Hydrogen Reduction of a Single Crystal of Nickel Oxide

By Yoshio IIDA and Kenzo SHIMADA

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In an earlier paper[1] it was shown that the reduction of nickel oxide was strongly affected by a small amount of additive incorporated in the nickel oxide lattice. Little attention has been paid to the mechanism of hydrogen reduction of metal oxide, while the mechanism of oxidation of metal has been studied successfully since Wagner's theory[2]. Recently Baba[3] explained the mechanism of hydrogen reduction of germanium dioxide by assuming that the reduction is governed by an autocatalytic behavior. Murata[4] reported that a diffusion process of cation or anion is a rate-determining process in the hydrogen reduction of iron oxide. In their experiments oxide powder was used as a specimen. As powder exhibits complicate properties resulting from particle size and shape, powder is thought to be unfavorable to the study of the mechanism of the hydrogen reduction. From these points it is desirable to study the hydrogen reduction of a single crystal. In the present study the hydrogen reduction of a single crystal of nickel oxide has been carried out to explain the mechanism of the reduction.

Experimental Procedure

A single crystal of nickel oxide was prepared by Tochigi-Kagaku Co. in a way similar to Verneuil's method[5]. Rectangle specimens of 6×4×3 mm. were cut out from the raw material. The specimens were not subjected to further treatment.

Nickel nitrate recrystallized four times was heated at 800°C for 10 hr. to obtain nickel oxide powder. The average particle size of the nickel oxide was about 0.5 μ according to an electron micrograph.

The weight loss during the reduction process was measured by the thermobalance with a sensitivity of 0.5 mg. The apparatus could be used in hydrogen or in vacuo. After the specimen was heated in vacuo at a desired temperature, it was reduced with hydrogen. Hydrogen was used from a commercially available tank after purifying it with concentrated sulfuric acid, hot platinum asbestos, potassium hydroxide and phosphorus pentoxide.

Results and Discussion

Time-dependent Study.—A comparison of a reduction-temperature curve of a single crystal of nickel oxide with that of nickel oxide powder when heated at a velocity of 100°C/hr. is shown in Fig. 1. It is seen that a rate of reduction of the single crystal is much lower than that of the powder. It should be noted that there is the stage at about 500°C in the case of the single crystal where the reduction slows down. In order to elucidate the mechanism of the hydrogen reduction of nickel oxide, the isothermal reduction of the single crystal was studied in the range of 300°C to 800°C. The results are shown in Fig. 2. To see whether

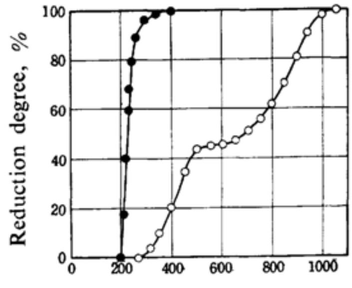

Fig. 1. Reduction-temperature curves of a single crystal of nickel oxide (○) and nickel oxide powder (●).

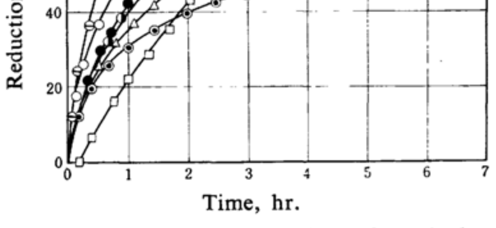

Fig. 2. Isothermal reduction of a single crystal of nickel oxide. □, 300°C: ●, 350°C: △, 400°C: ⊙, 500°C: ◑, 600°C: ○, 700°C: ⊖, 800°C

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[1] Y. Iida and K. Shimada, This Bulletin, to be published.

[2] C. Wagner, *Z. physik. Chem.*, **49**, 735 (1936).

[3] H. Baba, This Bulletin, **29**, 789 (1956).

[4] Y. Murata and N. Kasaoka, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **61**, 1440 (1958).

