The Influence of Magnesium Oxide upon the Reduction of Cobalt and Nickel Oxides

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Solid solutions of stable magnesium oxide in the reducible cobalt and nickel oxides have been prepared by heat treatment, and the influence of the stable oxide upon the reduction of the reducible oxides has been studied by continuously recording the weight of a sample during reduction in hydrogen gas. The results indicate a complicated mechanism in interaction between the oxides. Magnesium oxide was found to have a marked retarding influence upon the reduction of cobalt and nickel oxides.

The reactivities of solids are highly dependent upon the structures of their lattices and there is a close relationship between defects in the lattices and various physical and chemical properties of solids.

The influence of defects, primarily vacancies in metal oxide lattices, upon the oxidation of metals has been studied much more thoroughly than the influence of defects on the reverse reaction, the reduction of oxides. Most of the investigations of the effect of foreign substances upon the reducibility of solid oxides deal with the effect of small additions of foreign ions which have a different valence than the parent ions of the oxide^{1-3,6}, but also ions of the same valence as the parent ions should be able to change the number of defects if these added ions are capable of affecting the equilibrium of defects and thus changing the reactivity of the solid.

In the work reported here, we have studied the influence of relatively small additions of the stable magnesium oxide upon the reduction of the oxides of bivalent cobalt and nickel.

The oxides MgO, CoO, and NiO crystallize in the face-centered cubic system. MgO has a lattice parameter $a = 4.212 \text{ \AA}$ and forms solid solutions in all proportions with CoO ($a = 4.260 \text{ \AA}$) and NiO ($a = 4.195 \text{ \AA}$)⁴. Nickel forms only one stable oxide, NiO, whereas cobalt forms two oxides, CoO and Co₃O₄; the latter, however, exists only between 200° and 900°C⁵. Tests have shown that when a solid solution of MgO in CoO is formed at temperatures above 900°C

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Table 1. Synthesis of CoO—MgO and NiO—MgO solid solutions.

	CoO—MgO	NiO—MgO
1. Mechanical mixing		
2. Synthesis, 2 h in air	1200°C	1200°C
3. Grinding and mixing, 1 h		
4. Synthesis, 2 h in air	1200°C	1200°C
5. Grinding		
6. Pressing		
7. Synthesis and sintering	20 h 1150°C	20 h 1150°C
Rel. density of sintered specimens (%)	66	54

and this solution is rapidly cooled, only very small amounts of the spinel $(\text{Co,Mg})\text{Co}_2\text{O}_4$ are formed, and the bivalent solid solution is maintained down to room temperature.

EXPERIMENTAL

Analytical grade nitrates of cobalt and nickel were converted to oxides by heating at 1000°C in air. After grinding, these oxides were thoroughly mixed with analytical grade magnesium carbonate and heated for 2 h at 1200°C. In order to obtain a fully homogeneous

Fig. 1. Schematic drawing of the thermobalance: a balance, b twin coil, c amplifier, d recorder, e SiC-tube furnace, f specimen, g temperature regulator, h adjustable transformer, j ammeter, k potentiometer and thermocouple, l copper furnace, m drying tower (silica gel), n drying tower (Mg perchlorate), o flowmeter.

solid solution this material was thoroughly ground and mixed after the first heat treatment and heated once more to the same temperature. After the second heat treatment the powder was rapidly cooled to room temperature, ground and compressed into cylindrical specimens, 12.5 mm in diameter and 8.5 mm long, weighing about 4 g. The cylinders were sintered in air and then quenched to room temperature. Reference specimens consisting of CoO or NiO alone were prepared by the same procedure (Table 1).

Fig. 1 shows the apparatus used in the reduction experiments. The specimen (f) is suspended from a rod at the end of one beam of a thermobalance (a). A piece of soft iron and a permanent magnet fastened to the rod are surrounded by a stationary twin coil (b). When the equilibrium is disturbed, the piece of soft iron generates an electrical current in the coil, which after amplification (c) acts upon the permanent magnet and moves it back to the original balanced position. The required current gives information about the change in weight of the specimen and is continuously recorded (d) with an accuracy corresponding to ± 2 mg.

