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Original Research Paper

Nickel oxide powder synthesis from aqueous solution of nickel nitrate hexahydrate by a microwave denitration method

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ABSTRACT

Denitration of the aqueous solution of nickel nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$) by a microwave heating method was investigated. Since $Ni(NO_3)_2{\cdot}6H_2O$ aqueous solution cannot be heated to over 300 °C by microwave irradiation owing to the low microwave absorptivity of its intermediate, the final product of the denitration reaction (NiO) could not previously be obtained by microwave heating. We propose a novel NiO synthesis method that uses microwave heating without the risk of chemical contamination. In this technique, a NiO powder reagent (the same as the final product) was added to the solution of the raw material to function as a microwave acceptor. Moreover, the denitration efficiency to NiO could be improved by setting an adiabator around the reactor to increase the temperature homogeneity in the reactor, as well as raise the temperature at the periphery. Numerical simulations also reveal that the use of the adiabator results in remarkable changes in the electromagnetic field distribution in the reactor; consequently, temperature inhomogeneity decreases. Furthermore, the temperature dependence of the denitration efficiency to NiO, which is calculated from the simulated temperature distribution, approximately agrees with the experimental data. Accordingly, this indicates that the simulated results can estimate the progress of the denitration reaction to NiO using this microwave heating method.

1. Introduction

A microwave consists of both electric and magnetic fields and can produce heat due to its interactions with the dipole and electric charge of an object. A microwave heating method can selectively heat an object both rapidly and directly, as well as create a heat spot and overheat the sample. Since this method is expected to enable energy-saving heating that can improve the conversion and reaction rates, it has been widely used in various industrial processes and research fields, such as in drying processes, organic and inorganic reactions, sintering and solid-phase reactions at high temperatures, and other applications [1–5].

In the field of nuclear research, the aqueous solution of uranyl nitrate and plutonium nitrate is converted to the mixed oxide powder (MOX fuel) using the microwave heating method for direct denitration [6,7]. Hence, it is important to clarify the reaction mechanism of denitration of a metallic nitrate aqueous solution using microwaves.

The denitration mechanisms of nickel nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$) and copper nitrate trihydrated ($Cu(NO_3)_2{\cdot}3H_2O$) aqueous solutions have been investigated using conventional external heating sources [8–10]. Although the denitration of $Cu(NO_3)_2{\cdot}3H_2O$ aqueous solutions to CuO powder using microwave heating has been investigated [11], preparation of NiO powder from $Ni(NO_3)_2{\cdot}6H_2O$ aqueous solutions using the microwave denitration method has not yet been reported. NiO powder has been obtained by the thermal decomposition of nickel nitrate, nickel sulfate, and nickel acetate using conventional external heating [12–14]. Our previous report [15] detailed the denitration mechanisms of $Ni(NO_3)_2{\cdot}6H_2O$ and $Cu(NO_3)_2{\cdot}3H_2O$ aqueous solutions using microwave heating. In addition, the reason why NiO powder had not yet been synthesized from $Ni(NO_3)_2{\cdot}6H_2O$ aqueous solutions using microwave denitration has been discussed.

In view of this, in this study, we propose a novel method of synthesizing NiO powder from $Ni(NO_3)_2{\cdot}6H_2O$ aqueous solution using microwave heating, without adding "contaminants", in the form of

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Nomenclature

C_p	specific heat capacity [J/(mol K)]	ω	angular velocity (rad/s)
E	electric field vector (V/m)	ε	complex permittivity (F/m)
h	heat transfer coefficient [W/(m^2 K)]	ε'	relative permittivity (–)
H	magnetic field vector (A/m)	ε''	relative dielectric loss factor (–)
$\mathbf{j}_0$	current density (A/m^2)	ε_0	vacuum permittivity (F/m)
j	imaginary unit	μ	relative magnetic permeability (H/m)
k	thermal conductivity [J/(s m K)]	μ'	real part of relative magnetic permeability (–)
p	time-averaged power density (W/m^3)	μ''	imaginary part of relative magnetic permeability (–)
q	amount of heat generated per unit volume (W/m^3)	μ_0	vacuum permeability (H/m)
t	time (s)	ρ	density (kg/m^3)
T	temperature (K)	ϕ	packing fraction (–)

exogenous microwave acceptors, to the raw material solution. In many cases, carbon, which has a high dielectric loss factor, is often used as an added microwave acceptor, as it absorbs microwaves with high efficiency [16]; however, it remains in the final product as a contamination.

In this work, the effects on the process of the microwave denitration while using an adiabator are also investigated. Namely, the temperature distribution in the reactor and the efficiency of the denitration process to yield NiO powder are also evaluated by numerical simulation.

