Korean J. Chem. Eng., 35(11), 2321-2326 (2018)
DOI: 10.1007/s11814-018-0137-2

pISSN: 0256-1115
eISSN: 1975-7220

Optimization fluidization characteristics conditions of nickel oxide for hydrogen reduction by fluidized bed reactor

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(*Received 27 February 2018 • accepted 31 July 2018*)

Abstract−We evaluated the optimal conditions for fluidization of nickel oxide (NiO) and its reduction into high-purity Ni during hydrogen reduction in a laboratory-scale fluidized bed reactor. A comparative study was performed through structural shape analysis using scanning electron microscopy (SEM); variance in pressure drop, minimum fluidization velocity, terminal velocity, reduction rate, and mass loss were assessed at temperatures ranging from 400 to 600 °C and at 20, 40, and 60 min in reaction time. We estimated the sample weight with most active fluidization to be 200 g based on the bed diameter of the fluidized bed reactor and height of the stocked material. The optimal conditions for NiO hydrogen reduction were found to be height of sample H to the internal fluidized bed reactor diameter D was H/D=1, reaction temperature of 550 °C, reaction time of 60 min, superficial gas velocity of 0.011 m/s, and pressure drop of 77 Pa during fluidization. We determined the best operating conditions for the NiO hydrogen reduction process based on these findings.

Keywords: Fluidized Bed Reactor, Superficial Gas Velocity, Hydrogen Reduction, Reduction Rate, Pressure Drop

INTRODUCTION

Nickel (Ni) is a metal of high value used in vehicle batteries, cellular phones, and semiconductors. Ni is separated from NiO found in nature using a fluidized bed reactor before being commercially used [1,2]. The steel industry uses coke as a reductant in fluidized bed reactors to reduce NiO. This process generates CO_2 as a by-product, and requires installation of additional post-treatment process facilities to remove the CO_2 [3,4]. Using hydrogen as a reductant is considered an eco-friendly alternative for steelmaking processes, because the byproduct of the process is water instead of CO_2. Compared to the coke process, hydrogen reduction has faster gas-solid reactions, shorter reaction time, and allows for a low reaction temperature to be maintained. Processes using hydrogen are gaining prominence as eco-friendly methods, and they are expected to significantly contribute to reducing CO_2 emissions by 2100 [5]. Pollution is of great concern in advanced countries. Greenhouse gas reduction has been enforced under international treaties on climate change, and cutting out CO_2 emissions at their industrial sources is regarded as a priority in the 21st century [6,7]. Major factors in the hydrogen reduction process are reaction temperature, reaction time, and gas flow rate [8]. Hydrogen reduction of metal oxides in fluidized bed reactors has been studied extensively. The reducing gas is a critical component of the process due to its direct contact with the metal oxide particles. It is necessary to determine fluidization parameters for procurement of optimal fluidization conditions when particular laboratory equipment is in use [9-11]. A study of reduction rates and fluidization characteristics, such as gas flow rate, reaction temperature, and reaction time, is necessary to identify optimal experimental conditions. Fluidization results and products must be analyzed in depth as well [12,13].

In this study, NiO was reduced to Ni through hydrogen reduction in a laboratory-scale fluidized bed reactor. The flow rate of the hydrogen gas, reaction time, and reaction temperature were used as variables to determine optimal process conditions for reduction rates and fluidization results.

