Effect of Additives on the Hydrogen Reduction of Nickel Oxide

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The effect of additives on hydrogen reduction of metal oxide was previously studied in view of the dissociation pressure of the oxide by Grube[1] and Sano[2]. Parravano[3] recently studied the effect of additives on the reductive properties of nickel oxide from the point of view of a semiconductor and concluded that a direct correlation exists between the activation energy and the type of additives for the hydrogen reduction of nickel oxide.

The present investigation has been undertaken to determine the effect of additives on the temperature at which nickel oxide begins to be reduced by hydrogen, and to ascertain whether or not the properties of a semiconductor are related to the reductive properties of nickel oxide.

Experimental

Nickel nitrate recrystallized four times was heated at 800°C for 10 hr. to obtain nickel oxide powder. The average particle size of nickel oxide powder was about 0.5 μ according to an electron micrograph. Aluminum oxide powder obtained by heating c. p. aluminum hydroxide at 800°C for 10 hr. Cupric oxide powder was obtained by heating c. p. nitrate salt at 800°C for 10 hr.

Powders were mixed and pressed at a pressure of 1000 kg./cm^2 into tablets $10\times10^{\phi}$ mm. The compacts were heated at various temperatures in a silicon carbide furnace with a sintered corundum tubing.

Weight loss during the reduction process was measured by a thermobalance which had a sensitivity of 0.5 mg. and could be used in hydrogen, vacuum and, if necessary, in oxygen. Hydrogen was used from a commercially available tank after being purified with concentrated sulfuric acid, hot platinum asbestos, potassium hydroxide, and phosphorous pentoxide.

Electrical resistance was measured by a Wheatstone bridge in the range of room temperature to 400°C in air.

Results

Effect of Additive Aluminum Oxide.—In order to study the effect of additive aluminum oxide on reduction of nickel oxide, the reduction-temperature curves were obtained at the rate of heating of 100°C/hr. NiO-Al_2O_3 mixtures of 99 : 1, 95 : 5, and 50 : 50 mol. were heated at 1100°C for 4 hr. It is seen from Fig. 1 that the mixtures begin to be reduced at 300°C whereas pure nickel oxide begins to be reduced at 200°C. The reduction-temperature curve of the mixture 50 : 50 mol. ratio consisted of two stages. At the first stage the reduction takes place in the range of 300 to 400°C and the second stage reduction begins at 700°C.

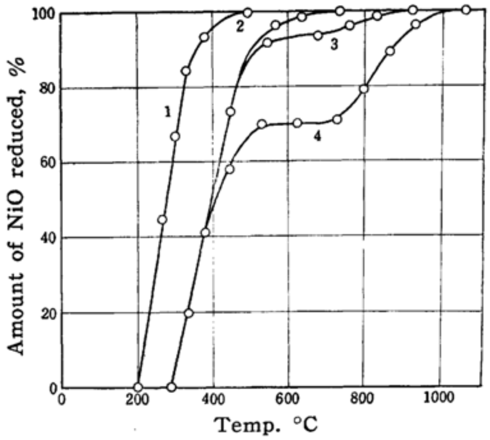

Fig. 1. Reduction-temperature curves of NiO-Al_2O_3 mixtures heated at 1100°C for 4 hr. Curve 1 is for pure NiO and curves 2, 3 and 4 are for the mixtures containing 1, 5 and 50 mol. % of Al_2O_3, respectively.

Effect of Additive Lithium Oxide.—A NiO-Li_2O mixture of 95 : 5 mol. ratio was heated for 4 hr. at 1100°C and the reduction-temperature curve was determined in the same way as described above. It is seen from Fig. 2 that the beginning temperature of reduction of the NiO-Li_2O mixture is about 260°C and is higher that of pure nickel oxide and lower than that of the NiO-Al_2O_3 mixture. The temperature at which reduction is completed is 800°C for the NiO-Li_2O mixture and is higher by 400°C than that of pure nickel oxide. It

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[1] G. Grube, O. Kuvashewuski and K. Zwinaues, *Z. Elektrochem.*, **45**, 881 (1939).

[2] K. Sano, *J. Japan Inst. Metals* (*Nippon Kinzoku Gakukai-shi*), **6**, 339 (1942).

[3] G. Parravano, *J. Am. Chem. Soc.*, **74**, 1194 (1952).

