TWO-STAGE FLUIDIZED-BED SYSTEMS FOR THE METAL POWDER PRODUCTIONS OF MOLYBDENUM AND NICKEL

KIM Yong Ha, KIM Hang Goo

Department of Chemical Engineering, Pukyong National University, Nam-gu, Busan, Republic of Korea,
yhkim@pknu.ac.kr

Abstract

As a pyro-metallurgical process, a fluidized-bed process can be employed because of its high transfer rates of heat and mass between gas and powder particles. The metal powder production usually needs to be divided to a few steps to obtain an efficiency of stepwise control or to solve some operational difficulties. In these cases, a multi-stage fluidized-bed system can be used to meet different operating conditions of steps. Hydrogen reduction processes of oxides by a two-stage fluidized-bed reactor are investigated in this study for the metal powder productions of molybdenum and nickel. For the molybdenum powder production, before the hydrogen reduction, a serial use of a single fluidized-bed reactor for the calcination of an ammonium molybdate to make a molybdenum oxide, is also investigated. As results, optimal or desirable operational conditions (temperature, residence time and gas consumption rate) for each fluidized-bed step are provided, as well as the process conceptions of the hydrogen reduction by the two-stage fluidized-bed reactors.

Keywords: Fluidized-bed, multi-stage, molybdenum oxide, nickel oxide, hydrogen reduction

1. INTRODUCTION

Metal powders are usually produced through the reduction of oxidic intermediate powders using reductants such as hydrogen gas and CO gas [1]. In the production of molybdenum powder of high purity, ammonium molybdates are usually the first intermediates, and are calcined into molybdenum oxides, which are the second intermediates, before the reduction. On other hand, in the production of nickel metal powder, nickel oxides are usually the intermediates. There are two types of commercial nickel oxide, Nickel (II) and Nickel (III) oxides. Nickel (II) oxide is the chemical compound with the formula NiO and is referred to green nickel oxide, whereas Nickel (III) oxide is known to have the formula Ni_2O_3 and referred to black nickel oxide [2]. The green nickel oxide is notable as being the only well-characterized oxide of nickel, whereas the black nickel oxide is not well characterized [3]. The hydrogen reduction of green nickel oxides has been extensively studied over the past decades and many results of kinetic, mechanistic and thermodynamic analyses have been reported. In this study, therefore, the hydrogen reduction behavior of the black Ni oxide powder was investigated.

In gas-solid reaction systems, fluidized-bed reactors are usually employed because of their high transfer rates of heat and mass between gas and powder particles. The metal powder production usually needs to be divided into a few steps to obtain an efficiency of stepwise control or to solve some operational difficulties. For these purposes, a multi-stage fluidized-bed system can be used to meet different operating conditions of steps. There have been a lot of investigations on the use of single fluidized-bed reactors, but few studies on the use of the multi-stage fluidized-bed systems have been reported due to technical difficulties.

In this study, the use of fluidized-bed reactors in the calcination and reduction steps will be presented with optimal or desirable operation conditions (which have been obtained by a serial of tests using a lab-scale fluidized- bed reactor) for each step. In addition, multi-stage fluidized-bed systems to produce molybdenum and nickel metal powder from their oxidic mediates will be finally introduced.

2.   EXPERIMENTAL

In this study, the ammonium molybdate sample was prepared from a molybdenite concentrate from Chile by crystallization after desulfurization and ammonia water leaching, and a commercial black nickel oxide concentrate from Vale company was used as a nickel oxide sample. The chemical compositions of the samples obtained by XRF (XRF-1700, SHIMADZU, Japan) are given in **Table 1**. A fluidized bed reactor used in this study has an inner diameter of 0.02 m at the lower part and 0.04 m at the upper part, a height of 0.7 m, and was made of SUS 310S. Ar gas was used as the inert gas until the oxide sample was preheated to the targeted temperature. After every experiment, the specimen was taken out of the fluidized-bed reactor and then was characterized by X-ray diffraction (XRD, D/Max 2500, Rigaku, Japan) and scanning electron microscopy (SEM, S-2400, HITACHI, Japan). The fractional conversion was identified by EDAX.