EXPERIMENT

1. Materials

For accurate observation of NiO powder fluidization behavior, the NiO powder were categorized using Geldart's classification, in which the flow characteristics are described with respect to particle size and density [14]. Prior to the experiment, physical properties and particle size of the NiO powder were measured. Particle size was found to be 26.9 μm using a particle size distribution analyzer (TSI, model 3603, USA). Results of the particle size analysis are shown in Fig. 1. The particle density of NiO is 6,990 kg/m^3. The NiO powder used in this study belonged to Geldart's Group A; particles in this group display favorable fluidization under low superficial gas velocity [15]. Based on Eq. (1), the mean value of the three measurements was determined to be the particle density of the NiO powder. The true and bulk density was measured using a pycnometer and the water as displacement fluid according to the standard

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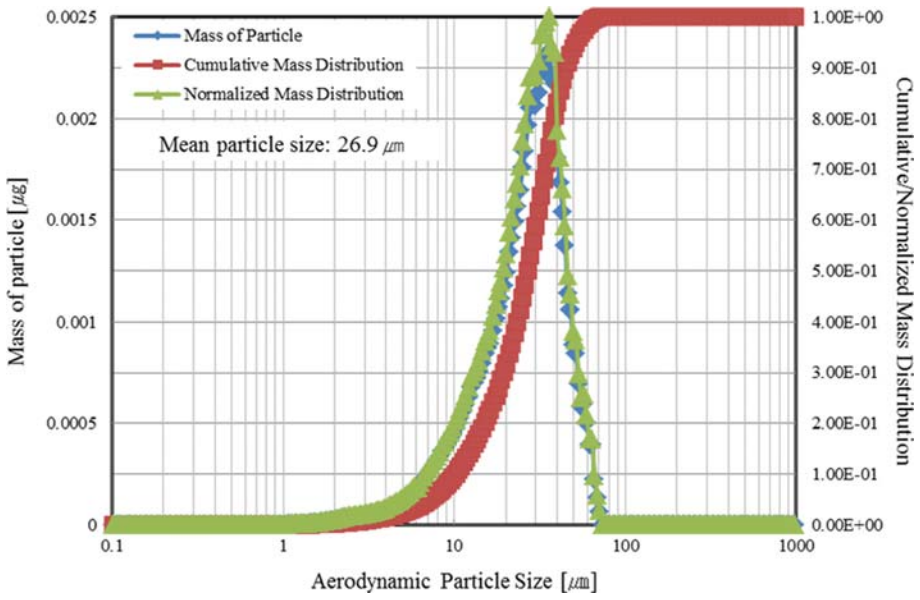

Fig. 1. Particle size distribution of the NiO powder used in the experiments.

