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Figure 1

Figure 1: Figure 1

Abstract

Full Text

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STUDY OF EQUILIBRIUM CONDITIONS DURING THE REDUCTION OF FERRITE $Mg_{0.5}Mn_{0.5}Fe_2O_4$ BY HYDROGEN

In the present work, a study was carried out of the reduction of ferrite $Mg_{0.5}Mn_{0.5}Fe_2O_4$ under equilibrium conditions at temperatures of 800, 900, and 1000°; the oxygen pressures during dissociation of the ferrite were calculated, and the composition of the solid phases formed at different stages of its reduction was determined.

Ferrite $Mg_{0.5}Mn_{0.5}Fe_2O_4$ is a solid solution of magnesium and manganese ferrites in the molar ratio 1 : 1.

The initial specimen was obtained by sintering a mixture of the oxides MgO, MnO, Fe_2O_5, taken in the required ratio, at 1200° for 30 hours in an atmosphere of CO_2. Reduction was carried out in a closed vacuum apparatus with circulation of the $H_2 + H_2O$ mixture until equilibrium was established. The water-vapor pressure was maintained equal to the pressure of saturated vapor at 0°. The hydrogen pressure in the equilibrium gas mixture was determined after freezing out the water vapor in a trap immersed in liquid nitrogen.

From the values

$$K_p = \frac{P_{H_2O}}{P_{H_2}}$$

P_{O_2} was determined (^{1}). The degree of reduction was determined from the consumption of hydrogen. Reduction to the oxide of composition $Mg_{0.5}Mn_{0.5}O$ was taken as 100%. Analysis of the solid phases coexisting with the equilibrium gas phase was carried out by X-ray diffraction by the Debye method in a camera 57.3 mm in diameter. The exposures were made in Fe–$K_{ }$ radiation with the use of a Mn filter.

Figure 2

Figure 2: Figure 2

Fig. 1. Change in the equilibrium oxygen pressure during reduction of ferrite Mg_{0.5}Mn_{0.5}Fe_2O_4 at temperatures:
1 –800°, 2 –900°, 3 –1000°

Figure 1 gives the oxygen pressures during dissociation of the ferrite as a function of the degree of reduction at different temperatures. Two regions can be distinguished, corresponding to two stages of reduction. In the first stage there is a sharp decrease in the dissociation pressure as reduction proceeds. The second stage corresponds to an almost horizontal region. X-ray examination of the solid products shows the presence of spinel and wüstite phases up to 33% reduction and of wüstite and metallic phases after 33% reduction.

Measurement of the lattice parameters of all three phases in the course of reduction is shown in Fig. 2. The spinel phase may be represented as a solid solution of the type $(MgFe_2O_4)_{x_1} \cdot (MnFe_2O_4)_{x_2} \cdot (Fe_3O_4)_{x_3}$, and the wüstite phase as a solid solution of the type $(MgO)_{y_1} \cdot (MnO)_{y_2} \cdot (FeO)_{y_3}$. The quantities $x_1 x_2 x_3$ and $y_1 y_2 y_3$ are not independent. The following method was used to determine them.

Fig. 2. Change in the lattice parameters of the spinel ($a_{\mathrm{Me3O_4}}$), wüstite (a_{MeO}), and metallic (a_{Me}) phases as a function of the degree of reduction of ferrite $Mg_{0.5}Mn_{0.5}Fe_2O_4$

From literature data ($^{2-7}$) it is known that in the corresponding solid solutions of the spinel and wüstite types Vegard' s rule (^{8}) is obeyed. Assuming that in ternary solid solutions as well the lattice parameter changes linearly with composition, in the concentration triangle with vertices $MgFe_2O_4$, $MnFe_2O_4$, Fe_3O_4 one can construct an isoparametric line of all compositions that have a lattice parameter equal to that experimentally observed at the given percentage of reduction.

In the concentration triangle with vertices MgO, MnO, FeO, an analogous isoparametric line can be constructed for all compositions having a lattice parameter equal to the experimental value found at the same percentage of reduction. It is now possible to determine those compositions of the wüstite phase that are obtained when the configuration point defining the composition of the spinel phase passes along the first constructed line. To do this, one must successively subtract from the initial ferrite composition the compositions lying on the mentioned line, taking into account the amount of oxygen removed at the given percentage of reduction. The compositions obtained lie on a line, at whose point of intersection with the isoparametric line in the wüstite concentration triangle the desired composition of the wüstite phase is found. Subtracting this composition from the initial ferrite gives the desired composition of the spinel phase.

Figure 3

Figure 3: Figure 3

The results of calculations for different stages of reduction are presented in Fig. 3, where the spinel and wüstite concentration triangles are superposed. The composition of the spinel phase changes along the line $B_1B_2B_3$, and the composition of the wüstite phase along the line $A_1A_2A_3$ up to 33%, and along the line $A_3 - A_5$ after 33% reduction.

Fig. 3. On the determination of the concentrations of the solid phases formed during reduction of ferrite $\mathrm{Mg_{0.5}Mn_{0.5}Fe_2O_4}$

Using these data, it is possible to explain satisfactorily the results presented in Figs. 1 and 2. Indeed, the decrease in the parameter of the wüstite phase up to 19% reduction occurs as a result of depletion of the solid solution in manganese monoxide and enrichment in ferrous oxide (segment A_1A_2, Fig. 3).

The increase in the lattice parameter after 19% is explained by depletion of the solid solution in magnesium oxide and further enrichment in ferrous oxide (segment A_2A_3). By 33% reduction, the solid solution contains only the wüstite phase of composition $0.5\mathrm{MgO}\cdot 0.5\mathrm{MnO}\cdot 2\mathrm{FeO}$ (point A_3). As reduction proceeds, the amount of ferrous oxide decreases, but the lattice parameter at

In this case it changes only slightly, since the solid solution $0.5\mathrm{MgO}\cdot 0.5\mathrm{MnO}$ and FeO have very similar values of the lattice parameters (region A_3—A_5). The metallic phase detected in the solid reduction product has a lattice parameter coinciding with the lattice parameter of pure iron, which remains constant within the limits of measurement error up to the end of reduction. Finally, the decrease in the lattice parameter of the spinel phase as reduction proceeds is explained by depletion of the solid solution in manganese and magnesium ferrites and enrichment in magnetite (region B_1B_2, Fig. 3).

The sharp drop in the equilibrium oxygen pressure during dissociation at the first stage of reduction (Fig. 1) is also consistent with the decrease in the concentration of magnesium ferrite and the increase in the concentration of magnetite in the spinel solid solution. As 33% reduction is approached, the dissociation pressure of the solid solution falls to values close to the dissociation pressure of magnetite ([9]).

At the second stage of reduction, the change in dissociation pressure with the composition of the solid solution $0.5\mathrm{MgO}\cdot 0.5\mathrm{MnO}\cdot (2-x)\mathrm{FeO}$ is very weakly expressed. Comparison of our data with analogous results obtained in works ([1,10]) for the solid solutions MnO—FeO and MgO—FeO showed that, for all three types of solid solutions, not only does the pressure-composition dependence have the same character, but the numerical values are also in good agreement.

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