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Abstract

Full Text

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Reduction of Manganese Ferrite by Hydrogen and Graphite

Manganese ferrite has a spinel-type crystal lattice, in which metallic ions can exist in different valence states (^1) and the oxygen content can deviate from stoichiometric (^2). Manganese ferrite has become widely used, since materials with valuable magnetic properties have been obtained on its basis. The conditions of its formation have been studied by many investigators (^3, ^4). Ferrite of stoichiometric composition was obtained by firing a mixture of oxides in an atmosphere of carbon dioxide (^4).

Fig. 1. Reduction of manganese ferrite by hydrogen at 500°.

The starting material for the present investigation was manganese ferrite, obtained by sintering an equimolar mixture of Fe_2O_3 and MnO at 1200° for 30 hours. Firing and cooling were carried out in a stream of CO_2. X-ray structural analysis of the product obtained showed that it is single-phase and has a lattice parameter of 8.50 Å, which agrees with literature data (^5).

When sintered in air, a single-phase ferrite with a parameter of 8.452 Å was obtained, i.e., a considerably smaller one, which indicates an increased oxygen content in the lattice as compared with the stoichiometric composition.

Reduction of manganese ferrite by hydrogen. The reduction of manganese ferrite by hydrogen was carried out in a closed apparatus with circulating gas. The water vapor formed was frozen out in a trap cooled with liquid gas. The rate of the reaction was judged from the decrease in the hydrogen pressure. Reduction was carried out at 400 and 500° and an initial hydrogen pressure of 400 mm.

The rate of reduction of manganese ferrite initially increases as reduction proceeds, reaching a maximum value approximately at 30-40% removal of oxygen (Fig. 1), after which it begins to decrease, and the process practically ceases when 75% of the oxygen has been removed from the ferrite. X-ray structural analysis shows that at this point the sample contains metallic iron and manganous oxide.

Reduction of manganese ferrite by graphite. Graphite powder, obtained by crushing Acheson electrodes and calcined in vacuum at 1000°, was used as the reducing agent. A mixture of 0.3 ferrite and 0.2 graphite was thoroughly mixed and placed in a quartz cup suspended from the spring of a MacBain balance. During

a vacuum of about 10^{-2} mm was maintained in the reaction space. The reaction rate was judged from the loss in weight and from the amount of evolved CO_2, which was trapped in a trap cooled with liquid nitrogen.

As the reduction process proceeds, the rate decreases (Fig. 2), and at about 25% there is a clearly expressed minimum on the kinetic curve. With further reduction the rate increases somewhat, and then falls to zero by the end of the process. Manganese ferrite is completely reduced by graphite at 1000°. X-ray structural analysis of ferrite samples reduced to different degrees showed that the spinel phase is detected only up to 20% reduction. In the X-ray pattern of a sample reduced by 20%, there are only weak lines belonging to the spinel phase, and the lines of a lattice of the NaCl type are sharply expressed. Possible phases with a lattice of this type may be the protoxides of iron, manganese, or their solid solutions. No metallic phase is detected at this stage. In samples reduced by more than 20%, two phases are present—the protoxide and metallic phases. The parameters of the crystal lattices of these phases do not change as the percentage of reduction increases, which indicates the presence of solid solutions of constant concentration.

Since the manganese content in the ferrite relative to iron does not exceed 35 at. %, according to the phase diagram of the Mn—Fe system (6), at 1000° the stable phase will be the γ-solid solution. The X-ray patterns show a predominant amount of the α-solid solution, which is formed as a result of decomposition of the γ-solution during cooling.

The gaseous reaction products evolved during the reduction of manganese ferrite by graphite contain about 70% CO_2 at the initial moment. As reduction proceeds, the carbon dioxide content decreases, and after 25% reduction only carbon monoxide is present in the gaseous reaction products.