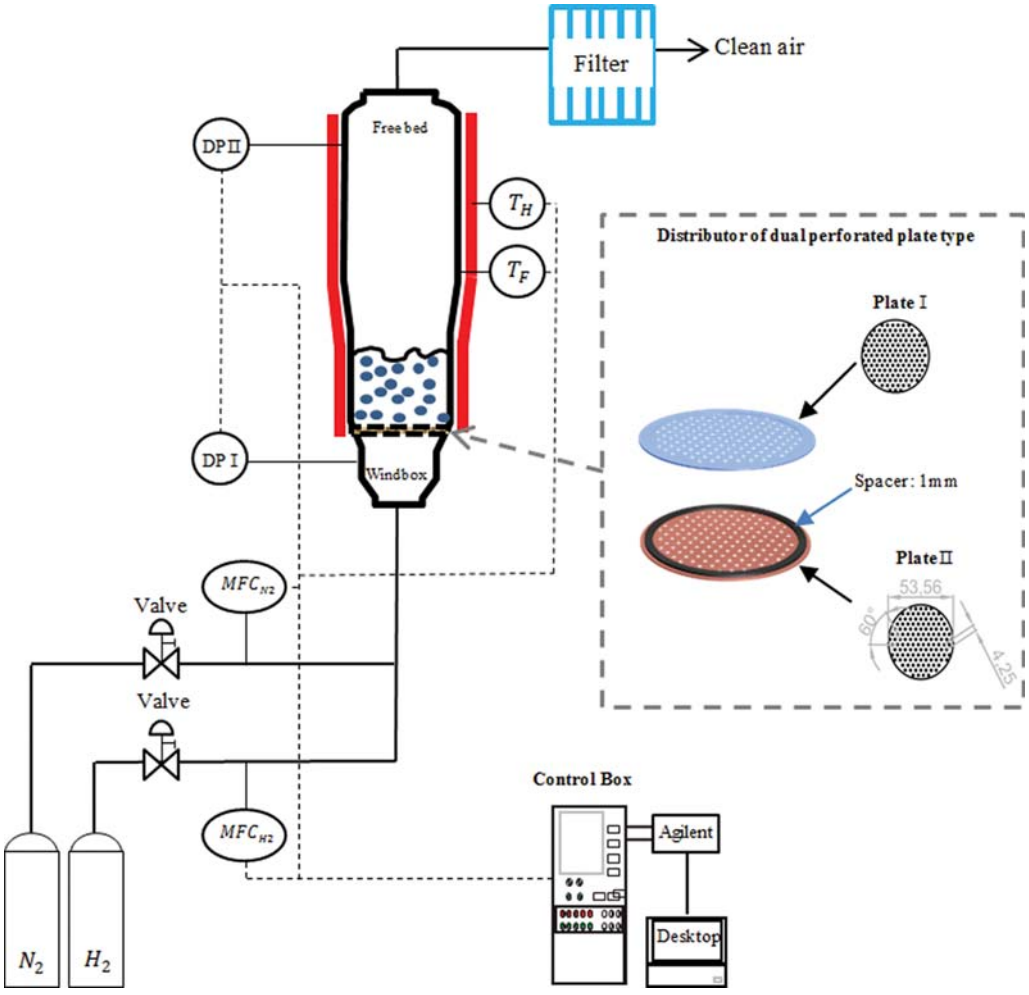

Fig. 2. Schematic diagram of the experimental apparatus.

MFC_{N2}. N_2 mass flow controller
MFC_{H2}. H_2 mass flow controller
DP I. Electronic remote sensor of pressure drop I
DP II. Electronic remote sensor of pressure drop II
T_H. Heating jacket temperature
T_F. Fluidized bed reactor temperature

Table 1. Experimental conditions

Parameter	Contents
Sample type	NiO (Particle density: 6990 kg/m^3, Mean particle size: 26.9 μm)
Fluidization gas	Nitrogen, Hydrogen
Gas flow rate	0 to 60 L/min
Superficial gas velocity	0 to 0.45 m/s
Sample weight	50 to 350 g
Reaction temperature	400 to 600 °C
Reaction time	20, 40, 60 min
Geometrical dimension	Bed diameter: 0.05 m, Bed height: 0.76 m
Distributor type	Double-layer perforated plate (Opening ratio of 2.2%)

ISO 12154:2014. An average value then was taken as basis for further calculations [16]. Based on the NiO powder mean particle size and thus calculated NiO particle density, from the Geldart's graph we conclude that our NiO powder would demonstrate good fluidization and was suitable for the experiment.

$$\text{Particle density} = \frac{\text{Mass of a single powder}}{\text{Volume the powder would displace surface were nonporous}} \quad (1)$$

2. Method

The fluidized bed reactor and laboratory equipment used in this study are shown in Fig. 2. Table 1 lists equipment, data, and experimental conditions. Before the experiment, N_2 gas was purged to ensure that there was no air in the fluidized bed reactor. Pressure drop ports were installed above the distributor and above the maximum bubbling height to measure the NiO powder pressure drop. After the hydrogen reduction experiment, the NiO powder was stored in product containers without air contact. Element quantification using scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) (HITACHI, S-4700, Japan) equipment was performed to compute the reduction rate from the oxygen and nickel compositions after the experiment. The NiO powder images before and after the experiment were analyzed to determine the NiO powder structure.

