Non-stoichiometry of Nickel Oxide

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The physical and chemical properties of nickel oxide have been studied extensively by many investigators[1]. Gray[2] and Iida[3] reported that the electrical properties of nickel oxide varied with the preparation method. Since nickel oxide is a *p*-type semiconductor containing an excess of oxygen, the change in the electrical properties are thought to be attributed to a concentration of an excess of oxygen which produces cation vacancy in nickel oxide. From the electrical neutrality of the crystal, $2x$ Ni^{3+} ions must be formed when there are x vacancies of Ni^{2+} in the crystal.

In the present experiment, the concentrations of Ni^{3+} ion in nickel oxide crystals prepared from various methods have been determined by chemical analysis and a concentration of cation vacancy has been calculated. The concentration of cation vacancy thus obtained has been compared with that obtained by the density and lattice parameter of nickel oxide.

Experimental

Recrystallized nickel nitrate was prepared by dissolving electro-deposited nickel of 99.9% purity in c. p. nitric acid. Nickel carbonate and nickel hydroxide were precipitated in an aqueous solution of nickel nitrate by ammonium carbonate and ammonium hydroxide. These nickel salts were heated for 3 hr. in air in the temperature range of 400 to 1300°C to obtain nickel oxide.

Electrical resistance was measured in the air from room temperature to 300°C by a method similar to that described by Griffith[4].

The density measurement was the same as that described by Culbertson[5] except that a weighing glass bulb sealed under evacuation was broken off in distilled water containing 0.001% of surface active reagent.

Powder diffraction patterns were recorded by a diffractometer with copper-target radiation. The lattice parameter of nickel oxide was determined by the diffraction peak of (420).

The chemical analysis of Ni^{3+} was made according to the directions of Verwey[6].

The composition ratio of Ni/O was determined by hydrogen reduction of samples at 700°C for 5 hr.

Results and Discussion

Non-stoichiometry of Nickel Oxide Prepared from Nickel Nitrate.—Nickel oxide was prepared by heating nickel nitrate for 3 hr. at temperatures of 400 to 1200°C. Experimental results are shown in Table I. It is seen from electron photographs that particle size increases with an increase in the heating temperature (Fig. 1). At low temperatures of 400 and 500°C, unit particle size can not be determined by an electron photograph because nickel oxide is in the form of very small particles or their aggregates. At 600°C it is about 0.2 μ and grows to 1 μ at 1000°C. Inasmuch as the width of diffraction peak (200) at half intensity did not vary with the heating temperature in the range of 400 to 1200°C, the crystallization of nickel oxide heated at 400 and 500°C is thought to be completed.

The composition ratio of O/Ni is larger than 1 below 600°C and is nearly 1 above 600°C. It is seen that nickel oxide prepared by heating the nitrate below 600°C has obviously an excess of oxygen. The lattice parameter of nickel oxide does not vary with the heating temperature within the experimental error. The density of nickel oxide increases with an increase in the heating temperature as shown in Table I. The change in the lattice parameter is more strongly dependent on the oxygen ion which has a larger ion radius than the nickel ion. From the consideration of a constant lattice parameter and the decreasing densities of nickel oxide with an excess of oxygen, it seems to be reasonable to assume that nickel oxide has a cation vacancy as mentioned previously[7].

It has been known[8] that the Ni^{3+} ion is not present in pure and dry nickel oxide. Chemical analysis, however, shows that the Ni^{3+} ion is evidently present in pure and dry nickel

