Hydrogen Reduction of Solid NiO-CoO-MgO Solutions

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Solid NiO—CoO—MgO solutions have been prepared for a study of the influence of the magnesium oxide content upon the hydrogen reduction of solid CoO—NiO solutions at 1000°C and 1050°C. With magnesium oxide contents above 17.1 mole-% the time dependence of the reduction can be expressed by the topokinetic equation

$$x = 1 - \exp(-kt^n)$$

where x is the fraction of CoO and NiO reduced after time t , k is the reaction rate constant, and the value of the exponent n ($0 < n < 1$) depends upon the concentration of magnesium oxide in the solid solution. The value of n approaches unity for binary solid solutions of CoO and NiO.

Addition of magnesium oxide retards the reduction rate of CoO or NiO to an extent that depends in a complicated way upon its concentration and the reduction temperature and it appears as if several different mechanisms are involved simultaneously¹.

This paper deals with an investigation of the hydrogen reduction at high temperatures of certain ternary solid oxide solutions in the system CoO—NiO—MgO with the purpose of determining the influence of high contents of magnesium oxide on the reducibility of the system CoO—NiO.

EXPERIMENTAL

Analytical grade nitrates of cobalt and nickel were converted to oxides by heating at 1000°C in air. After grinding the oxides were thoroughly mixed. Two base batches were prepared in the ratios of 2 moles of NiO to 1 mole of CoO and 2 moles of CoO to 1 mole of NiO. Different amounts of analytical grade magnesium carbonate were added to the finely ground base batches and ternary solid solutions were prepared by promoting diffusion in the solid state by three two-hour heat treatments in air at 1200°C. Between the heat treatments, the solid solutions were ground and mixed. Before the last heat treatment the powders were compressed into cylindrical compacts (diameter 12.5 mm, height 8.5 mm, weight 4 g).

Since magnesium oxide forms solid solutions with both cobalt(II) and nickel oxides in all proportions², it was expected that similar solid solutions would be formed in the ternary system. X-Ray analyses confirmed that this is the case (Fig. 1).

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Fig. 1. Lattice parameters for solid solutions of MgO in $2\text{CoO}-1\text{NiO}$ and $2\text{NiO}-1\text{CoO}$.

Fig. 2. Reduction of solid solutions of MgO in $2\text{NiO}-1\text{CoO}$ as a function of time. Temperature 1050°C . ▲ 17.1 mole-% MgO; △ 31.8 mole-% MgO; ● 55.6 mole-% MgO; ○ 73.8 mole-% MgO.

Fig. 3. Reduction of solid solutions of MgO in $2\text{CoO}-1\text{NiO}$ as a function of time. Temperature 1050°C . ▲ 17.1 mole-% MgO; △ 31.8 mole-% MgO; ● 55.6 mole-% MgO; ○ 73.8 mole-% MgO.

Fig. 4. Reduction of solid solutions of MgO in 2CoO-1NiO as a function of time. Temperature 1000°C. $\times$ 9 mole-% MgO; $\blacktriangle$ 17.1 mole-% MgO; $\triangle$ 31.8 mole-% MgO; $\bullet$ 55.6 mole-% MgO; $\circ$ 73.8 mole-% MgO.

The reduction experiments were performed in a recording thermobalance described elsewhere¹. The experimental conditions were the same as described in Ref.¹ except that the rate of flow of hydrogen gas was 40 l/h (NTP). Two reduction temperatures were used, 1000°C and 1050°C. Below 1000°C the reduction rates for specimens with high magnesium oxide contents were very low and 1050°C was the upper limit for the furnace. Only CoO and NiO are reduced at these conditions.

RESULTS

Figs. 2-4 show the reduction ratio plotted against reduction time for the systems 2 CoO-1 NiO-(MgO) and 2 NiO-1 CoO-(MgO). The content of

Fig. 5. $\text{Log}\{-[\ln(1-x)]/k\}$ plotted against $\log t$ for solid solutions of MgO in 2NiO-1CoO. Temperature 1050°C. $\blacktriangle$ 17.1 mole-% MgO; $\triangle$ 31.8 mole-% MgO; $\bullet$ 55.6 mole-% MgO; $\circ$ 73.8 mole-% MgO. $\text{Log } k = 0.9036 - 2$.