The hydrogen reduction of NiO is a clean technology process with water as a byproduct. The reduction equation (NiO to Ni) and the equation for the theoretical reduction rate are shown in Eqs. (2) and (3), respectively [17].

$$NiO\ (solid)+H_2\ (gas)\rightarrow Ni\ (solid)+H_2O\ (gas) \quad (2)$$

$$\text{Reduction rate [\%]} = \text{Oxygen content in NiO[\%]} - \text{Oxygen content in product [\%]}/\text{Oxygen content in NiO [\%]} \times 100 \quad (3)$$

RESULTS AND DISCUSSION

1. Pressure Drop

The pressure drop in the NiO powder layer increases proportionally as the superficial gas velocity increases. Minimum fluidization velocity refers to the point where the drag exerted on the solid by the gas equals gravity; it is also where fluidization starts to actively take place. When superficial gas velocity increases and reaches terminal velocity, the particle drag cannot resist the flow speed and the sample is ejected from the reactor [18]. When the superficial gas velocity increases in the bubbling regime, the powder drag cannot endure the fluid velocity, and the NiO powder thus flows out of the fluidized bed reactor. This state of fluidization is referred to as pneumatic conveying, and the fluid velocity at this time is defined as the terminal velocity [19]. Fig. 3 shows the pressure drop results plotted against increasing superficial gas velocity in the reaction temperature range of 400 to 600 °C. Fig. 4 represents the minimum fluidization velocity and terminal velocity results. Minimum fluidization velocity ranged from 0.011 to 0.037 m/s and pressure drop varied from 41 to 151 Pa under fluidization conditions; terminal velocity was found to be 0.15 to 0.375 m/s. In conclusion, the results were associated with mass loss according to the increase in temperature, as shown in Fig. 7. It is determined that as the temperature increased, the amount of oxygen in NiO decreased, and the weight of the powder also decreased, which caused a pressure drop and a decrease in minimum fluidization velocity and terminal velocity.

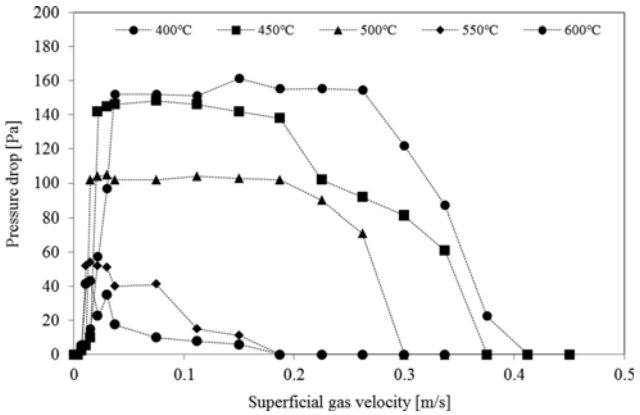

Fig. 3. Results of the pressure drop as a function of the superficial gas velocity.

2. Sample Weight

Using too much NiO powder may lead to an increased pressure drop and less active fluidization; thus, choosing the correct weight of sample is crucial for fluidization [20]. Fig. 5 depicts reduction rate for the temperature range of 400 to 600 °C and sample weight of 50 to 350 g. As the reaction temperatures increased from 400 to

