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## Abstract

## Full Text

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### CHEMISTRY

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## ON EQUILIBRIUM CONDITIONS IN THE REDUCTION OF MAGNESIUM FERRITE BY HYDROGEN

The reduction of magnesium ferrite has been studied in works (<sup>1-3</sup>). However, information on changes in the solid phase occurring during the reduction of magnesium ferrite under equilibrium conditions is absent from the literature. The present work is devoted to this question. The initial magnesium ferrite was obtained by sintering a mixture of MgO and Fe<sub>2</sub>O<sub>3</sub> oxides of chemically pure grade in a stoichiometric ratio of 1 : 1. Sintering was carried out at 1200° for 30 hours in air. X-ray diffraction established that the initial sample was single-phase and had a lattice parameter of  $8.382 \pm 0.005 \text{ \AA}$ .

**Fig. 1.** Equilibrium oxygen pressures during dissociation of magnesium ferrite at different degrees of reduction

X-ray analysis of the reduction products was carried out by the Debye method in a camera 57.3 mm in diameter on a URS-55 apparatus. A tube with an Fe anode was used;  $\beta$ -radiation was filtered out with a Mn filter. An asymmetric film loading was used. The lattice parameters of the reduced samples were calculated by extrapolation according to Bradley and Jay (<sup>4</sup>).

Determination of the equilibrium conditions during the reduction of magnesium ferrite was carried out in a closed vacuum apparatus with circulation of an H<sub>2</sub> + H<sub>2</sub>O mixture. The water vapor pressure in the system was maintained constant and equal to the saturated vapor pressure at 0°. After equilibrium had been established, the water vapor was frozen out in a trap immersed in liquid nitrogen, and the hydrogen pressure was determined with a McLeod manometer. The degree of reduction was determined from the consumption of hydrogen.

Reduction to MgO was taken as 100%. The equilibrium oxygen pressure  $P_{\text{O}_2}$  during dissociation of the ferrite was calculated from the equation

$$P_{\text{O}_2}^{1/2} = K_p \cdot K_{\text{H}_2\text{O}},$$

where

$$K_p = \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}}$$

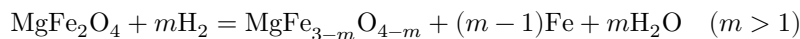
was obtained experimentally, and  $K_{\text{H}_2\text{O}}$  is the equilibrium constant of the water-vapor dissociation reaction at the same temperature, calculated by the formula of D. Chipman and A. Samarin (<sup>5</sup>).

Equilibrium conditions were investigated for the reduction of magnesium ferrite at a temperature of 900°. The oxygen pressures calculated from the above equation are presented in Fig. 1, from which it follows that, as reduction proceeds, the equilibrium oxygen pressure during ferrite dissociation gradually decreases. The course of the curve indicates the formation of solid solutions of variable composition. X-ray diffraction analysis

showed that for samples reduced by less than 33%, spinel and wüstite phases are present in the solid product. From the lines of the spinel phase it was possible to determine its parameter at 10.9 and 16.7% reduction. It proved to be  $8.397 \pm 0.005 \text{ \AA}$  for both degrees of reduction. For the sample reduced to 25.8%, the lines of the spinel phase are weak, and an exact determination of the lattice parameter is difficult. At 31.3% reduction the spinel phase is not detected. The lattice parameter of the wüstite phase present in the reduction product increases from  $4.237 \text{ \AA}$  at 10.9% reduction to  $4.291 \text{ \AA}$  at 31.3% reduction (Fig. 2).

For samples reduced by more than 33%, wüstite and metallic phases are found in the solid product. The lattice parameter of the metallic phase remains constant, within the limits of measurement error, as reduction proceeds and is equal to  $2.863 \pm 0.002 \text{ \AA}$ , which coincides with the lattice parameter of pure iron. For the wüstite phase, however, the lattice parameter decreases from  $4.291 \text{ \AA}$  at 31.3% to  $4.230 \text{ \AA}$  at 96.7% reduction (Fig. 2).

The observed dependence of the lattice parameter of the wüstite phase can be satisfactorily explained if one considers the change in the concentration of the solid solution as reduction proceeds. After 33% reduction, the composition of the wüstite phase can be determined from the degree of reduction:



where  $m$  is a quantity equivalent to the percentage of reduction. Knowing the concentration of ferrous oxide and magnesium oxide in the wüstite solid solution

Fig. 2. Dependence of the lattice parameter of the wüstite phase on the degree of reduction of  $\text{MgFe}_2\text{O}_4$

Figure 2: Fig. 2. Dependence of the lattice parameter of the wüstite phase on the degree of reduction of  $\text{MgFe}_2\text{O}_4$

at 49.2, 66.3, and 97.7% reduction, and using the experimentally found values of the lattice parameters of the solid solutions for these degrees of reduction, one can find by extrapolation the values of the lattice parameters for pure MgO and FeO. It is known <sup>(6)</sup> that Vegard' s rule is obeyed for these solid solutions. The lattice parameters determined in this way proved to be 4.222 and 4.326 for MgO and FeO, respectively. It is probable that, in the reduction process, a wüstite solid solution is formed with a small deviation from the stoichiometric composition  $\text{MeO}$ , which also requires a somewhat elevated value for the lattice parameter of the ferrous oxide entering this solution.