Table 1 Composition (wt.%) of samples used in the study

Molybdenite	Mo	S	Fe	Cu	Al	Si
MoS_2	41.82	24.92	1.51	1.74	4.01	4.01
Nickel Oxide	Ni	O	Fe	Ca	Mn	Si
Black	80.87	17.86	0.33	0.16	0.45	031

3.   RESULTS AND DISCUSSION

3.1.   Molybdenum metal powder production

The ammonium molybdate prepared from the molybdenite concentrate had particle sizes ranging 5~100 μm, an average size of 30 μm, and a tapping density of 2.22 g/cm^3, which can be classified as Geldart A. An optimal fluidized velocity was found to lie in the range of 0.35÷0.67 m/s at 500 °C. When ammonium molybdate is heated, ammonium molybdate decomposes in a stepwise procedure and gives off NH_3 and H_2O, leaving MoO_3 as the final product. The stepwise decomposition is reported in literature as follows; $(NH_4)_6Mo_7O_{24} \cdot 4H_2O \rightarrow (NH_4)_4Mo_5O_{17} \rightarrow (NH_4)_2Mo_4O_{13} \rightarrow (NH_4)_2Mo_{14}O_{43} \rightarrow (NH_4)_2Mo_{22}O_{67} \rightarrow MoO_3$ [4, 5]. According to the analytical results of TGA, DTA and XRD (**Figure 1**) in this study, the stepwise decomposition was observed in the range of 110 ÷ 380 °C, and finished around 400 °C. The experimental results for the fluidized-bed decomposition of ammonium molybdate are shown in **Figure 2**, and optimal conditions are found to be as follows: a temperature range of 400 ÷ 500 °C, a residence time of 30 ÷ 40 min, and a specific (air) gas consumption rate of 600 ÷ 700 Nm^3/t-AM.
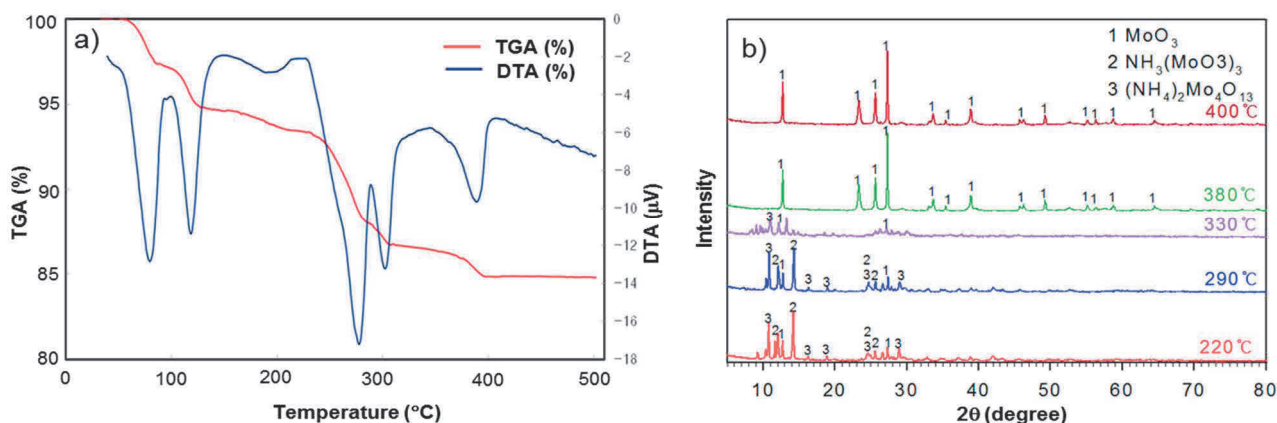