The furnace tube, 25.4 mm wide, is filled with ceramic pellets up to the specimen in order to ensure a full heating of the reducing gas to the furnace temperature, which is measured with a thermocouple (k) at a point close to the specimen. Another thermocouple (g) actuates the temperature regulating device (h—j). Nitrogen and hydrogen introduced into the furnace are first deoxidized in a heated tower containing finely divided copper (l) and then dried over silica gel (m) and magnesium perchlorate (n). The gas flow was kept constant at 23.5 l/h (NTP) during all runs.

Before each experiment the furnace was brought to the reduction temperature, and the tube was flushed with nitrogen with the specimen suspended in the cool upper part of the furnace. After changing to hydrogen, the specimen was rapidly lowered to a fixed position in the hot zone, and the reduction time was counted from this moment. The short heating-up time of the specimen is thus included in the reduction time, but the error thus introduced is small.

Fig. 2. Reduction of CoO—MgO as a function of time. Temperature 600°C. The figures beside the curves give the MgO contents of CoO in mole-%.

Fig. 3. Reduction of CoO—MgO as a function of time. Temperature 700°C.

Fig. 4. Reduction of CoO—MgO as a function of time. Temperature 800°C.

RESULTS

The investigation was mainly concerned with the effect of MgO upon the reduction of CoO with hydrogen, but for comparison some experiments were also run with the system NiO—MgO. The results of the different runs are shown in Figs. 2—6, where the reduction ratio is plotted as a function of the reduction time at temperatures between 600°C and 1000°C. Figs. 7 and 8 show the degree of reduction of CoO after certain fixed times at 700°C plotted against the content of MgO.

As shown by Figs. 2—8, MgO greatly retards the reduction of CoO. At low temperatures, 600—800°C, this influence is, however, very complex and therefore the curves have been divided into three groups which relate to specimens with low, medium, and high MgO contents.

In group I (0.15—1.0 mole-% MgO) the reduction rate decreases with increasing MgO content in solid solution at all three reduction temperatures (Figs. 2—4, 7—8).

Group II starts at 1.5 mole-% MgO. The upper limit for MgO in this group varies with the reduction temperature (600°C: 1.5—7.1 % MgO; 700°C: 1.5—

Fig. 5. Reduction of CoO—MgO as a function of time. Temperature 800°C. Note the different time scale compared with Fig. 4 owing to the very slow reaction.

Fig. 6. Reduction of CoO—MgO as a function of time. Temperature 900°C (—) and 1000°C (---).

Fig. 7. Degree of reduction after 10, 20, and 40 min as a function of MgO content. Temperature 700°C.

Fig. 8. Degree of reduction after 10 and 20 min as a function of MgO content. Temperature 800°C.

5.8 % MgO; 800°C: 1.5–4.3 % MgO). The influence of the MgO content upon the reduction rate is also different at different temperatures. At 600°C the reduction rate of CoO decreases with increasing MgO content (Fig. 2). After a relatively rapid reduction during the first 5 min, the reduction rate drops and then remains almost constant. The first part of the reduction process at 700°C proceeds most rapidly in the samples of highest MgO content, but later the relative reduction rates change so that, finally, after 2 h the specimens high in MgO are reduced at the lowest rate (Figs. 3 and 7). The reduction rate is lower in group II than in group I except during the first 5 min. At 800°C the influence of the MgO content upon the reduction rate is so high that the second group is similar to the first group (Figs. 4, 8).

Group III comprises the specimens with the highest MgO contents. This group is missing at 600°C but appears at 700°C with 5.8 mole-% and at 800°C with 4.3 mole-% MgO. Group III is characterized by a high initial reduction rate and a very slow final one (Figs. 3–8). The ease of reduction decreases with increasing MgO content. At higher reduction temperatures, at 900°C and 1000°C (Fig. 6), where specimens with low MgO contents are so rapidly reduced that it is difficult to record their weight loss accurately, specimens with high MgO contents are reduced at a low rate.