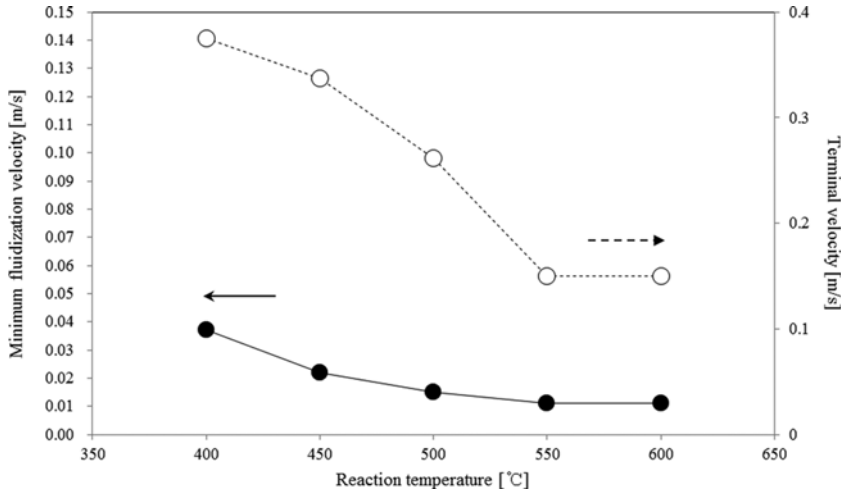

Fig. 4. Minimum fluidization velocity and terminal velocity at different reaction temperatures.

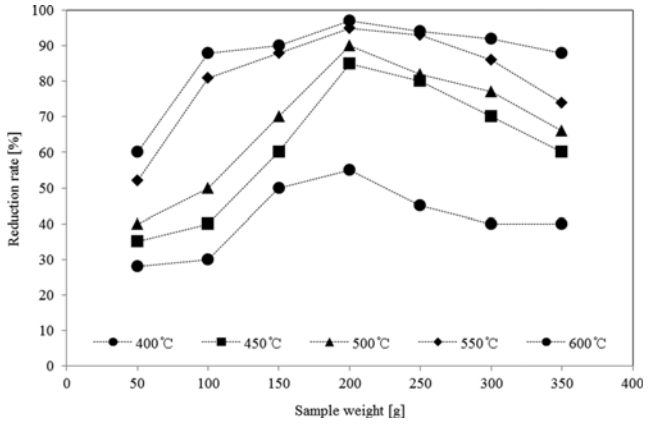

Fig. 5. Reduction rate versus sample weight at reaction temperatures ranging from 400 to 600 °C.

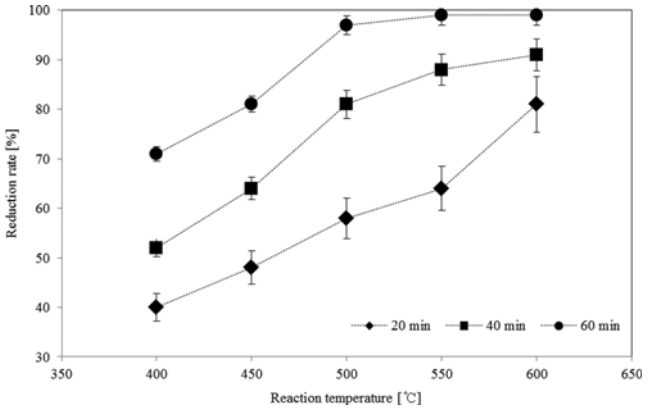

Fig. 6. Reduction rate versus reaction time at reaction temperatures ranging from 400 to 600 °C.

600 °C, the reduction rates increased from 28 to 60% for a 50 g sample, from 55 to 97% for a 200 g sample, and from 40 to 88% for a 350 g sample. The reduction rate decreased with increasing sample weight, and increased with increasing temperature. As it is known from gas theory, gas will expand as the temperature increases. Inside the windbox the flow rate and thus the gas velocity changes according the temperature. It is difficult to refer to it during tests. Thus the flow rate of 6 L/min is referred to as the flow rate at normal conditions. The fluidization phenomenon occurs when adequate weight of NiO powder is present in a fluidized bed reactor. For a fixed gas flow rate of 6 L/min, up to the sample weight of 200 g, the reduction rate increases due to the increase in turbulence for which a certain bed height is required and the hydrogen gas/solid contact time is increased. If the weight of NiO powder increases, the bubbling regime moves toward the fixed bed with no fluidization and channeling. In this case, NiO and hydrogen have a lower reaction rate, resulting in a decrease in the reduction rate. The ratio of the stocked height of sample H to the internal fluidized bed reactor diameter D was H/D=1, which generally resulted in the highest reduction rate, regardless of the reaction temperature.