Figure 1 Decomposition of ammonium molybdate with temperature: a) TGA and DTA, b) XRD pattern
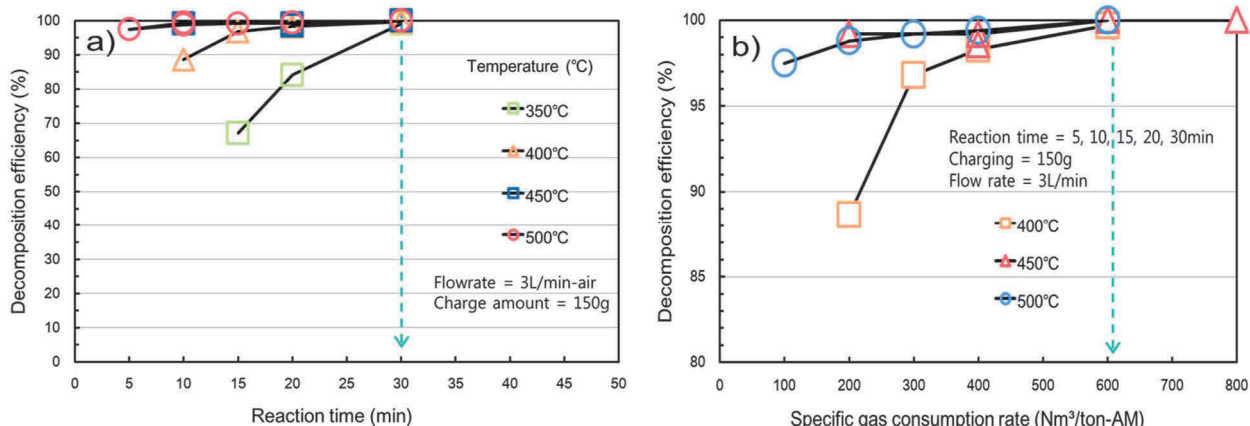
Figure 2 Experimental results for the fluidized-bed decomposition of ammonium molybdate: a) effects of temperature and residence time, b) effects of specific gas consumption rate

The next step is the reduction of the decomposed (or calcined) ammonium molybdate, i.e. MoO_3. The reduction of molybdenum oxide is necessarily carried out in two steps to prevent the defluidization by the sublimation of MoO_3 at temperatures above about 650 °C and to prevent the formation of coarse metal powder due to the presence of water vapor developed during the reaction [1, 6, 7, 8]. In the first stage, molybdenum trioxide is reduced at a temperature in the range of 500 ÷ 550 °C to produce molybdenum dioxide ($MoO_3 + H_2 \rightarrow MoO_2 + H_2O$), and in the second stage, the molybdenum dioxide begins to reduce to molybdenum in the temperature range of 850÷900 °C ($MoO_2 + 2H_2 \rightarrow Mo + 2H_2O$). In this study, a two-stage reduction by hydrogen of the decomposed ammonium molybdate is also examined and the results are shown in **Figure 3** and **Figure 4**.
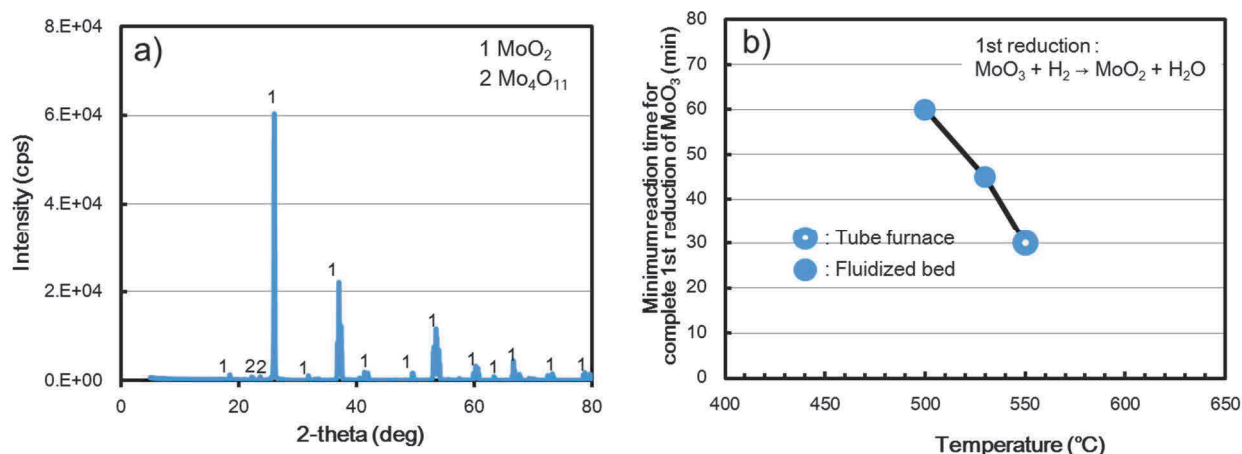

Figure 3 Experimetal results for the first stage reduction of MoO_3: a) XRD pattern in which Mo_4O_{11} phase is almost disappeared, b) plot of the minimum residence time versus temperature

