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Abstract

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ON THE REDUCTION OF NICKEL FERRITE BY GRAPHITE

The mechanism of crystal-chemical transformations during the reduction of metal oxides by graphite has been studied in detail for iron oxides ([1]). In the reduction of more complex chemical compounds, in whose crystal lattice there are atoms of different metals, substantially different regularities may be expected.

Ferrites—compounds of the type $Me^{2+}Fe_2^{3+}O_4$ with the spinel structure—deserve comprehensive investigation, since by their physical properties they are valuable materials in semiconductor technology. In addition, in a number of metallurgical operations processes occur with the formation of ferrites and their subsequent interaction.

The material for the present investigation was nickel ferrite, obtained by sintering an equimolar mixture of Fe_2O_3 and NiO oxides in air at 1200° for 30 h. X-ray diffraction analysis of the product obtained showed that it was a pure ferrite with a crystal-lattice parameter of 8.333 (±0.005) Å. As the reducing agent, graphite from Acheson electrodes was used, calcined in vacuum at 1100°.

The ferrite was thoroughly ground with graphite and subjected to reduction. The amount of graphite was three times greater than that theoretically required for complete reduction. The crucible with the sample was suspended from the quartz spring of a McBain balance with a sensitivity of 0.001 g. The apparatus was connected to vacuum pumps, and the gaseous reaction products were continuously pumped out (at a vacuum of the order of 10^{-4} mm Hg) from the reaction space during the experiment. The carbon dioxide was captured in a trap immersed in liquid nitrogen, and its amount was periodically determined from the pressure after thawing in a definite volume. For continuous conduct of the experiment, several traps connected in parallel were used.

Figure 1 shows the change in the rate of the process of reduction of nickel ferrite by graphite at 950° as a function of the amount of oxygen removed. At the beginning, up to 20%, a certain decrease in the rate is observed. After 45–50% of the oxygen has been removed from the sample, the reduction rate increases sharply, reaching a maximum value at 80%.

This character of the kinetics indicates the substantial role of crystal-chemical transformations in the reduction process.

The solid products of reduction of nickel ferrite at different stages of reduction were examined by X-ray diffraction. The phase composition and the crystal-lattice parameter were determined.

It turned out that the product of reduction of nickel ferrite by graphite in the first stages of reduction (up to 20%) is almost pure metallic nickel with a lattice parameter of 3.517–3.520 Å. After 20% reduction, an increase in the lattice parameter of the metallic phase is observed, which indicates an increase in the iron content in the nickel.

The dependence of the lattice parameter of the metallic phase on the oxygen content in the solid phase is given in Fig. 2. The concentration of iron in nickel up to 20% reduction, calculated from the data of Bradley, Jay, and Taylor (^{2}), does not exceed 3 at.%, while at 35% it is 20 at.%. With further reduction, the lattice parameter of the metallic phase remains unchanged and only after 50% reduction begins to increase again, reaching, at 70% reduction, a value of 3.581 Å. This value of the parameter is close in magnitude to the parameter of the face-centered crystal lattice of the solid solution in the two-phase region of the phase diagram of the Fe–Ni system and corresponds to the limiting concentration of iron in nickel at room temperature.

Fig. 1. Change in the rate of reduction of nickel ferrite by graphite at 950°

The lattice parameter of the spinel phase of the initial ferrite at the beginning of reduction increases from 8.333 to 8.362 Å at 20% reduction and remains constant upon further reduction (Fig. 3).

The wüstite phase appears in specimens reduced by 35%. At 50% reduction, in addition to the metallic and ferrite phases, a considerable amount of wüstite is detected.

The metallic phase with a body-centered lattice, which is a solid solution of nickel in iron, is detected in very small amounts at 70% reduction.

Fig. 2. Change in the lattice parameter of the metallic phase in the products of reduction of nickel ferrite by graphite at 950°

Fig. 3. Change in the lattice parameter of nickel ferrite during reduction by graphite at 950°

The change in the lattice parameters of the spinel phase and of the metallic reduction products indicates that the process of reduction of nickel ferrite by graphite at 1000° is accompanied by diffusion of metal ions in the crystal lattice.

As a result of the removal of oxygen by the reducing agent, the surface layer of the ferrite is enriched in Ni^{2+} and Fe^{2+} ions. Some of these excess ions form the metallic phase, while others diffuse into the depth of the crystal lattice. Both of these processes lower the free energy of the surface layer, which is increased owing to the excess of metallic ions. Those ions that are less strongly bound to oxygen, i.e., nickel ions, pass preferentially into the metallic phase. The iron ions, under the action of the concentration gradient, diffuse into the lattice.

ferrite, and the nickel ions outward. This process is accompanied by an increase in the crystal-lattice parameter of the ferrite, which thereby approaches magnetite. The rate of reduction at this stage gradually decreases.

After 20% reduction, the lattice parameter of the spinel phase no longer changes, which indicates the cessation of substitution of nickel ions in the ferrite by iron ions. Since the ferrite is now already substantially depleted in nickel, upon its further reduction the reaction products become dominated by iron ions, which, dissolving in nickel, increase the lattice parameter of the metallic phase.

The transformation of magnetite into wüstite occurs, as is known ([1]), by diffusion of iron ions into the interior of the crystal lattice. Therefore, in the range from 35 to 50% reduction, in which magnetite is reduced to wüstite, no enrichment of the metallic phase with iron is observed, and its parameter remains unchanged. Only after all the magnetite has transformed into wüstite, i.e., after 50% reduction, do the iron ions formed during reduction again diffuse into the metallic phase, which is accompanied by an increase in the parameter of its crystal lattice. The kinetic picture of reduction after 50% corresponds to the reduction of wüstite.

When the concentration of iron in nickel reaches the maximum solubility in the face-centered lattice of the solid solution, a phase with the body-centered lattice of α-iron appears in the metallic reduction products; it is formed as a result of further reduction of wüstite and also, possibly, as a result of the decomposition of a supersaturated γ-solid solution of iron in nickel.

Thus, the mechanism of reduction of nickel ferrite by graphite in vacuum is determined both by diffusion of ions in the surface layer and by bulk diffusion of ions into the interior of the crystal lattice. It differs from the case of reduction by gases, for example by hydrogen at 400°, when bulk diffusion is of no substantial importance and the rearrangement of the lattice is effected mainly through surface diffusion of ions.

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Note: Figure translations are in progress. See original paper for figures.