3. Reduction Rate

Reaction temperature and reaction time are crucial factors for reduction of metal oxides, and it is important to identify the ideal conditions [21]. Based on the pressure drop, as shown in Fig. 3, the optimal flow rate 6 L/min in this study was determined by the minimum fluidizing velocity, superficial gas velocity of 0.015 m/s, and the bed diameter of 0.053 m.

Fig. 6 illustrates reduction rate according to changes in the reaction time from 20, 40 to 60 min at each temperature. The rates varied between 40 and 71% at a reaction temperature of 400 °C, and varied between 81% and 99 at 600 °C. The reduction rate increased as reaction temperature and reaction time increased. Reduction rate of 99% was obtained for a reaction time of 60 min and a reaction temperature of either 550 or 600 °C; however, 550 °C is preferred as the more efficient operating temperature for its lower operating cost and stable operation. The original NiO powder mass of the metal oxides is reduced as the oxygen is separated during reduction [22]. When oxygen is removed during reduction process from NiO, leaving behind only Ni, the resulting weight reduction can be expressed as a mass loss. The weight of mass loss in the reduction process in the fluidized bed reactor is an indicator

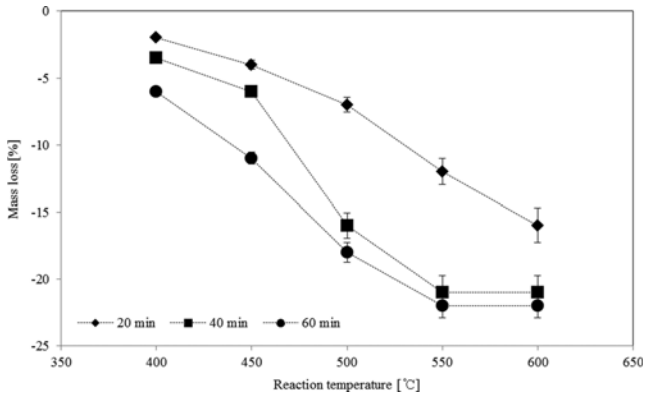

Fig. 7. Comparison of the mass loss as a function of reaction time and reaction temperature.

that can be used to assess the produced metal rate. Fig. 7 shows the mass loss at different reaction times and temperatures. The loss increased with increasing reaction temperature and time. The 'mass loss-reaction time' slope was gentle for the reaction time of 20 min, and similar trends were observed for 40 and 60 min reaction times. An average difference of 1% was observed between reaction temperatures of 550 and 600 °C.

4. Structure Shape

Metal oxides can go through a variety of changes during the reduction process. Therefore, it is crucial to conduct structural analysis using SEM images [23]. Fig. 8 shows x5,000, x10,000, and x20,000 SEM images for comparison of the original NiO powder with the product obtained after the experiment. The conditions of the original NiO powder were a superficial gas velocity of 0.015 m/s, reaction temperature of 550 °C, and reaction time of 60 min.