For the first stage, the minimum residence time which is required for the complete disappearance of Mo_4O_{11} phase (**Figure 3a**), is plotted versus temperature in **Figure 3b**, in the temperature range of 500÷550 °C. For example, the minimum residence time for the first stage is 45 min at 530°C. In the consideration of amount of MoO_3 sample (50g) and hydrogen flow rate (2 liter/min), the specific (hydrogen) gas consumption rate per ton of MoO_3 is in the range of 1200÷2400 Nm^3/t-MoO_3. For the second stage, the minimum residence time which is required for the complete disappearance of MoO_2 phase (**Figure 4a**), is plotted versus temperature in **Figure 4b**, in the temperature range of 850÷900 °C. The minimum residence time for the second stage is 45 min at 900 °C. In consideration of the amount of MoO_2 sample (50g) and the hydrogen flow rate (2 liter/min), the

specific (hydrogen) gas consumption rate per ton of MoO_2 is in the range of $1200\div2400$ Nm^3/t-MoO_2. Using all the data above, a multi-stage fluidized-bed process to produce molybdenum metal powder from ammonium molybdate can be established shown in **Figure 5**.
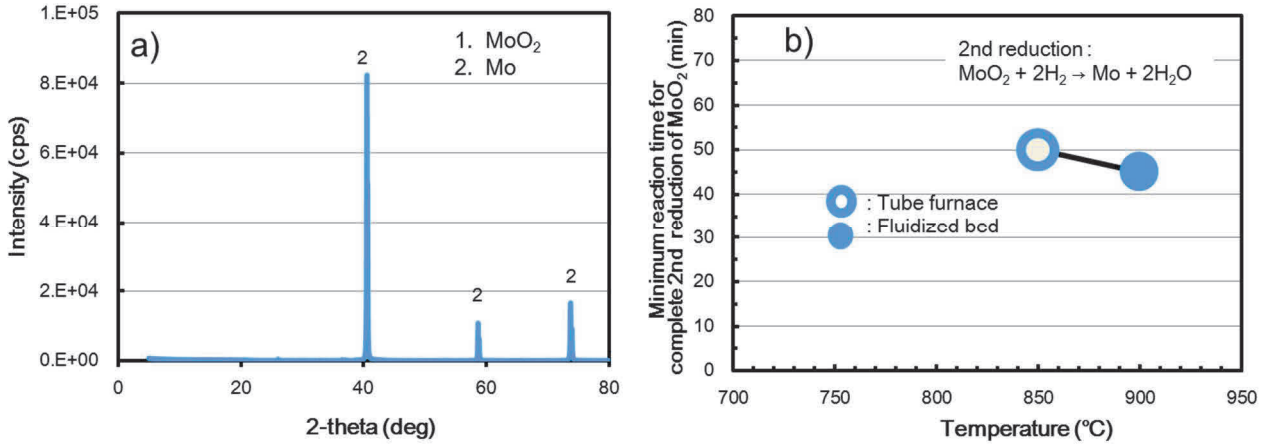

Figure 4 Experimetal results for the second stage reduction of MoO_2: a) XRD pattern in which MoO_2 phase is almost disappeared, b) plot of the minimum residence time versus temperature
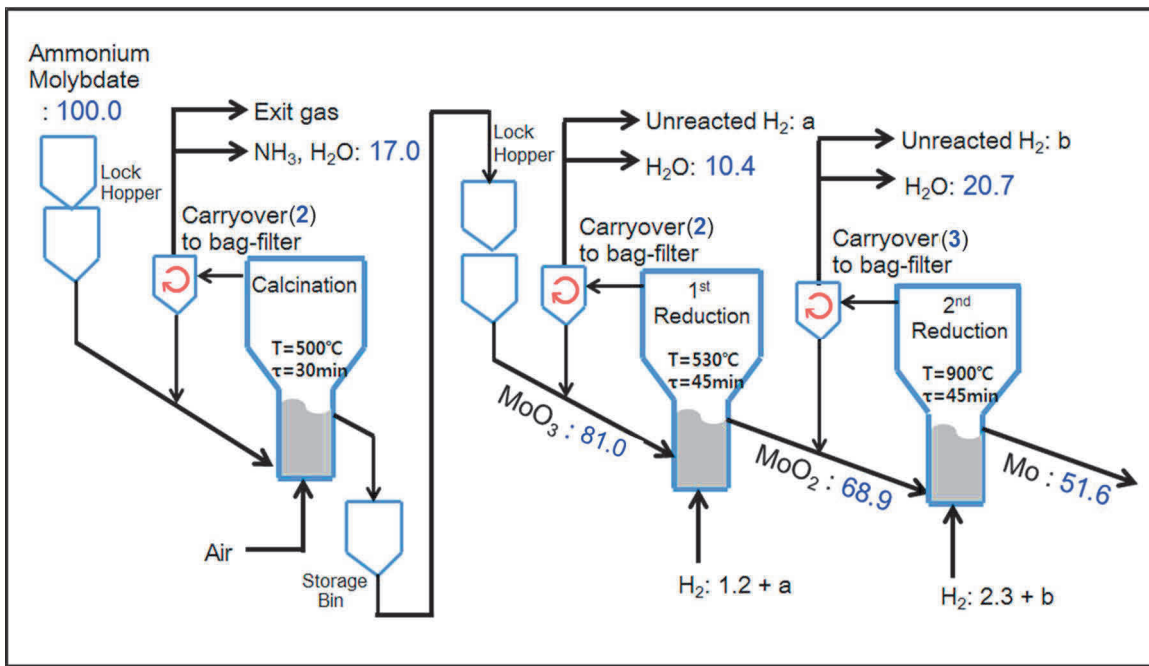