The general effect of MgO in solid solution with NiO is to retard the reduction rate of NiO. Fig. 9 shows that increasing amounts of MgO render the decomposition of NiO more difficult. A comparison of Fig. 9 with Figs. 2–4 reveals that 1.5 mole-% MgO has about the same retarding effect upon the

Fig. 9. Reduction of NiO—MgO as function of time. Temperature 600°C (—), 700°C (---) and 800°C (----).

reduction rate of NiO as on that of CoO and that in both cases the retarding effect diminishes as the reduction temperature rises. At 7.5 mole-% MgO the curves indicate a sluggish reaction of NiO over the whole investigated range and a lower reduction rate than for the corresponding sample of CoO—MgO.

DISCUSSION

The results of this investigation show that MgO in solid solution with CoO or NiO has a very marked influence upon the reduction of the latter two oxides by hydrogen, a fact that can not be accounted for by an interaction of differently charged cations. The shapes of the reduction-time curves are different for the three concentration groups and this indicates that several mechanisms of interaction between MgO and CoO may be operating.

Already small additions of MgO (group I) have a strong retarding effect upon the reduction of CoO. This effect can be interpreted by recalling that CoO like NiO is a non-stoichiometric compound of the *p* type, *i.e.* an oxide with cation vacancies^{7,8}. Neglecting other possible lattice effects, the defect equilibrium due to the non-stoichiometry can be illustrated as follows:

where the sum of Co^{3+} ions (electron holes) is responsible for the electronic conductivity and $\square_{\text{Co}}^{2+}$ (cation vacancies) represents the degree of non-stoichiometry. While it is quite easy to understand that small amounts of foreign cations with different valences are able to shift this defect equilibrium, it is more difficult to understand why cations of the same valence should exert a similar effect. This is, however, possible if these foreign cations are able to change the defect equilibrium in the lattice due to some interaction with the parent cations.

With some justification we can expect that Mg^{2+} is able to interact with Co^{2+} and Co^{3+} in the CoO lattice and cause the shift mentioned. We know that the electronic conductivity decreases sharply on adding MgO to the CoO lattice; this indicates a shift in the equilibrium (1)⁹. On the assumption that the reduction rate is determined by diffusion processes in the solid phase¹⁰, this kind of shift could explain the influence of dissolved MgO upon the reduction rate.

Fig. 10. Reduction of CoO, CoO + 5.8 mole-% MgO (solid solution) and CoO + 5.8 mole-% MgO (mechanical mixture) as a function of time.

With increasing MgO contents above *ca.* 1.5 mole-% MgO (group II), the reactivity of the solid solution gradually changes and the reduction rates are relatively high at 4–6 mole-% MgO. In all probability this phenomenon depends on facilitated nucleation of the metallic phase. The lattice parameters for CoO ($a = 4.260$ Å) and MgO ($a = 4.212$ Å) differ slightly, and by adding MgO strain is produced in CoO by lattice distortion. As the amount of MgO is increased, this distortion which accelerates the reduction becomes more pronounced and dominates over the defect-healing effect above a certain concentration of MgO. There is also the possibility that higher MgO contents facilitate the nucleation process by providing more suitable nucleating sites at the phase boundaries between the unreduced MgO phase and the metallic cobalt.

For specimens with higher MgO contents (group III) it may be assumed that the distortion of the CoO lattice causes a high initial reduction rate, but that the retarding influence due to the dilution of CoO with MgO soon begins to dominate, as can be seen in Figs. 3 and 4.

The reduction rate of CoO was decreased by the presence of MgO in solid solution for all compositions studied owing to atomic interactions between the different cations. Experiments with only mechanical mixtures of the two oxides have shown that MgO has a weak accelerating influence upon the reduction of CoO (Fig. 10). In a mixture MgO evidently loosens up the aggregate of oxide particles and thus facilitates the circulation of gas around the CoO particles. Note that the experiments of Fig. 10 were made with raw materials differing from those used in the other runs and also in a different apparatus; hence these curves are not directly comparable with those of the earlier figures.

The few experiments carried out with the system NiO–MgO indicate that the same reduction retarding mechanism dominates at low contents of MgO as in the system CoO–MgO. The distortive influence of MgO ($a = 4.212$ Å) upon the NiO lattice ($a = 4.195$ Å) is, however, small and therefore it can be expected that the diluting effect of higher contents of MgO will dominate over the distorting effect and thus prevent the reaction rate from changing in the same way as with CoO.

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