2. Materials and methods

2.1. Microwave denitration experiment

20.0 g of high-purity nickel nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$) reagent (Sigma–Aldrich) was dissolved in 15.0 mL of distilled water and 0–8.5 g of crystalized NiO powder (Sigma–Aldrich, Purity = 99%, Mass median diameter = 2.0 μm) was added as a microwave acceptor. This aqueous solution or suspension, used as the starting material, was placed in a three-neck 100 mL Pyrex flask, which served as the reactor.

Microwave denitration experiments were conducted using the microwave heating equipment (Shikoku-keisoku, μ-Reactor) shown in Fig. 1, which consisted of a magnetron, PID controller, cavity, and K-type thermocouple. The starting material was irradiated and heated using a 2.45 GHz microwave generated by the magnetron and directed into the cavity fabricated by the stainless steel. The agitator was not used during the microwave irradiation. The microwave output was kept at 750 W until the preset reaction temperature was attained, at which point the output was adjusted (40–770 W) to keep the reaction temperature constant using the PID controller. Here, the temperature measured by a thermocouple at the center of the reactor was defined as the reaction temperature. Water vapor and nitrogen oxide gas generated by the reaction were exhausted by air fed into the reactor at the constant flow rate of 100 mL/min. The evaporated water was captured by a condenser and the noncondensable gas was absorbed by distilled water in a gas washing bottle.

To investigate the effects of temperature distribution in the reactor, denitration experiments were also conducted while covering the reactor with an adiabator which was constructed of silica-alumina and its surface is made of aluminum foil, using a $Ni(NO_3)_2{\cdot}6H_2O$ aqueous solution containing 6.0 g of added NiO powder.

It was assumed that the nitrogen oxide gas was converted to a HNO_3 aqueous solution and then completely dissociated to H^+ and NO_3^- in the gas washing bottle. The decomposition of $Ni(NO_3)_2{\cdot}6H_2O$ is expressed by the following chemical reaction:

$$Ni(NO_3)_2 \cdot 6H_2O \rightarrow NiO + 2HNO_3 + 5H_2O.$$

Accordingly, the amount of generated HNO_3 can be calculated from pH measurements (pH meter; Horiba, F-53). The crystalline phases of the final product were identified from powder X-ray peak patterns measured by X-ray diffraction (XRD; Rigaku, RINT-2000). Surface conditions were measured by a Fourier-transform infrared (FT-IR) spectrometer using the attenuated total reflectance (ATR) method (Thermo Scientific, iS5).

2.2. Numerical simulation of the reactor

To evaluate the progress of the microwave denitration, the temperature distribution in a reactor should be calculated. Since microwaves generate heat by their interaction with the dipole and electric charge of an object, the temperature distribution depends on the object's internal electric and magnetic fields.

The electromagnetic field in an object is expressed by the following Maxwell's equations (Ampere's and Faraday's laws):

$$\nabla \times \boldsymbol{H} = \varepsilon_0 \varepsilon \frac{\partial \boldsymbol{E}}{\partial t} + \boldsymbol{j}_0 \tag{1}$$

$$\nabla \times \boldsymbol{E} = -\mu_0 \mu \frac{\partial \boldsymbol{H}}{\partial t} \tag{2}$$

where $\boldsymbol{E}$ is the electric field vector, $\boldsymbol{H}$ is the magnetic field vector, and $\boldsymbol{j}_0$ is the current density. ε is the relative permittivity and μ is the relative magnetic permeability. ε_0 and μ_0 represent the vacuum permittivity and vacuum permeability, respectively.

Combining these laws with Gauss' laws leads to the following equations [17]:

$$\nabla \times \boldsymbol{H} = j\omega\varepsilon_0\varepsilon\boldsymbol{E} + j_0 \tag{3}$$

$$\nabla \times \boldsymbol{E} = -j\omega\mu_0\mu\boldsymbol{H} \tag{4}$$

where ω is the angular frequency, and j is the imaginary unit. An electromagnetic field of the object can be calculated by these equations.

The time-averaged power density, p, can be obtained from Eq. (5) [18]:

$$p = \frac{\omega}{2}\left(\varepsilon_0\varepsilon''\|E\|^2 + \mu_0\mu''\|H\|^2\right) \tag{5}$$

where ε'' and μ'' are imaginary parts of relative permittivity and relative magnetic permittivity, respectively.

On the other hand, thermal conductivity can be described by Fourier's law [19,20]:

$$\rho C_p \frac{\partial T}{\partial t} = \nabla \cdot (k\nabla T) + q \tag{6}$$

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