Figure 5 Process flow diagram of a multi-stage fluidized-bed system to produce a molybdenum metal powder from an ammonium molybdate

3.2. Nickel metal powder production

Many investigations have reported on the hydrogen reduction of nickel oxides and some of them have reported a sintering phenomenon (pore blocking or particle agglomeration) during the hydrogen reduction at high temperatures [9-11]. Jun et al. [10], especially, examined a two-stage reduction process for the production of high-purity ultrafine Ni particles (below 10 μm) in a micro-fluidized bed reactor to prevent the defluidization by the particle agglomeration. The single- and two-stage reduction processes were also examined in this study using a black nickel oxide that has approximately ten times bigger particle size (below 100 μm), and a similar

agglomeration phenomenon was observed in single-stage fluidized-bed reduction at a temperature above 500 °C, as shown in **Figure 6a** and **Figure 6c**. This agglomeration phenomenon could be prevented by using a two-stage fluidized-bed operation (the first reduction at a low temperature and the second reduction at a high temperature) as shown in **Figure 6c** and **Figure 6d**.
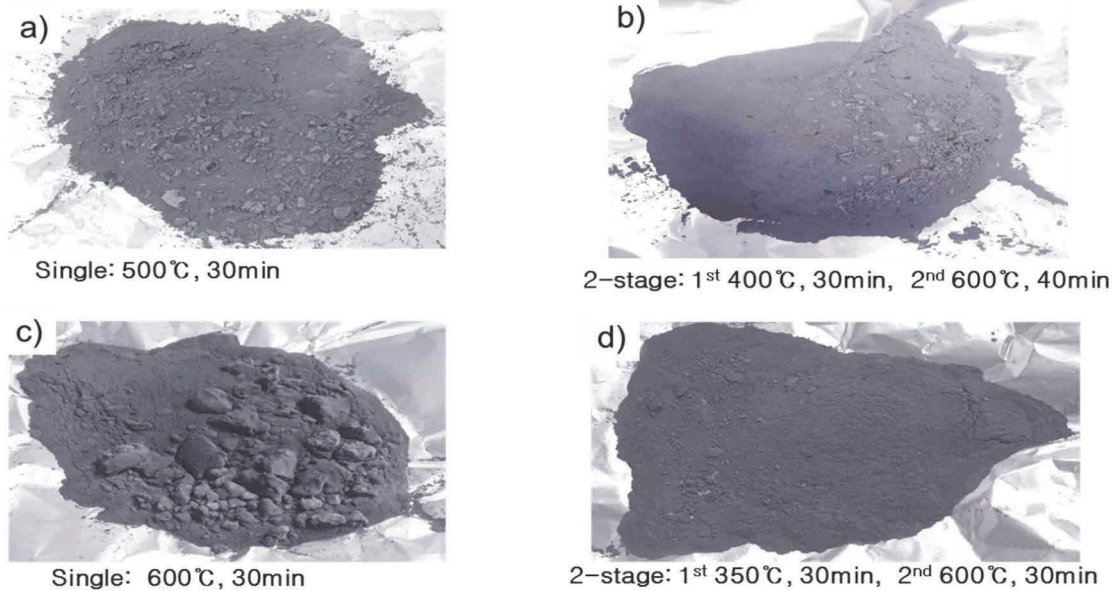