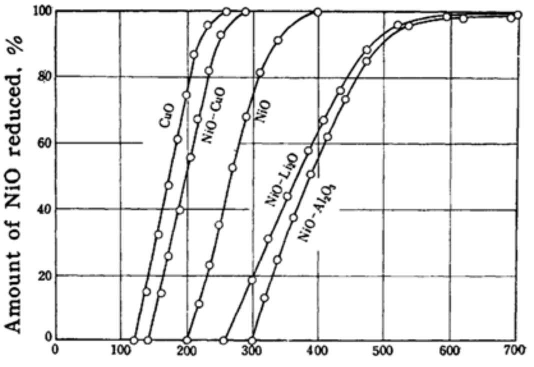

Fig. 2. Reduction-temperature curves of CuO, NiO and mixtures of NiO and 5 mol. % of CuO, Li_2O and Al_2O_3, respectively. CuO, NiO and the mixtures were heated at 1100°C for 4 hr.

may be concluded that the heated NiO-Li_2O mixture becomes more difficult to reduce than to do pure nickel oxide.

Effect of Additive Cupric Oxide. — The reduction-temperature curve for the NiO-CuO mixture of 95 : 5 mol. ratio heated for four hours at 1100°C was determined at the same rate of heating. It is seen from Fig. 2 that the beginning temperature of reduction for the NiO-CuO mixture is 160°C and is lower than that for nickel oxide. To confirm the fact more evidently, the isotherms of reduction at 160, 140 and 120°C were obtained using the same samples described above. The result is shown in Fig. 3. Pure nickel oxide started to be reduced after an induction period of two hours at 180°C and the amount of nickel oxide reduced was about 80% even after a reducing period of 10 hr. at 180°C. NiO-CuO compact of 95 : 5 mol. ratio heated at 1100°C, however, could be reduced completely after a two hour reducing period at 160°C without an induction period. At 140°C the amount of reduced nickel oxide was 100% after an eight hour reducing period, and even at 120°C the reduction occurred slowly after a two hour induction period. It may be concluded that nickel oxide in the heated NiO-CuO mixture can be reduced at a lower temperature than pure nickel oxide.

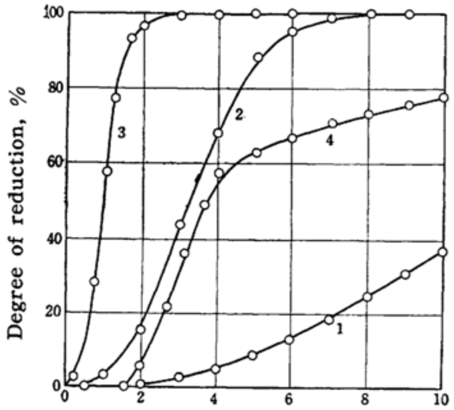

Fig. 3. Comparison between isothermal reduction of NiO-CuO mixture of 95:5 mol. ratio heated at 1100°C and that of pure NiO. Curves 1, 2 and 3 represent reduction of the NiO-CuO mixture at 120, 140 and 160°C, respectively. Curve 4 represents reduction of pure NiO at 180°C.

In order to see how additive cupric oxide enhances the reduction of nickel oxide by hydrogen, the isotherms of reduction at 140°C for NiO-CuO mixtures of 95 : 5 mol. ratio heated at 700 and 1100°C are compared with the unheated mixtures. The result is shown in Fig. 4. The unheated mixture was reduced by 5% at 140°C for one hour and then ceased to be reduced. Although the mixture heated at 700°C behaves at the initial time of reduction in the same way as the unheated mixture, the one heated at 700°C can be reduced again after a two hour reducing period. The mixture heated at 1100°C can be reduced more rapidly and is reduced by 100% for eight hours at 140°C. It is concluded from the experimental results that cupric oxide in the unheated mixture does not enhance the reduction of nickel oxide but cupric

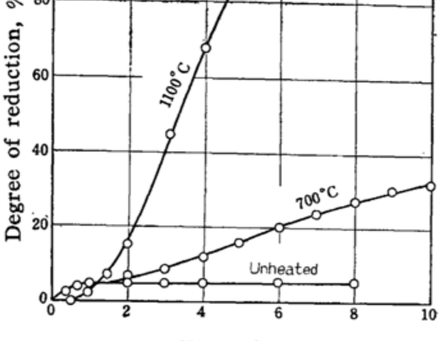

Fig. 4. Isothermal reduction of NiO-CuO mixture of 95:5 mol. ratio heated at 700 and 1100°C, respectively for 4 hr. and of that unheated. The reduction temperature is 140°C.

oxide in the heated mixture enhances the reduction.