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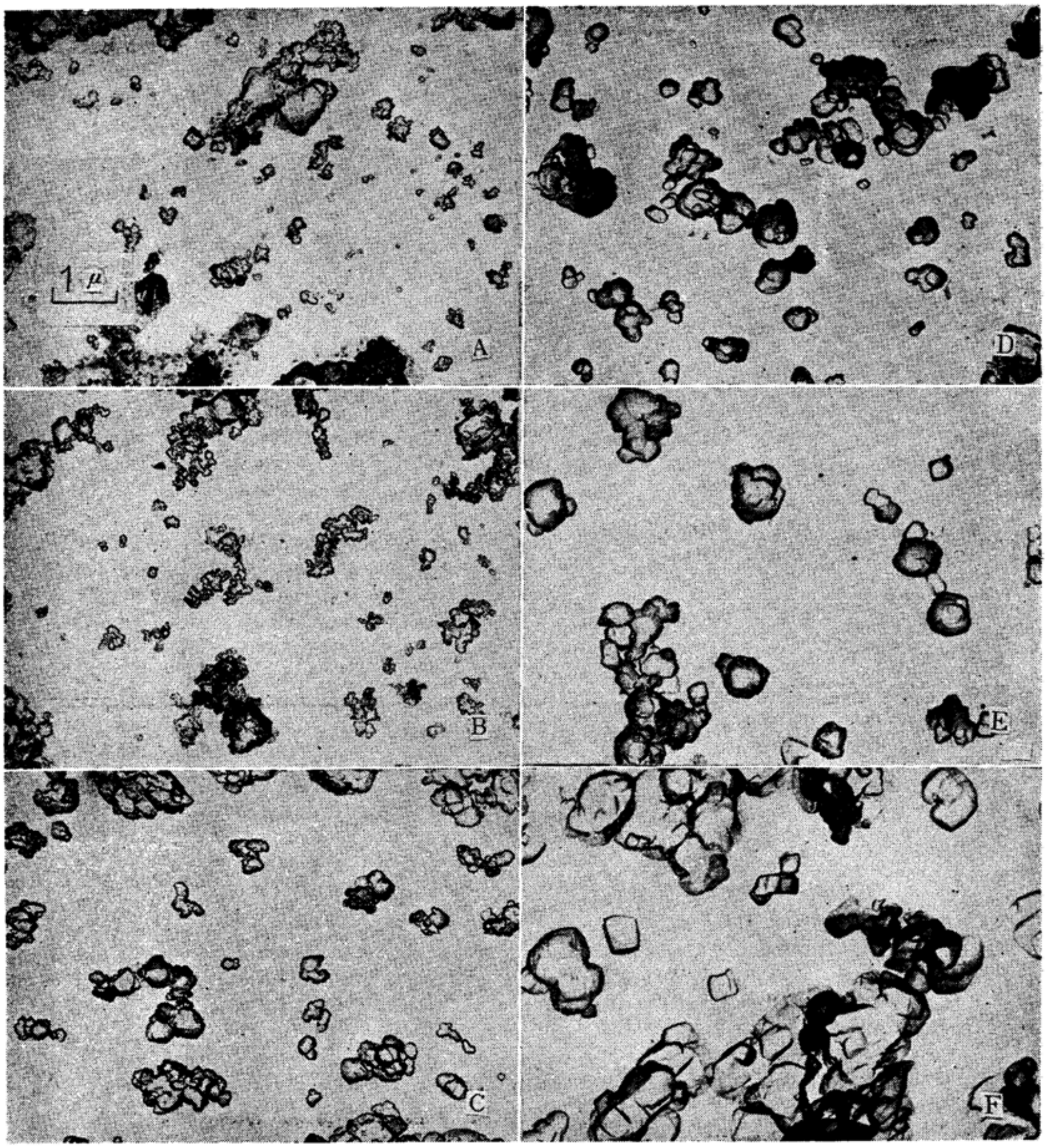

Fig. 1. Electron photographs of nickel oxides prepared by decomposition of nickel nitrate at (A) 400°C, (B) 600°C, (C) 700°C, (D) 800°C, (E) 900°C and (F) 1000°C.

oxide and decreases with the calcining temperature of nickel nitrate. From the reason mentioned above, a concentration of cation vacancy can be calculated as shown in Table I.