[5] J. Nakazumi, ibid., **59**, 1304 (1956).

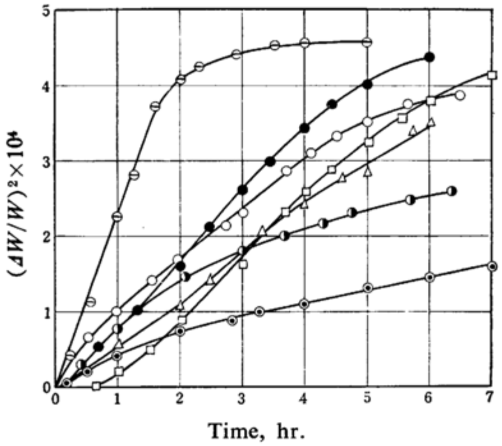

Fig. 3. Parabolic plot of isothermal reduction of a single crystal of nickel oxide. □, 300°C: ●, 350°C: △, 400°C: ⊙, 500°C: ◑, 600°C: ○, 700°C: ⦶, 800°C.

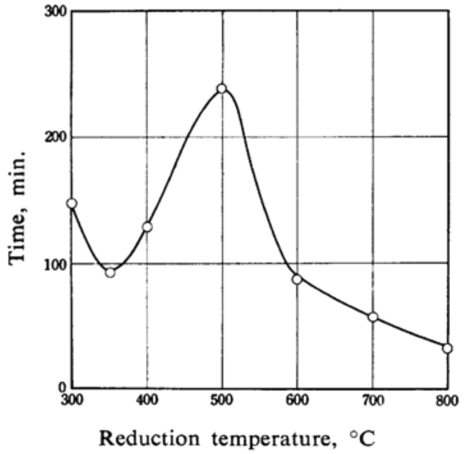

Fig. 4. Time required to obtain 50% reduction at various temperatures.

the isotherms can be expressed by the parabolic law, a square of the reduction loss per gram is plotted against the reduction time. Fig. 3 shows that the reduction of the single crystal does not obey the parabolic law. A rate of reduction of the single crystal does not always increase with an increase in the reduction temperature. In Fig. 4, the time required to obtain 50% reduction is plotted against the reduction temperature. It is seen that the time at 350°C is shorter than that at 300°C whereas the time increases with an increase in the reduction temperature in the range of 350°C to 500°C. Since the time is reversely proportional to the rate of the reduction, the rate is lowest at 500°C and then increases with an increasing temperature as do ordinary chemical reactions. The stage at which the reduction does not proceed in the reduction-temperature curve of the single crystal at 500°C is attributed to the lowest rate of the reduction at 500°C. In the reduction of nickel oxide powder or other metal oxide such as ferric oxide and tungsten oxide powder, these phenomena were not observed.

Microscopical Examination. — Reduction of the single crystal oxide proceeds layer by layer as shown in Fig. 5. The specific gravity of the single crystal of nickel oxide is 6.8 and that of nickel is 8.90. As a volume ratio of nickel oxide is 6.8/8.9=0.76, the specific volume of nickel is lower than that of nickel oxide. Accordingly, the nickel layer formed on the nickel oxide by the hydrogen reduction should be very porous. The reduction mechanism is considered schematically as follows. Hydrogen passes through the porous nickel layer, and reacts with nickel oxide at the boundary of nickel and nikel oxide. The water formed as a result of the reduction is released from the boundary. The penetration of hydrogen through the porous nickel layer is very easy because of its small molecular size. However, the desorption of water through the nickel layer is thought to be very difficult because of its large molecular size. By this reduction schema, the desorption of water formed is considered to be a rate-determining step in the hydrogen reduction process. Nickel formed on the surface of nickel oxide by the reduction is composed of very fine particles, and the particles start to sinter with an increase in the reduction temperature[6,7]. It is expected that the number and size of the pores decrease at higher temperatures by sintering, and the desorption of water through the pores is retarded. It may be attributed to