Fig. 2. Reduction of manganese ferrite by graphite: 1—without additive; 2—with addition of K_2CO_3

Effect of additives on the reduction of manganese ferrite by graphite. Potassium and sodium carbonates were tested as additives. An additive in an amount of 1% of the ferrite weight was thoroughly ground together with it and with graphite. Reduction was carried out by the same method as without the additive. Additives of potassium and sodium carbonate exert an accelerating effect on the process of reduction of manganese ferrite (Fig. 2). X-ray studies were carried out on the solid products of the reduction of manganese ferrite with

Fig. 3. Dependence of the lattice parameter of the monoxide phase on the degree of reduction

Figure 2: Fig. 3. Dependence of the lattice parameter of the monoxide phase on the degree of reduction

addition of K_2CO_3. A phase with a spinel-type lattice, analogous to the initial ferrite, is present in the sample reduced by 18.93% and is not detected at 28.9% reduction.

In all samples a phase with an NaCl-type lattice was found, corresponding to the monoxide phase MeO. Its parameter increases with increasing percentage reduction, approaching the value of the MnO lattice parameter but not reaching it (Fig. 3). At 89.9% the lattice of this phase is strongly distorted, and the lattice parameter cannot be determined. The metallic phase was first detected at 30% reduction. This phase has a body-centered cubic lattice of the α-Fe type, the parameter of which at first increases slightly and then, having reached a value of 2.865 Å, remains constant, indicating that its concentration is unchanged. In the sample reduced by 90%, a γ-solid solution with a lattice parameter of 3.618 Å is observed.

On the basis of the experimental material presented above, the mechanism of reduction of manganese ferrite may be represented as follows. When oxygen is removed, an excess of metallic ions arises on the surface of the crystal lattice; these ions, on the one hand, may diffuse into the interior of the ferrite lattice and, on the other, may form a metallic phase. The occurrence of one or the other process depends on the ratio of the rates of oxygen removal and reaction diffusion.

Fig. 3. Dependence of the lattice parameter of the monoxide phase on the degree of reduction

In reduction by hydrogen, the rate of oxygen removal exceeds the diffusion rate, since the process takes place at comparatively low temperatures (400–500°). The ions formed on the surface do not have time to diffuse into the ferrite lattice, and some of them form nuclei of the metallic phase. Predominantly iron ions pass into the metallic phase, since they are less strongly bound to oxygen. Manganese ions, diffusing into the lattice, rearrange it into an NaCl-type lattice characteristic of the solid solutions MnFe_{1−x}O. The latter is gradually enriched in manganese, approaching the MnO lattice. Further reduction of MnO at this temperature does not occur, and the process practically ceases when 75% of the oxygen has been removed from the oxide.

In reduction by graphite in vacuum at a temperature of 1000°, the rate of oxygen removal is commensurate with the diffusion rate. The metallic ions have time to diffuse into the interior of the spinel lattice and rearrange it into an NaCl-type lattice. The metallic phase is formed only after this rearrangement has been completed (i.e., after 25% reduction) and is a solid solution of manganese in iron of constant concentration.

Additions of potassium and sodium carbonates accelerate the reduction process. The single-zone character of the process, typical of reduction by graphite (7,8), disappears; the metallic phase appears earlier than in reduction without additions, i.e., before 25% reduction. The metallic phase is formed predominantly by iron ions; therefore the monoxide phase that appears is enriched in manganese, as evidenced by the increase in the lattice parameter.

As reduction proceeds further, manganese also passes into the metallic phase, forming a γ-solid solution, which decomposes on cooling, and α-phase lines are obtained on the X-ray pattern. With increasing manganese concentration, the γ-phase becomes stable and does not decompose on cooling; therefore, at 90% reduction, γ-phase lines are observed on the X-ray pattern.

Thus, in the case of the reduction of manganese ferrite as well, additions of alkali-metal salts accelerate the stage of chemical interaction of the reducing agent with the compound being reduced, which is associated with a change in the electronic state of the lattice due to the incorporation into it of monovalent ions (9).

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