From the viewpoint of a semiconducting mechanism, electrical conductivity of nickel oxide should increase with an increase in an excess of oxygen or in a concentration of cation vacancy. The experimental resuls show that the conductivity increases with the cation vacancy. As nickel oxide calcined at low temperatures has a small particle size, the conductivity is thought to increase with an increase in the particle size in view of the contacting resistance of the powder. The conductivity of nickel oxide calcined at low temperatures, however, is high in spite of its small particle size according to the experimental results. Furthermore, Table I shows that the activation energy of the conductivity of nickel oxide decreases with an increase in the cation vacancy. From these facts it is concluded that nickel oxide calcined at low temperatures is obviously a non-stoichiometric compound and has Ni^{3+} ions and cation vacancies, consequently.

Table I shows that the concentration of vacancies calculated from the densities is higher than that from chemical analysis of the

TABLE I. PHYSICAL AND CHEMICAL ANALYSIS OF NICKEL OXIDE PREPARED FROM DECOMPOSITION OF NICKEL NITRATE

Calcining temp., °C	400	500	600	700	800	900	1000	1200
Ratio of O/Ni	1.10	1.04	1.01	0.995	0.995	0.995	0.993	0.995
Density observed, g./cc.	5.74	6.28	6.40	6.48	6.53	6.62	6.65	6.80
Lattice parameter, Å	4.1798	4.1801	4.1792	4.1788	4.1788	4.1788	4.1788	4.1756
Electrical conductivity at 300°C, Ω cm.	6.8×10^{-4}	4.9×10^{-4}	4.1×10^{-4}	2.1×10^{-4}	1.0×10^{-4}			
Activation energy of the conductivity, kcal./mol.	8.5	9.5	10.0	10.3	10.5	11.0	11.4	
Ni^{3+}, at. %	1.07	0.41	0.31	0.27	0.11	0.040	0	0
Density calculated, g./cc.	6.789	6.787	6.792	6.794	6.794	6.794	6.794	6.809
Number* of vacancy per cc.	1.71×10^{21}	1.30×10^{21}	1.00×10^{21}	8.01×10^{20}	6.73×10^{20}	4.42×10^{20}	3.65×10^{20}	2.10×10^{19}
Number** of vacancy per cc.	2.79×10^{20}	1.24×10^{20}	8.62×10^{19}	7.40×10^{19}	3.02×10^{19}	1.09×10^{19}		

* Values calculated from the densities.

** Values calculated from Ni^{3+} atomic per cent.

TABLE II. COMPOSITION RATIO OF O/Ni OF NICKEL OXIDE PREPARED VARIOUS NICKEL SALTS

Calcining temp., °C	400	500	600	700	800	900	1000
Nitrate	1.10	1.04	1.01	0.995	0.995	0.995	0.993
Hydroxide	1.12	1.07		1.02		1.00	0.997
Carbonate	1.21	1.09		1.02		1.00	0.991

TABLE III. ACTIVATION ENERGY OF ELECTRICAL CONDUCTIVITY OF NICKEL OXIDE PREPARED FROM VARIOUS SALTS (kcal./mol.)

Calcining temp., °C	400	500	600	700	800	900	1000
Nitrate	8.5	9.5	10.0	10.3	10.5	11.0	11.4
Hydroxide	7.7	8.3	—	10.3	—	—	—
Carbonate	5.3	6.3	—	7.4	—	8.2	9.3

Ni^{3+} ion. As a measurement is liable to give too low density values to small particles because of the incomplete desorption of gases even under the cautious density measurement, the disagreement may be attributed to the lowering of observed density. Further experiment, however, is necessary to determine which method is better to obtain the concentration of vacancy in nickel oxide.

Effect of Starting Material. — As nitrogen peroxide which may be responsible for an excess of oxygen in nickel oxide may be formed when nickel nitrate is decomposed, it is of interest to know whether the excess of oxygen in nickel oxide can be formed when nickel carbonate or nickel hydroxide is decomposed. Table II shows that the excess of oxygen is formed in the nickel oxides prepared from nickel carbonate and hydroxide as well as from nitrate. It is seen that the excess of oxygen is higher in nickel oxide from carbonate than in nickel oxides from nitrate and hydroxide. Electrical conductivity measurement shows that the activation energy of electrical conductivity decreases with an increase in the excess of oxygen for all nickel oxides and is the lowest for nickel oxide obtained from carbonate. It is confirmed that the excess of oxygen can be formd in nickel oxide prepared from other salts which are different from the nitrate. No reasonable explanation, however, has yet been found to make clear why the excess of oxygen is the highest in nickel oxide from carbonate, although nickel carbonate, hydroxide and nitrate start to decompose at about 250°C and their purity is essentially the same.

