Effect of Compacting and Grinding on the Hydrogen Reduction of Nickel Oxide

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(Received February 10, 1960)

It has long been known that metal is hardened as a result of plastic deformation when it is pressed or rolled. Recently, it has been reported that the physical or chemical properties of non-metallic substances such as oxide[1], ionic crystal[2] and mineral[3] also vary when they are ground or pressed. Although these phenomena are not explained completely at present, increasing interest is being shown in the plastic deformation of ionic crystal.

In the previous paper[4] dealing with the hydrogen reduction of nickel oxide, it was shown that the rate of reduction was affected by the crystal distortion induced by the dissolution of minor additives. It is thought to be desirable to see how the reduction of nickel oxide is affected by grinding or compacting. In the present paper the isothermal reduction of nickel oxide, in a single crystal form or in powder form, subjected to grinding or compacting has been studied, consideration being given to the surface area of the specimens.

Experimental

Chemical pure nickel sulfate recrystallized four times was heated at 850°C for 10 hr. to obtain nickel oxide powder. The average unit-particle size of nickel oxide was about 0.5 μ according to its electron micrograph. Nickel oxide was compacted into tablets at various pressures of 0 to 2000 kg./cm^2. A single crystal of nickel oxide was prepared by the method similar to that described by Verneuil[5].

The rate of reduction by hydrogen was determined by a thermobalance with a sensitivity of 0.5 mg. and could be used in hydrogen and in vacuo. Since the rate of reduction of nickel oxide by hydrogen at 200°C was a suitable magnitude for a comparison of the rates of specimens subjected to various treatments, the isothermal reduction was carried out at 200°C in the present study. In all cases of this experiment, nickel oxide of a constant weight of 500 mg. was heated up to 200°C in a vacuum of 10^{-3} mmHg and reduced at a constant temperature of 200°C by hydrogen whose flowing velocity was 100 cc./min.

Hydrogen from a commercially available cylinder was used after being purified with concentrated sulfuric acid, hot platinum asbestos, potassium hydroxide and phosphorus pentoxide.

The surface area of nickel oxide powder was determined by the B. E. T. method[6] in which nitrogen was the absorbent.

Results and Discussion

Effect of Compacting Pressure.—The bulk density of nickel oxide pressed at various pressures of 0 to 2000 kg./cm^2 was measured from the ratio of weight of dimension. Table I shows that the bulk density increases and the calculated porosity decreases with an increase

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[1] J. B. Wachtman, *J. Am. Ceram. Soc.*, **37**, 291 (1954). A. S. Keh et al., *Acta Metallurgica*, **7**, 694 (1959).

[2] S. Sonoike and T. Ninomiya, *Metal Physics* (*Kinzoku-Buturi*), **1**, 67 (1955); H. Kanzaki, ibid., **1**, 108 (1955).

[3] H. Takahashi, This Bulletin, **32**, 235, 245, 252 (1958).

[4] Y. Iida and K. Shimada, ibid., **33**, 8 (1960).

[5] J. Nakazumi, *J. Chem. Soc. Japan. Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **59**, 1304 (1956).

[6] S. Brunauer, P. H. Emmett and E. Teller, *J. Am. Chem. Soc.*, **60**, 309 (1938).

TABLE I. BULK DENSITY, POROCITY AND SURFACE AREA OF NICKEL OXIDE PRESSED AT VARIOUS PRESSURES

Compacting pressure, kg./cm^2	0	200	500	1000	2000
Bulk density, g./cc.	1.7	2.1	2.5	3.0	3.4
Surface area, m^2/g.	1.60	—	1.54	1.67	1.50
Porosity, %	75	69	63	56	50

in the compacting pressure. Although the surface area could be thought to decrease with an increase in the pressure, it does not vary with the pressure as shown in Table I. From these data it is found that a contact point which is formed by an atomic distance between nickel oxide particles and which prevents the adsorption of nitrogen, does not decrease with the pressure in spite of the decreasing porosity. In the previous paper$^{7)}$ dealing with the oxidation of nickel powders it was shown that a surface area of nickel powders with a ductile property did not vary with the compacting pressure in the range of 0 to 1000 kg./cm^2. In view of the results concerning nickel powders, the results shown in Table I can be accepted as correct.

The effect of compacting pressure on the isothermal reduction of nickel oxide is shown in Fig. 1. It is seen that the rate of reduction increases with an increase in the compacting pressure below 1000 kg./cm^2. It should be noted that the amount of reduced nickel oxide in 5 hr. at 200°C is only 50% for an unpressed nickel oxide whereas it is 100% for nickel oxide pressed at 1000 kg./cm^2. Inasmuch as the surface area does not vary with the compacting pressure as shown in Table I, the accelerated reduction by compacting can be attributed to the crystal distortion which may be induced by compacting. Although the mechanism of hydrogen reduction of nickel oxide compact is very complicated$^{8)}$ and not yet understood clearly, the porosity of the compact is thought to play an important role in the reduction which is a chemical reaction of solid with gas. The rate is lower at 2000 kg./cm^2 than at 1000 kg./cm^2. It is found that the effect of porosity on the reduction exceeds that of compacting when the pressure is relatively high and the porosity is small.

From these data it is expected that the rate becomes higher when nickel oxide compact pressed at a high pressure is ground into fine powders and its porosity becomes larger. Fig. 2 shows that the reduction is promoted further when the compact pressed at 1000 kg./cm^2 is ground into powders. It is seen that the rate of reduction of nickel oxide powder prepared by compacting and grinding is obviously higher than that of the nickel oxide powder subjected to no mechanical treatment and having the same porosity. This means that the effect of mechanical treatment on the hydrogen reduction is large and the effect of the porosity is small.