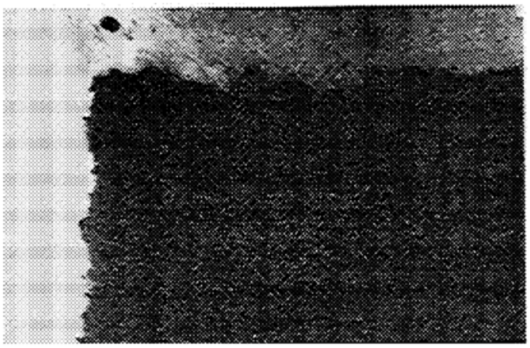

Fig. 5. A section of a single crystal of nickel oxide reduced partially. A white part is a reduced nickel phase and a brack part is an unreduced nickel oxide phase. (×20)

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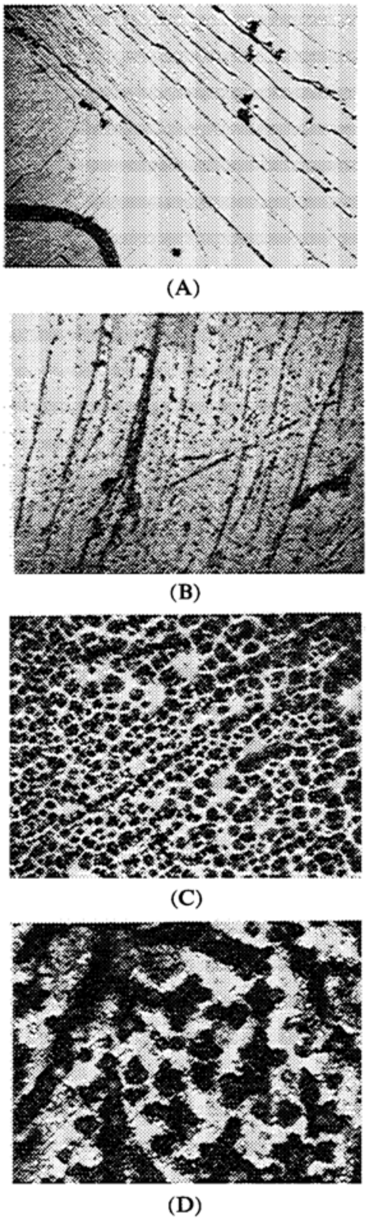
[6] R. Ueda, *J. Japan Inst. Metals* (*Nippon Kinzoku Gakkai-Shi*), **23**, 292 (1959).

[7] P. H. Emmett, "Catalysis" Vol. I The Waverly Press, Inc., New York (1954), p. 371.

the change of the pores by sintering that the rate of reduction decreases in the range of 350 to 500°C.

While the sintering is enhanced above 500°C, a pressure of water vapor increases and thus the water vapor passes through the nickel layer forming large pores at higher temperatures. Water vapor can easily be released through the large pore and then the reduction process is promoted above 500°C as shown in Fig. 4.


(A)

(B)

(C)

(D)

Fig. 6. Microphotographs of the surface of a single crystal of nickel oxide reduced at various temperatures. (A) is for the unreduced crystal; (B), for the crystal reduced at 400°C: (C), for the crystal reduced at 800°C: and (D), for the crystal reduced at 1000°C. (×400)

A microscopical examination shows that these explanations are correct. Fig. 6a is a microphotograph of the free surface of the unreduced single crystal. Fig. 6b shows that there are many small pores on the surface of the single crystal reduced at 400°C. It is seen in Figs. 6c and 6d that the pores become larger when the single crystal was reduced at 800 and 1000°C. From these facts it is concluded that the release of water from the boundary of the metal and the oxide is a rate-determining step in the hydrogen reduction of the single crystal of nickel oxide.