Figure 6 Reduced black nickel oxide powders : a) single stage at 500 °C and 30 min, b) the first stage at 400°C and 30 min and the second stage at 600 °C and 40 min, c) single stage at 600 °C and 30 min, d) the first stage at 350°C and 30 min and the second stage at 600 °C and 30 min (at the sample amount of 75 g and at the hydrogen flow rate of 6 liter/min)

From the results of this study and the literature survey, optimal (or desirable) operation conditions for a two-stage fluidized-bed reduction by hydrogen can be established as follows: 1) for the first reduction; a temperature range of 350 ÷ 400 °C, a residence time of 30 ÷ 40 min, and a specific (hydrogen) gas consumption rate of 1600 ÷ 3200 Nm^3/t-NiO, 2) for the second reduction; a temperature range of 550 ÷ 600 °C, a residence time of 20 ÷ 30 min, and a specific (hydrogen) gas consumption rate of 1600 ÷ 2400 Nm^3/t-NiO.
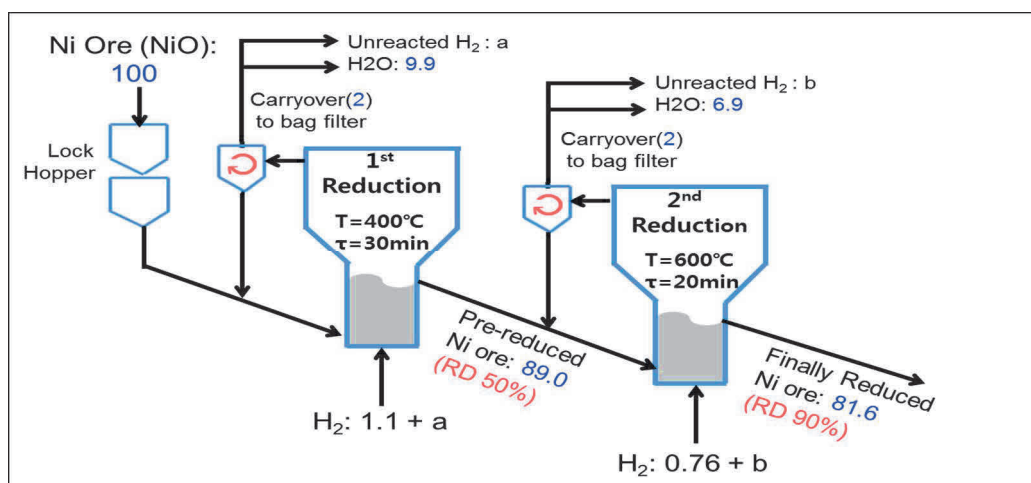

Figure 7 Process flow diagram of a two-stage fluidized-bed system to produce a nickel metal powder

Using all the data above, a two-stage fluidized-bed process to produce nickel metal powder, of which reduction degree (i. e. the percentage of the removed oxygen from the total oxygen in the black nickel oxide) is around 90 %, from a black nickel oxide can be suggested as can be seen in **Figure 7**.

4. CONCLUSION

In this study, the use of multi-stage fluidized-bed systems to produce molybdenum and nickel metal powder from their oxidic mediates, was investigated and optimal (or desirable) conditions for each step have been obtained by a serial of tests with a lab-scale fluidized- bed reactor.

For the production of molybdenum metal: 1) for the calcination of ammonium molybdate; a temperature range of $400 \div 500$ °C, a residence time of $30 \div 40$ min, and a specific (air) gas consumption rate of $600 \div 700$ Nm^3/t-AM, 2) for the first reduction by hydrogen; a temperature range of $500 \div 550$ °C, a residence time of $30 \div 60$ min, and a specific (hydrogen) gas consumption rate of $1200 \div 2400$ Nm^3/t-MoO_3, 3) for the second reduction by hydrogen; a temperature range of $850 \div 900$°C, a residence time of $40 \div 50$ min, and a specific (hydrogen) gas consumption rate of $1200 \div 2400$ Nm^3/t-MoO_2

For the production of nickel metal: 1) for the first reduction by hydrogen; a temperature range of $350 \div 400$ °C, a residence time of $30 \div 40$ min, and a specific (hydrogen) gas consumption rate of $1600 \div 3200$ Nm^3/t-NiO, 2) for the second reduction by hydrogen; a temperature range of $550 \div 600$°C, a residence time of $20 \div 30$ min, and a specific (hydrogen) gas consumption rate of $1600 \div 2400$ Nm^3/t-NiO.

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