The Reduction of Gamma-Irradiated Nickel Oxide by Hydrogen

By Toshiro YAMASHINA and Takaaki NAGAMATSUYA

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In the process of reducting nickel oxide by hydrogen, it has been observed by several investigators that the reduction started after an induction period.[1-3] According to Hauffe,[1] the induction period should correspond to the period required for the nuclei formation of metallic nickel. Parravano[2] investigated the reduction process of nickel oxide from the view point of the electronic state of the semiconductor. Because the nickel oxide is a p-type semiconductor containing excess oxygen, it may be expected that the reduction process of nickel oxide could be affected by its physical properties, such as the electronic state and its non-stoichiometry. In this work, a gamma-irradiated nickel oxide will be found to behave in an unusual manner in the reduction process by hydrogen, depending upon the radiation dose.

Pure nickel oxide samples were obtained by decomposing and firing c. p. nickel nitrate in an atmosphere of air for five hours at 500°C. The reduction velocities were measured in an all-glass, closed system of a Gulbransen-type microbalance[4] with a sensitivity of 7.21×10^{-7} g./div. The reaction temperature was 190°C and the hydrogen pressure, 60 mmHg. The hydrogen used in these experiments was prepared by diffusing it through a palladium film. The irradiation was carried out with Co-60 gamma-rays, the intensity of which was 5.85×10^{5} r./hr.; the total dose reached about 2×10^{8} r.

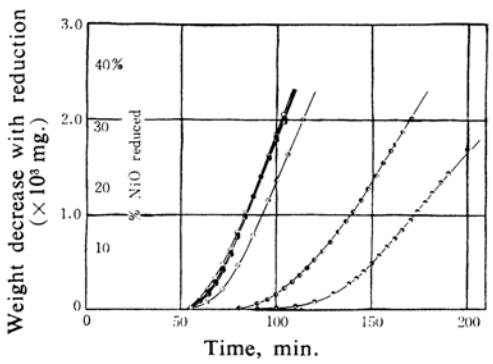

Fig. 1. The reduction curves of gamma-irradiated nickel oxide by hydrogen.

○ not irradiated ● 2.93×10^{5} r.
◑ 1.0×10^{7} r. ◉ 5.85×10^{7} r.
◐ 8.5×10^{7} r. ◓ 1.07×10^{8} r.

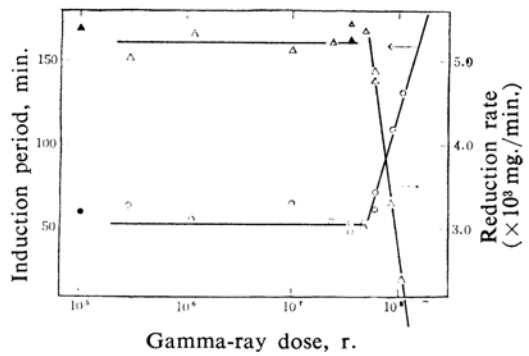

Fig. 2. Induction period and reduction rate as a function of irradiation dose.
▲, ● not irradiated

The reduction curves of the irradiated nickel oxide are presented in Fig. 1. The reduction velocities were found to decrease with the radiation dose, being remarkable over a total dose of 5.8×10^{7} r. The induction periods and the reduction rates are plotted as a function of the irradiation dose in Fig. 2, for which the induction periods were obtained by extraporating the curves in Fig. 1 to the time axis while the reduction rates were estimated from the slope of the linear part after the induction period. It is to be noted that both values changed abruptly at irradiation doses above 5×10^{7} r. In order to explain the above phenomena, other measurements with a change of irradiation dose were made. The measurement of chemisorbed oxygen by means of iodometry[5,6] showed the same tendency as that in the induction periods and the reduction rates with irradiation; in other words, no change in the excess oxygen in nickel oxide was revealed up to irradiation dose of 5×10^{7} r., while an abrupt increase of excess oxygen was

1) K. Hauffe and A. Rahmel, *Z. physik. Chem. N. F.*, 1, 104 (1954).
2) G. Parravano, *J. Am. Chem. Soc.*, 74, 1194 (1952).
3) Y. Iida and K. Shimada, This Bulletin, 33, 8 (1960).
4) T. Shibata and G. Okamoto, *Denki Kagaku*, 32, 293 (1964).
5) S. W. Weller and S. E. Volts, *J. Am. Chem. Soc.*, 76, 4695 (1954).
6) M. Nachman, I. Maxim and T. Braun, *J. Phys. Chem. Solids*, 20, 307 (1961).

observed above 1×10^8 r. The excess oxygen in nickel oxide was found to be 0.04—0.05 atm. % in the case of both unirradiated and irradiated less than 5×10^7 r., while 0.12 atm. % in that of 2×10^8 r. irradiated. No differences in BET surface area were observed in any case.

On the basis of results presented above, it may be concluded that the reduction of nickel oxide by hydrogen is greatly influenced by non-stoichiometry with gamma-irradiation. Detailed observations, such as hydrogen adsorption and catalysis by the gamma-irradiated nickel oxide, are now being made.

Faculty of Engineering
Hokkaido University
Sapporo