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## Abstract

## Full Text

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# REDUCTION OF COPPER FERRITE $CuFeO_2$ BY GRAPHITE

Ferrite of monovalent copper has the composition $Cu^{1+}Fe^{3+}O_2^{2-}$ and a rhombohedral structure ($^{1-3}$). In the present work we investigated the kinetics of reduction of the ferrite by graphite and the crystallochemical transformations occurring in this process.

The ferrite was obtained by sintering a mixture of stoichiometric composition $Cu_2O + Fe_2O_3$ at 1000° in a stream of $CO_2$ for 28 hr. X-ray studies showed that the samples were single-phase. Reduction by graphite was carried out in a vacuum of the order of $10^{-2}$ mm Hg. The reaction rate was determined from the loss in weight of the charge, established at definite time intervals by means of spring quartz balances, and from the amount of carbon dioxide evolved during the same intervals, which was frozen out in a trap immersed in liquid nitrogen. The procedure is described in detail in (4).

The results of experiments on the kinetics of reduction at 900, 950, 1000, and 1050° are presented in Fig. 1, from which it is seen that copper ferrite is reduced stepwise. At 900° the process ends at 25% reduction. At higher temperatures the reduction proceeded further. At first, up to 50% reduction, the reaction rate decreases, after which its acceleration is again observed. The kinetic curves have a well-defined minimum and maximum.

The gaseous reaction products in the reduction of $CuFeO_2$ by graphite are $CO_2$ and CO. In the initial stage, up to 33% reduction, the gas phase consists practically only of carbon dioxide; by 50% reduction the ratio of CO to $CO_2$ becomes equal to 1 : 1. With further reduction the amount of carbon dioxide gradually decreases.

The stepwise character of the reduction of copper ferrite is confirmed by X-ray structural investigation of the composition of the solid phases at various degrees of reduction.

Fig. 1. Reduction of $CuFeO_2$ by graphite at different temperatures

Figure 1: Fig. 1. Reduction of $CuFeO_2$ by graphite at different temperatures

| Reduction, % | 11 | 22 | 30 | 40 | 46 | 75 |
|---|---|---|---|---|---|---|
| Phases | $CuFeO_2$, Cu, $Fe_3O_4$ | $Fe_3O_4$, Cu, $CuFeO_2$ | $CuFe_3O_4$, traces, $CuFeO_2$ | Cu, $Fe_3O_4$, FeO | Cu, FeO, $Fe_3O_4$ | Cu, FeO |

At the early stage of reduction, in the solid reaction products, along with the starting ferrite, copper and magnetite are found, the latter giving on the radiographs the diffraction pattern of spinel. By 30% reduction the phase of the initial ferrite disappears, and by 40% wüstite appears as a result of the reduction of magnetite. After 50% of the oxygen has been removed, autocatalytic reduction of wüstite begins, and copper, wüstite, and iron are found in the solid reaction products.

The ferrites, the mechanism of whose reduction was studied earlier (4–6), had the spinel structure and formed continuous series of solid sol—

tions with one of the reduction products—magnetite. The reduction of these ferrites by graphite at relatively high temperatures and low partial pressures of the reducing agent was accompanied by bulk diffusion of metal ions in the solid phase. The ferrite of monovalent copper does not form solid solutions with magnetite, as is shown by studies of the dependence of the equilibrium oxygen pressures in the gas phase on the degree of reduction. Detailed results of this work will be published later. The absence of mutual solubility between the initial oxide and the products of its reduction makes it possible to assume that the reduction process of monovalent copper ferrite is not accompanied by appreciable bulk diffusion of metal cations or oxygen ions through the layer of solid reaction products. In this process an important role is played by surface diffusion. As a result of the latter, during reduction, crystals of copper and magnetite grow on the surface of the ferrite particles.

**Fig. 1.** Reduction of $CuFeO_2$ by graphite at different temperatures

In our case, when the specimen was a powder with a small particle size and the process proceeded at high temperatures and low partial pressures of the reducing agent, the transformation of the ferrite into magnetite and copper was completed before the reduction of magnetite began. The latter proceeded as described in work (7).

Thus, the reduction of rhombohedral copper ferrite at 950, 1000, and 1050° proceeds stepwise, with the formation in the first stage of copper and magnetite. Subsequently, magnetite is reduced through wüstite to iron.

Analysis of the data obtained shows that, in the reduction of $CuFeO_2$ ferrite to magnetite and copper, surface diffusion plays a substantial role.

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