine complex of Ni:

\[
\text{Ni}^{2+}(\text{aq}) + 6\text{NH}_3(\text{aq}) = \text{Ni(NH}_3)_6^{2+}(\text{aq})
\]

As the solution is alkaline, the hexammine complex can be considered as Ni(NH₃)₆(OH)₂, which decomposes and precipitates as Ni(OH)₂ when the droplets are heated:

\[
\text{Ni(NH}_3)_6(\text{OH})_2(\text{aq}) = \text{Ni(OH})_2(s) + 6\text{NH}_3(g)
\]

The hexammine complex may also exist as Ni(NH₃)₆(NO₃)₂, which in the solid state begins to decompose at 80 °C and converts to NiO at 380 °C [9]. The precipitation of Ni(OH)₂ takes place within