Discussion

In an earlier paper[4] dealing with the solid state reaction of nickel oxide with aluminum oxide, it was shown that when the mixture NiO-Al_2O_3 was heated, a solid solution of aluminum oxide in nickel oxide and a spinel $NiAl_2O_4$ were formed. From these facts it is concluded that nickel in pure nickel oxide starts to be reduced at 200°C whereas nickel in the solid solution and that in the spinel starts to be reduced at 300 and 700°C, respectively.

Fensham[5] showed that a solid solution is formed when a mixture of nickel oxide and lithium oxide is heated at 1100°C. It was also shown[6] that a solid solution is formed when a mixture of nickel oxide and cupric oxide is heated at 1100°C.

Parravano[3] showed that by incorporation of 5 mol. % of aluminum oxide, the activation energy and the rate of hydrogen reduction of nickel oxide did not differ from those of pure nickel oxide. This result seems to be inconsistent with the result of the present investigation. In Parravano's experiment the mixture of NiO-Al_2O_3 was heated at 600°C to dissolve aluminum oxide into the nickel oxide crystal, while in this study the mixture was heated at 1100°C. The temperature 600°C seems to be too low to form a solid solution of NiO-Al_2O_3 completely. This may be the reason for the disagreement.

It was shown by Verwey[7] that nickel oxide is a semiconductor of *p*-type and its electrical conductivity is affected by incorporation of foreign ions. According to the principle of valency control[7], the semiconductivity of nickel oxide decreases by the incorporation of cations with higher valency than two, and increases by the incorporation of monovalent cations. The electrical and reductive properties of nickel oxide incorporated with various additives are shown in Table I. Nickel oxide with various additives was heated at 1100°C for 4 hr. Cationic holes in the nickel oxide lattice increase by the incorporation of Al^{+3} ion and decrease by the incorporation of Li^+ ion from the point of view of the electron-neutrality principle.

It can be seen that nickel oxide incorporated with Li^+ or Al^{+3} is less readily reducible than pure nickel oxide although Li^+ ion has the reverse effect on the semiconductivity compared with Al^{+3} ion. On the other hand, nickel oxide incorporated with Cu^{+2} is more easily reducible than pure nickel oxide, although it has a lower semiconductivity than that of pure nickel oxide. In view of the above facts it is concluded that the effect of impurities on the reductive properties of nickel oxide can not be explained reasonably by the properties of a semiconductor.

Previous reports[1,8] on the effect of additives on hydrogen reduction of oxide showed that the reduction is promoted by the formation of a solid solution of a reduced metal into additives. Niobium could be reduced with hydrogen as an Nb-Ni alloy by the addition of nickel powder[1]. In the present study it is, however, shown that the reductive properties of nickel oxide are not affected merely by the addition of cupric oxide, but affected by the dissolution of a small quantity of cupric oxide into nickel oxide crystal by heating. As the reduced nickel can form no solid solution with unreducible lithium oxide or aluminum oxide, the dissolution of lithium oxide or aluminum oxide should have no influence on the hydrogen reduction according to the above mechanism. The experimental results, however, show that the reduction of nickel

TABLE I. ELECTRICAL AND REDUCTIVE PROPERTIES OF NiO AS A FUNCTION OF IMPURITY DISSOLUTION

	Electrical resistance at 300°C Ω cm.	Activation energy of electrical conductivity kcal./mol.	Change in the number of vacancies	Reduction beginning temp. °C
NiO	10^5	20		200
NiO+Al_2O_3 (5 mol. %)	10^7	22	Increase	300
NiO+Li_2O (5 mol. %)	10	4	Decrease	260
NiO+CuO (5 mol. %)	10^2	10	Unchange	160

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[4] Y. Iida, *J. Japan Soc. Powaer Metallurgy* (*Huntai oyobi Hunmatsu-Yakin*), **6**, 55 (1959). (in English).

[5] P. Fensham, *J. Am. Chem. Soc.*, **76**, 968 (1954).

[6] Y. Shimomura, *J. Japan Inst. Metals* (*Nippon Kinzoku Gakukai-shi*), **17**, 421 (1953).