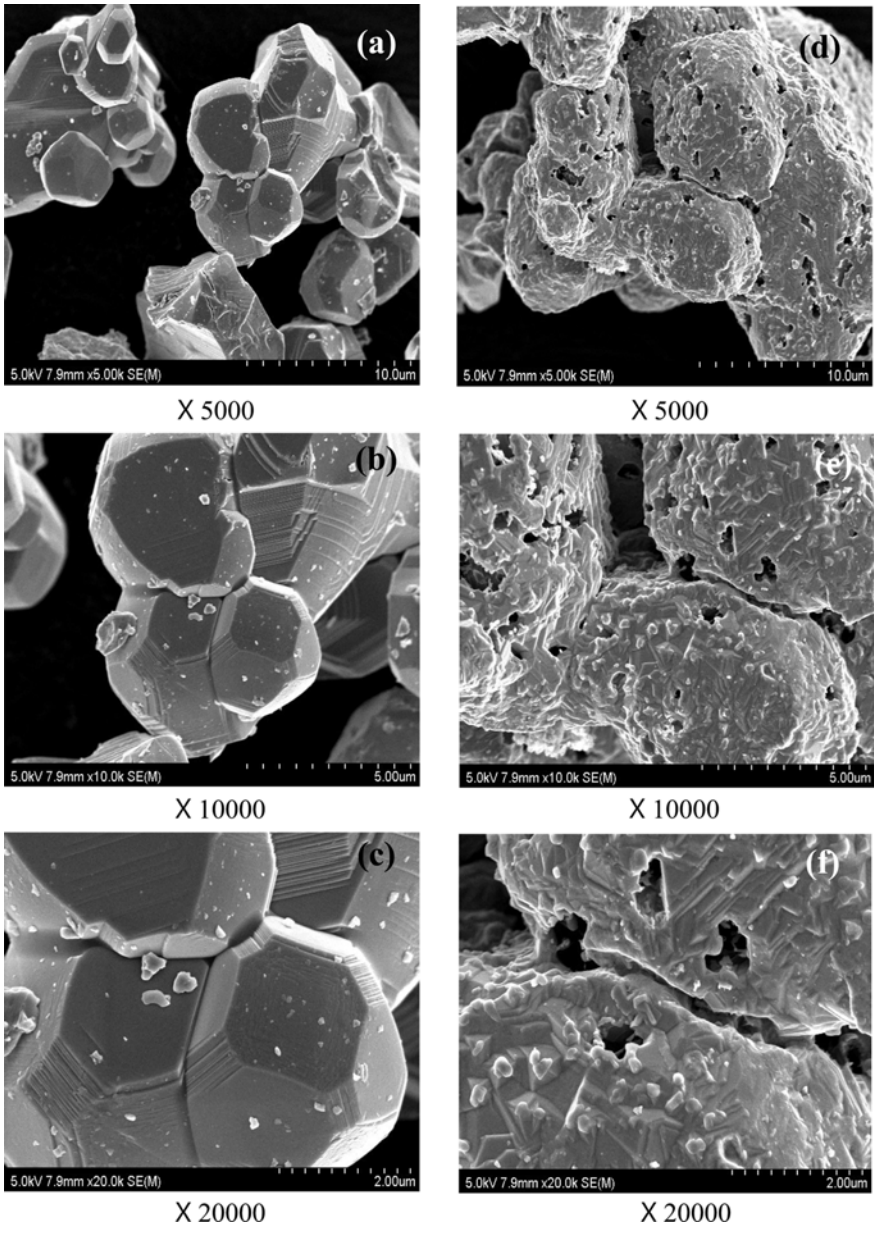

Fig. 8. SEM images of the NiO powder before reduction (a)-(c) and after reduction (d)-(f).

Before the experiment, octagonal shapes were observed in the NiO powders; after the experiment, the products contained air pockets and microcracks.

CONCLUSIONS

Hydrogen reduction of NiO powder was performed in a laboratory-scale fluidized bed reactor. The highest reduction rate of 99% was achieved under the following conditions: superficial gas velocity of 0.015 m/s, reaction temperature of 550 °C, and reaction time of 60 min. As the reaction temperature increased, the pressure drop and minimum fluidization velocity decreased, which were determined to have been caused by the decreased weight of NiO powder associated with mass loss. Oxygen was completely reduced at 550 °C. Fluidization was most active when the height of the stocked NiO powder in the fluidized bed reactor was equal to the bed diameter of the reactor. The structural analysis of images under optimal conditions revealed formation of air pockets and numerous microcracks, which were visible to the naked eye.

ACKNOWLEDGEMENTS

This research was supported by the Ministry of Trade, Industry & Energy (MOTIE), Korea Evaluation Institute of Industrial Technology (KEIT) through the Encouragement Program for The Industries of Economic Cooperation Region.

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