Fig. 6. $\text{Log}\{-[\ln(1-x)]/k\}$ plotted against $\log t$ for solid solutions of MgO in 2CoO-1NiO. Temperature 1050°C. $\blacktriangle$ 17.1 mole-% MgO; $\triangle$ 31.8 mole-% MgO; $\bullet$ 55.6 mole-% MgO; $\circ$ 73.8 mole-% MgO. $\text{Log } k = 0.2000 - 1$.

Fig. 7. $\text{Log}\{-[\ln(1-x)]/k\}$ plotted against $\log t$ for solid solutions of MgO in 2CoO-1NiO. Temperature 1000°C. $\times$ 9 mole-% MgO; $\blacktriangle$ 17.1 mole-% MgO; $\triangle$ 31.8 mole-% MgO; $\bullet$ 55.6 mole-% MgO; $\circ$ 73.8 mole-% MgO.

magnesium oxide is expressed in mole-%. The forms of the curves suggested that the reduction can be described by a time function of the type

$$x = 1 - \exp(-kt^n)$$

Fig. 8. The value of the exponent n for different volume fractions of MgO in the metallic phase. Δ 2NiO—1CoO, 1050°C; $\circ$ 2CoO—1NiO, 1000°C; $\times$ 2CoO—1NiO, 1050°C.

where x = fraction of the oxides CoO and NiO that has been reduced

t = reduction time in minutes

k = reaction rate constant

n = an exponent, whose value depends upon the concentration of MgO.

When the double logarithm of the unreduced fraction of the cobalt and nickel oxides ($1-x$) was plotted against the logarithm of the reduction time for the various compositions, straight lines with different slopes were obtained (Figs. 5—7). All lines have the same trend to the origo except that for the specimen with the lowest magnesium oxide content, 9 mole-%, in Fig. 7. The reason for this is probably that the mechanism of interaction of the stable and reducible oxides at low magnesium oxide contents is another than at high contents¹.

The values of the exponent n for the various solid solutions were determined from the slopes of the lines in Figs. 5—7 and are plotted in Fig. 8 against the volume fraction of magnesium oxide in fully reduced Co—Ni—MgO. A slightly curved line drawn through the data points to a value for unity of n at zero magnesium oxide content.

X-Ray analyses of the specimens after reduction showed that the reduced metals form a cobalt-nickel alloy with the same metal ratio as in the original solid oxide solution.

DISCUSSION

The results of studies of the reduction of pure nickel oxide and nickel oxide to which certain additions had been made, have been reported in the literature^{3,4}. These investigations were, however, made using low temperatures (150—300°C) where differences between the outer and inner layers of the materials have been rate determining for the reduction process. By making use of the rapid diffusion at high temperatures, such effects have been eliminated in the experiments reported in this paper.

Both cobalt and nickel oxides are p -type compounds with cation vacancies and electron holes. In Ref.¹ it was tentatively suggested that the addition of small amounts of magnesium oxide retards the reduction of these oxides by

changing the defect equilibrium in the lattices of the latter. At high magnesium oxide contents the oxide is reduced with difficulty owing to the dilution of unreduced cobalt oxide by the magnesium oxide, and the reduction rate decreases with increasing magnesium oxide content. In the work reported here the amounts of magnesium oxide in solid solution with CoO—NiO were so high that the dilution effect dominated.

In cases like this the reduction mechanism is complicated because there are two solid phases, the reduced metal and the unreduced oxide solution in the system, and the latter varies in composition during the process. The topokinetic equation

$$x = 1 - \exp(-kt^n) \quad (1)$$

was fitted to the data. This equation is valid for reactions where the reaction rate is governed by the formation and growth of nuclei⁵.

The results indicate that the reduction process follows the topokinetic equation, and Fig. 8 shows that the value of n increases continuously as the amount of magnesium oxide in solid solution with CoO—NiO decreases and approaches unity at zero magnesium oxide content.

Thus the extrapolated time function for the reduction of CoO—NiO without added magnesium oxide is

$$x = 1 - \exp(-kt) \quad (2)$$

which is the kinetic equation for a reaction of the first order and which implies that the reduction rate at time t is proportional to the fraction of unreduced CoO—NiO, which is plausible. Eqn. (2) has not been verified, as no experiments on the reduction of CoO—NiO without added magnesium oxide were made at high temperatures, and no kinetic data are found for this system in the literature.

It is interesting to note that solid solutions with high cobalt oxide contents were easier to reduce than those with high nickel oxide contents. This result is understandable considering that cation vacancies and electron holes are much higher in number in cobalt oxide than in nickel oxide.

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