Isothermal Change in Electrical Conductivity. —From the above experiments, it has been evident that the nickel oxide obtained by heating nickel salts at low temperatures exhibits a vacant cation structure and its electrical properties vary with the cation vacancy and the concentration of cation vacancy decreases with the increasing heating temperature. It seems to be desirable to determine the isothermal change in electrical conductivity of the nickel oxide. Nickel nitrate was heated at 300°C for 3 hr. to obtain nickel oxide with a high concentration of the vacancy whose ratio of O/Ni is 1.36. The isothermal change in the electrical conductivity at 300, 400 and 500°C is shown in Fig. 2. It is seen that the behavior of electrical conductivity varies with heating temperature. At 300°C, the electrical conductivity increases with the heating time while it decreases with the heating time at 500°C. At 400°C, the conductivity increases initially in a heating period of 2 hr. and then decreases with the time. Since the cation deficient structure of nickel oxide is thought to be formed during the decomposition process of nickel nitrate and to be uncompleted in 3 hr. at 300°C, the conductivity increases with the time when it is reheated at 300°C. At 400°C, the uncompleted cation deficient structure is completed in an initial heating period. This may be the result in the initial inrease in the conductivity at 400°C.

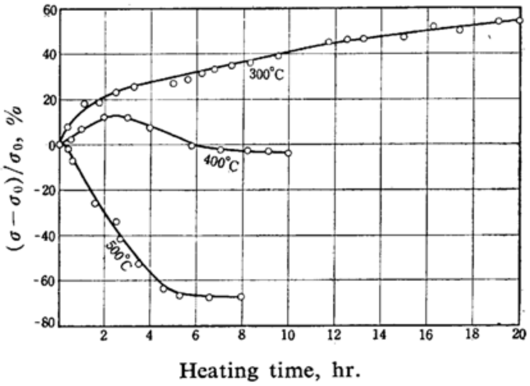

Fig. 2. The isothermal change in electrical conductivity of nickel oxide at various temperatures. Nickel oxide was made by decomposition of nickel nitrate at 300°C for 3 hr.

The cation deficient structure of nickel oxide is expressed by the following equation according to Hauffe[9]

$$\mathrm{NiO}+2\oplus+\square'' \rightleftharpoons \frac{1}{2}\mathrm{O}_2$$

where $\square''$ represents the vacancy of nickel site and $\oplus$, a positive hole of the electron. There are equilibrium states at various temperatures between the concentration of the vacancy and oxygen pressure following the above equation. Since nickel oxide calcined at 300°C has a higher concentration of vacancy than the equilibrium state at 400°C, the vacancies greater than the equilibrium value diffuse to the surface of the crystal and disappear. The decreasing conductivity at 400°C in Fig. 2 can be explained by the diffusion of vacancy.

Summary

Nickel oxide obtained by heating nickel nitrate, carbonate and hydroxide at low temperatures exhibits a non-stoichiometric structure. An excess of oxygen decreases with an increase in the heating temperature of nickel salts. Concentration of Ni^{3+} determined by chemical analysis increases with the excess of oxygen. Densities of nickel oxide or activation energy of electrical conductivity decrease with an increase in the excess of oxygen, whereas lattice parameter does not vary. Isothermal change in electrical conductivity of nickel oxide shows that the decrease in vacancies may be attributed to the diffusion of vacancies to the crystal surface. The concentration of vacancies calculated from the density is higher than that from the concentration of Ni^{3+} ion. The disagreement may be attributed to the density measurement technique.

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