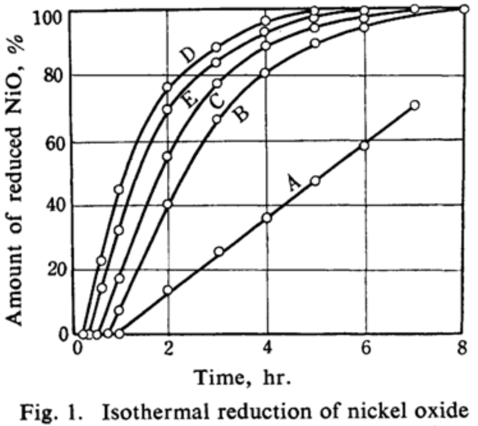

Fig. 1. Isothermal reduction of nickel oxide pressed at various pressures. The reduction temperature is 200°C. A is for nickel oxide unpressed, B, for nickel oxide pressed at 200 kg./cm^2, C, at 500 kg./cm^2, D, at 1000 kg./cm^2, and E, at 2000 kg./cm^2, respectively.

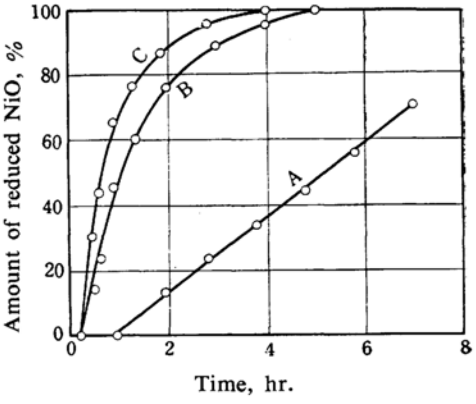

Fig. 2. Effect of compacting and grinding on the hydrogen reduction of nickel oxide at 200°C. A is for nickel oxide without compacting, B, nickel oxide compacted at 1000 kg./cm^2, and C, nickel oxide ground after compacting at 1000 kg/cm^2.

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7) Y. Iida, S. Ozaki and K. Shimada, *Reports of the Government Industrial Research Institute, Nagoya* (*Nagoya Kogyo Gijitsu Shikenjo Hokoku*), 10, 569 (1957).

8) Y. Iida and K. Shimada, This Bulletin, to be published.

Effect of Grinding.—Isothermal reductions of a single crystal of nickel oxide and of nickel oxide powders prepared by grinding of the crystal were compared with that of nickel oxide prepared by ignition of nickel sulfate. The results in Fig. 3 show that the rate of reduction of nickel oxide prepared by grinding of the single crystal is larger than those of a single crystal and nickel oxide prepared by ignition of nickel sulfate. It is a natural result from the consideration of the surface area that the rate of reduction of nickel oxide powders prepared by grinding of the single crystal exceeds that of the single crystal. The particles size of nickel oxide prepared by grinding of the single crystal is about 50 μ by a microphotograph and its surface area is too small to be determined by the B. E. T. method. The particle size of nickel oxide prepared by ignition of nickel sulfate is about 0.5 μ and is evidently smaller than that of nickel oxide prepared by grinding of the single crystal. The rate of reduction of nickel oxide prepared by ignition, however, is lower than that of nickel oxide prepared by grinding. As the single crystal was prepared from nickel oxide by igniting C. P. nickel sulfate, the purity of both nickel oxides is thought to be essentially the same. From the viewpoint of the surface area of nickel oxides, these facts cannot be understood reasonably.

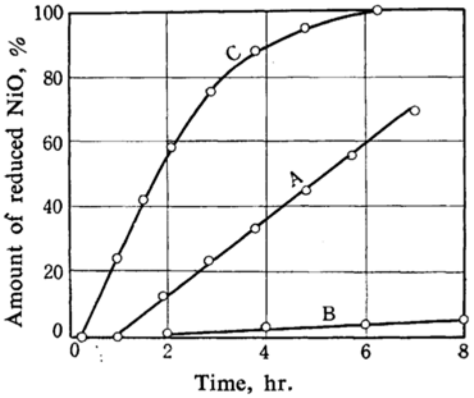

Fig. 3. Effect of grinding of a single crystal on the hydrogen reduction of nickel oxide at 200°C. A is for nickel oxide powders from ignition of nickel sulfate, B, a single crystal of nickel oxide and C, nickel oxide powders from grinding of the single crystal.

Recently, it was reported that a change in physical properties of sodium chloride[2], zinc oxide* and kaoline[3] by grinding or compressing might be attributed to the crystal distortion which was caused by the plastic deformation. From these considerations it is concluded that the accelerated reduction of nickel oxide prepared by grinding of the single crystal results from the crystal distortion induced by grinding. On the basis of these data, it seems reasonable to assume that nickel oxide, either in powder form or single crystal form, shows plastic deformation which results in the accelerated hydrogen reduction, when it is compacted or ground.

Summary

The rate of hydrogen reduction of nickel oxide increases with an increase in the compacting pressure although the bulk density of nickel oxide increases and the surface area does not vary with the pressure. The rate of reduction of nickel oxide which is prepared by the grinding of a single crystal and has a large particle size of 50 μ is higher than that of nickel oxide which is prepared by ignition of nickel sulfate and has small particle size of 0.5 μ. It seems reasonable to conclude that the accelerated reduction is attributed to the crystal distortion which may result from plastic deformation by grinding or compacting.

The authors wish to express their sincere thanks to Tochigi Kagaku Kogyo Co. for the presentation of the single crystal.

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* It is easily observed that zinc oxide turns yellow when it is ground after sintering.