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Abstract

Full Text

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ON THE REDUCTION OF CALCIUM FERRITES BY HYDROGEN UNDER EQUILIBRIUM CONDITIONS

At present there are a number of works on the reduction of monocalcium ferrite under equilibrium conditions. Watanabe and Matsuoka (⌢1) proposed a two-stage reduction scheme to metallic iron and calcium oxide. S. T. Rostovtsev and E. I. Leshchinskaya (⌢2) established that the reduction of monocalcium ferrite in the first stage proceeds according to the scheme:

$$2CaFe_2O_4 + xH_2 \rightleftarrows Ca_2Fe_{(4-2x)}O_{(8-3x)} + 2xFeO + xH_2O$$

with the formation of a phase of variable composition, which at the end of the stage passes into dicalcium ferrite; the two following equilibrium stages of the process lead to the reduction of FeO to metallic iron and of dicalcium ferrite to metallic iron and calcium oxide.

According to the data of Schenck (⌢3), Chirilli and Burdese (^{4,}5), the reduction of monocalcium ferrite proceeds in five equilibrium stages with the formation of phases of constant composition.

In the present work, the reduction of monocalcium and dicalcium ferrite by hydrogen under equilibrium conditions at 900° C was studied. Samples of the initial ferrites were prepared by the procedure described earlier (⌢6). The composition of the solid reduction products was monitored by the X-ray method. For the identification of ferrites of various compositions, data on their X-ray spectra known from the literature (^{7,}8,⌢4) were used. A vacuum procedure was used for carrying out experiments on equilibrium reduction (^{9,}10).

Fig. 1. Dependence of the H_2O content in the gas phase on the degree of reduction of monocalcium ferrite under equilibrium conditions

Figure 1 shows the change in the equilibrium composition of the gas phase (H_2O, %) as a function of the degree of reduction (α) of the initial ferrite. Reduction to metallic iron and calcium oxide was taken as 100%. The form of the curve indicates the stepwise character of the equilibrium reduction of monocalcium ferrite.

The first equilibrium stage (α = 0-8.34%) corresponds to the coexistence of solid phases for which the equilibrium composition of the gas phase is close to 100% H_2O. X-ray structural analysis established the composition of the solid phases: initial ferrite $CaFe_2O_4$, dicalcium ferrite $CaFe_2O_5$, and ternary ferrite $CaO \cdot FeO \cdot Fe_2O_3$ or ($CaFe_3O_5$). Thus, the chemical reaction corresponding to the first stage of the equilibrium reduction of $CaFe_2O_4$ can be expressed by the following equation:

$$4CaFe_2O_4 + H_2 \rightleftarrows Ca_2Fe_2O_5 + 2CaFe_3O_5 + H_2O$$

Similarly, from the composition of the solid phases, chemical equations were compiled for the remaining equilibrium stages of reduction:

II stage:

$$4CaFe_3O_5 + H_2 \rightleftarrows 2CaFe_5O_7 + Ca_2Fe_2O_5 + H_2O$$

$$\alpha = 8.34\text{–}12.5\%; \quad K_{\mathrm{pII}} = 1.27$$

III stage:

$$2CaFe_5O_7 + H_2 \rightleftarrows 8FeO + Ca_2Fe_2O_5 + H_2O$$

$$\alpha = 12.5 \div 16.7\%; \quad K_{p\mathrm{III}} = 0.785$$

IV stage:

$$FeO + H_2 \rightleftarrows Fe + H_2O$$

$$\alpha = 16.7\text{—}50.0\%; \quad K_{p\mathrm{IV}} = 0.6$$

V stage:

$$Ca_2Fe_2O_5 + 3H_2 \rightleftarrows 2CaO + 2Fe + 3H_2O$$

$$\alpha = 50.0\text{—}100.0\%; \quad K_{p\mathrm{V}} = 0.389$$

Dicalcium ferrite is reduced in one stage to metallic iron and calcium oxide. This is also confirmed by experiments carried out at 900° with pure, specially prepared dicalcium ferrite.

The results of the equilibrium study made it possible to approximately determine the enthalpies of formation from the elements of the ternary calcium ferrites $CaO \cdot FeO \cdot Fe_2O_3$ and $CaO \cdot 3FeO \cdot Fe_2O_3$, as well as the thermal effects of the intermediate reduction reactions. In this connection, because of the difficulty of directly determining the equilibrium constant of the first reduction stage, the method of combination was used to calculate the enthalpy of the ternary ferrite $CaO \cdot FeO \cdot Fe_2O_3$, i.e., algebraic addition of the equations of the chemical reactions for stages II-V. Thus, the enthalpy of the indicated compound is determined from the hypothetical constant of the equation:

$$CaFe_3O_5 + 4H_2 \rightleftarrows CaO + 3FeO + 4H_2O$$

The entropies of the ternary ferrites were determined by the Kelley method [11] by algebraic addition of the entropies of the constituent oxides. The results of the thermodynamic calculations are given below:

Type of compound	S_{298}, e.u.	ΔH°_{298}, kcal/mole
$CaO \cdot FeO \cdot Fe_2O_3$	44.4	−433.33
$CaO \cdot 3FeO \cdot Fe_2O_3$	73.0	−567.17

Reaction	ΔH_{298}, kcal/mole
$4CaFe_2O_4 + H_2 \rightleftarrows Ca_2Fe_2O_5 + 2CaFe_3O_5 + H_2O$	12.8
$4CaFe_3O_5 + H_2 \rightleftarrows 2CaFe_5O_7 + Ca_2Fe_2O_5 + H_2O$	31.6
$2CaFe_5O_7 + H_2 \rightleftarrows 8FeO + Ca_2Fe_2O_5 + H_2O$	29.9
$FeO + H_2 \rightleftarrows Fe + H_2O$	8.7
$Ca_2Fe_2O_5 + 3H_2 \rightleftarrows 2CaO + 2Fe + 3H_2O$	33.1

The somewhat overestimated value, in comparison with the known value, of the thermal effect for the reduction reaction of wüstite can be explained by the fact that wüstite contains a certain amount of dissolved calcium oxide, as indicated by the increased value of the crystal-lattice parameter of FeO obtained in reduction stage (III) ($a = 4.326$ Å).

The sufficient sensitivity of the vacuum method used for studying equilibria made it possible to show experimentally that the equilibrium reduction of monocalcium ferrite proceeds in clearly expressed stages to phases of constant composition, i.e., without the formation of solid solutions.

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

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