Study on the Reduction of Nickel Oxide Powder.—It is of interest to see whether the reduction of nickel oxide powder can be explained by the above mechanism. Nickel oxide powders of which praticle size was about 1 μ were compressed to a tablet of 10 $\phi \times 5$ mm. at a pressure of 1000 kg./cm^2. The bulk density of the tablet was 3.2 g./cc. and its porosity was 52%, which was thought to be sufficient for the penetration of hydrogen or the release of water. It is expected that each nickel oxide powder can be reduced homogeneously all over the tablet, and the reduction of each powder is governed by the above mechanism. The tablet was reduced at 180 and 250°C. Fig. 7 shows the section of the tablet reduced incompletely. It is seen that the reduction proceeds layer by lager in spite of the porous tablet. At 250°C at which there is no induction period, the reduction starts at the exterior of the tablet. At a reduction temperature of 180°C at which there is an induction period of reduction, the reduction starts at the interior of the tablet. It is generally accepted that a rate of oxidation of nickel is negligibly small below 300°C[8]. The outer oxide layer observed in the reduction of 180°C can not be attributed to the re-oxidation with oxygen contained in hydrogen or with water formed. These facts can not be explained completely by the mechanism reported in the previous literatures[2,3]. At present there is no

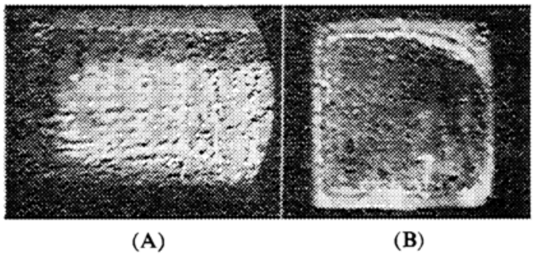

(A) (B)

Fig. 7. A section of a compact of nickel oxide powder reduced at 250°C (A) and 180°C (B). (×10)

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8) A. E. Gulbransen and K. F. Andrew, *J. Electrochem. Soc.*, **101**, 128 (1954).

alternative but to say that the reduction of nickel oxide powder proceeds topochemically.

Crystal Growth of Nickel Reduced.—It is reported[9] that oxide film formed on the metal surface by oxidation has a preferential orientation related to the crystal orientation of the metal. No attention has been paid to the crystal growth of the reduced metal on the metal oxide by the hydrogen reduction from the viewpoint of the crystal orientation of the reduced metal and the metal oxide.

The plane of cleavage of the single crystal of nickel oxide is known to be (100) plane[5]. The nickel layer reduced on the (100) plane of the single crystal of nickel oxide at 1000°C was etched and examined microscopically. The result is shown in Fig. 8, where a square etch pit is seen. It is concluded that nickel formed on (100) plane of nickel oxide by the reduction has (100) plane as perferential orientation.

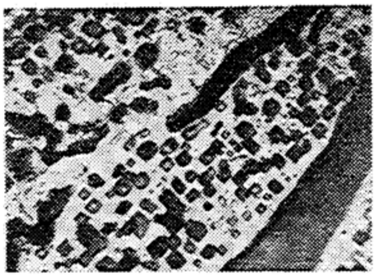

Fig. 8. Etch pit of reduced nickel. The etching reagent is concentrated nitric acid. (×400)

Summary

In the hydrogen reduction of a single crystal of nickel oxide, the rate of reduction does not always increase with an increase in the reduction temperature. In the range of 350 to 500°C the rate decreases with the temperature, and the rate is the lowest at 500°C. These facts are explained reasonably by the microscopical examination of the surface of the reduced nickel. It is concluded that the desorption of the water formed through the pores is a rate-determining step in the reduction of the single crystal of nickel oxide. The nickel formed on (100) plane of nickel oxide by the reduction has (100) plane as a preferential orientation.

The single crystal of nickel oxide was kindly presented to us by Tochigi Kagaku Kogyo Co.

Government Industrial
Research Institute
Kita-ku, Nagoya

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[9] I. S. Kerr, *J. Inst. Metals*, **85**, 379 (1956).