**Table 1**

**Concentration of solid phases formed during the reduction of magnesium ferrite**

Phase	10.9	16.7	25.8	31.3	49.2	66.3	97.7
MgO	$(\text{MgO})_{0.86}$	$(\text{MgO})_{0.0144}$	$(\text{MgO})_{0.0364}$	$(\text{MgO})_{0.0585}$	$(\text{MgO})_{0.0639}$	$(\text{MgO})_{0.0630}$	$(\text{MgO})_{0.0502}$
$\text{MgFe}_2\text{O}_4$	$(\text{MgFe}_2\text{O}_4)_{0.22}$	$(\text{MgFe}_2\text{O}_4)_{0.98}$	$(\text{Fe}_3\text{O}_4)_{0.78}$	$(\text{Fe}_3\text{O}_4)_{0.94}$	—	—	$(\text{FeO})_{0.08}$
Me	—	—	—	—	Fe	Fe	Fe

Reduction (%)

Now it is also possible to determine the concentration of the components of the wüstite phase in the products reduced up to 33%. By successively subtracting from the initial ferrite composition the compositions found for the wüstite phase, taking into account the oxygen removed at the given percentage of reduction, we obtain the compositions of the spinel phase at different stages of reduction. The results of these calculations are presented in Table 1, from whose data it follows that at low percentages of reduction a wüstite phase is formed whose composition is close to magnesium oxide. As the degree of reduction increases, enrichment in ferrous oxide occurs, and at 31.3% the composition of the wüstite phase corresponds to  $\text{Mg}_{0.35}\text{Fe}_{0.65}\text{O}$ . The lattice parameter in this region increases. After 33% reduction, the wüstite phase is depleted in ferrous oxide to the composition  $\text{Mg}_{0.92}\text{Fe}_{0.08}\text{O}$  at 97.7%. The lattice parameter at this stage decreases as reduction proceeds.

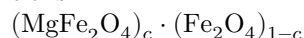
**Fig. 2.** Dependence of the lattice parameter of the wüstite phase on the degree of reduction of  $\text{MgFe}_2\text{O}_4$

Fig. 3. Dependence of the lattice parameter on the composition of solid solutions  $(\text{MgFe}_2\text{O}_4)_c \cdot (\text{Fe}_2\text{O}_4)_{1-c}$

Figure 3: Fig. 3. Dependence of the lattice parameter on the composition of solid solutions  $(\text{MgFe}_2\text{O}_4)_c \cdot (\text{Fe}_2\text{O}_4)_{1-c}$

The spinel phase, which represents a solid solution of magnesium ferrite with magnetite, rapidly approaches  $\text{Fe}_3\text{O}_4$  in composition as reduction proceeds. The concentration of the components in the spinel phase can be determined by an independent method. For this purpose, the change in the lattice parameter was studied for solid solutions of composition  $(\text{MgFe}_2\text{O}_4)_c - (\text{Fe}_3\text{O}_4)_{1-c}$ . These were prepared by sintering mixtures of both ferrites at  $1200^\circ$  for 30 h in a  $\text{CO}_2$  atmosphere. The lattice parameters were determined with an RKE camera on a URS-70 instrument with an accuracy of  $\pm 0.002 \text{ \AA}$ . The results are presented in Fig. 3. It follows from it that the change in the lattice parameter of the solid solution with its concentration is, to a first approximation, linear. By the same method, the lattice parameters of the spinel phase in the reduced samples were determined. The concentrations of the components in the solid solution, found using the dependence shown in Fig. 3, agree with the data of Table 1. It is confirmed that the composition of the spinel phase in the sample reduced to 16.7% is close to  $\text{Fe}_3\text{O}_4$ . This indicates that the additivity rule for the parameter of the solid solution  $(\text{MgO})_x \cdot (\text{FeO})_{1-x}$  is obeyed regardless of whether it is in contact with metal (after 33% reduction) or in contact with the spinel phase (up to 33% reduction).

**Fig. 3.** Dependence of the lattice parameter on the composition of solid solutions



The results of the present work show that the considerations expressed in the literature <sup>(2)</sup> concerning the instability of  $\text{Fe}_3\text{O}_4$  in contact with solid solutions  $(\text{MgO})_x \cdot (\text{FeO})_{1-x}$  have no experimental confirmation.

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