[7] E. J. Verwey, P. W. Haaijman, P. C. Romijn and G. W. Osterhout, *Philips Res. Reports*, **5**, 173 (1950).

[8] Z. Bankloh, *Z. anorg. u. allgem. Chem.*, **233**, 424 (1937).

oxide is retarded by the dissolution of lithium oxide or aluminum oxide. From these considerations it is concluded that the effect of the dissolution of various oxides on the reduction is not explained completely by the formation of a solid solution.

The reduction of a metal oxide has been considered to be an autocatalytic reaction[9]. Therefore, the accelerated reduction by the addition of cupric oxide is thought to be attributed to the catalytic behavior of metallic copper formed predominantly by hydrogen reduction. It is, however, important to note that cupric oxide does not promote the reduction when cupric oxide is mixed in nickel oxide, but cupric oxide dissolved in the nickel oxide lattice promotes the reduction. From this fact, it is concluded that copper formed predominantly in the reduction process exhibits no catalytic behavior.

In order to know the relation between the reductive properties of nickel oxide incorporated with impurities and the heat of formation of these impurities, the heats of formation of nickel oxide, aluminum oxide, lithium oxide and cupric oxide are given in Table II using the values of Seybolt[10]. It can be seen that the beginning temperature of the reduction of nickel oxide incorporated with other oxides with a greater heat of formation than nickel oxide is higher than that of pure nickel oxide whereas an oxide with a smaller heat of formation than nickel oxide has the reverse effect.

TABLE II. HEAT OF FORMATION OF VARIOUS OXIDES AT 298°K (BY SEYBOLT)

Oxide	NiO	Li_2O	1/3 Al_2O_3	CuO
Heat of formation kcal./mol.	−51.3	−134.0	−126	−30.4

Further, it is seen from Fig. 4 that the induction period of both the unheated mixture NiO-CuO and of that heated at 700°C is shorter than the induction period of that heated at 1100°C. It is evident that the reduction of cupric oxide is retarded by the incorporation of nickel oxide, which has a greater heat of formation than that of cupric oxide.

To see whether this explanation applies to the hydrogen reduction of any other oxide, ferric oxide containing 5 mol. % of aluminum oxide and cupric oxide respectively and pure ferric oxide were heated at 1200°C for 3 hr. and reduced at 350°C isothermally. The results are shown in Fig. 5. It is evident that the dissolution of aluminum oxide which has a greater heat of formation than ferric oxide retards the reduction of ferric oxide and the dissolution of cupric oxide which has a smaller heat of formation than ferric oxide promotes the reduction.

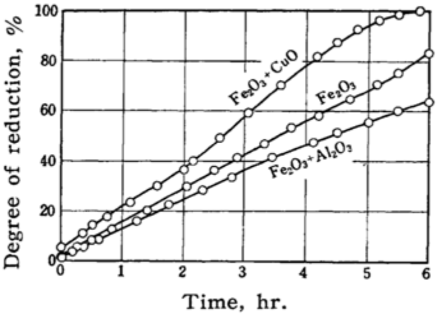

Fig. 5. Isothermal reduction of pure Fe_2O_3 and Fe_2O_3 containing 5 mol. % of CuO and Al_2O_3, respectively. Samples are heated at 1200°C for 3 hr. and reduced at 350°C isothermally.

In view of the above facts the most reasonable conclusion to be drawn from available data is that hydrogen reduction of metal oxide is promoted by the incorporation of another oxide with a greater heat of formation than that of oxide, and is retarded by the incorporation of an oxide with a smaller heat of formation.

Summary

The effect of additive impurities on the hydrogen reduction of nickel oxide has been studied. The additives have no influence on the reduction unless they dissolve into nickel oxide crystal. The reduction is promoted by the dissolution of cupric oxide and is retarded by the dissolution of lithium oxide and aluminum oxide. The effect of additives on the reduction is not explained reasonably by their catalytic behavior. There is no direct correlation between the reductive properties of nickel oxide and the type of additives from the point of the semiconducting behavior of these materials. The effect of additives on the reduction is related to their heats of formation.

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[9] A. F. Benton and P. H. Emmett, *J. Am. Chem. Soc.*, **46**, 2728 (1924).

[10] A. U. Seybolt and J. E. Burke, "Procedures in Experimental Metallurgy", John Wiley & Sons, Inc., New York (1953), p. 175.