FERRITE FORMATION IN MIXTURES OF MAGNESIUM OXIDE AND HEMATITE POWDERS

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At present there is considerable interest in the kinetics and mechanism of ferrite formation reactions [1-5]. In the work described below, the \( \text{MgO} + \text{Fe}_2\text{O}_3 = \text{MgFe}_2\text{O}_4 \) reaction was chosen with the aim of establishing how the composition of the gaseous environment and stoichiometry imperfections, attributable to this composition, in the starting oxides affect the mechanism and intensity of ferrite formation.

Magnesium oxide and hematite powders obtained from extra pure preparations were annealed for 4 h in air at 1300°C. This treatment was performed to "coarsen" the active preparations and even out the influence of nonequilibrium defects on experimental results. The oxide powders (< 0.25-mm fraction) were then heated for 6.5 h at 1000°C in a flow of gas under a given oxygen partial pressure in order to obtain specimens of various degrees of deviation from stoichiometry. Experiments were conducted in pure oxygen, air, and technical nitrogen (\( \text{PO}_2 = 10^{-3} \) atm). In addition, nonstoichiometric oxide powders were prepared by prolonged (24 h) heating in sealed quartz capsules a certain quantity of magnetite as a getter and filled after evacuation with nitrogen with an addition of water vapor.

The oxide powders were mixed in equimolar amounts and the resultant mixtures were subjected to isothermal heating at 1000°C under dynamic (series A) and static (series B) conditions. In series A experiments, a sample of mixed oxides was placed in a platinum boat, which was quickly introduced into a furnace preheated to 1000°C and held in a flow of gas under the same oxygen partial pressure as in the preparation of the individual oxides. In series B experiments, oxide mixtures in the form of powders or tablets produced under a pressure of 5 tons/cm² were sealed in quartz capsules with a minimum free volume (evacuated or filled with the gas mixture used for treating the starting oxides) and introduced into a furnace preheated to 1000°C. To determine the degree of ferritization, use was made of the techniques of chemical and x-ray phase analyses.

DISCUSSION OF RESULTS

The experimental results obtained, which are illustrated in Fig. 1 and Tables 1 and 2, enable us to draw the following conclusions:

1. Under comparable ferritization conditions (1000°C, 2 h), the reaction is much more rapid in tableted specimens than in loose powder mixtures (for \( \text{ZnO} - \text{Fe}_2\text{O}_3 \) and \( \text{ZnO} - \text{Al}_2\text{O}_3 \) mixtures, the opposite effect has been observed [6, 7]).

2. A fall in the chemical potential of the oxygen, which ensures that the oxides are nonstoichiometric and remains constant during the ferritization process, is accompanied by an acceleration of the reaction (this effect, too, is the reverse of that observed with \( \text{ZnO} - \text{Fe}_2\text{O}_3 \) and \( \text{ZnO} - \text{Al}_2\text{O}_3 \) mixtures).

3. Under comparable experimental conditions (1000°C, 2 h), the reaction is more rapid under static than under dynamic conditions.

To explain these phenomena, it is necessary to assume that, under increased oxygen pressures, cation counterdiffusion in a rigid oxygen lattice is the dominant mechanism of spinel formation. The rate of
the process is then determined by the mobility of the slowest component, which, judging from the data in [5], is the magnesium ion. The spinel phase forming under these conditions has a fixed nonstoichiometric composition [according to [8], $(\text{MgO})_{0.00}\text{MgFe}_2\text{O}_4$].

The unreacted oxides form no solid solutions with each other and remain "pure." The absence of impurity defects in the oxides hinders diffusion and, consequently, the spinel formation process as a whole. The lowest ferrite yield is observed (curve 1). The mechanism proposed by Schmalzried [2] for magnesium oxide transport,

\[ \text{MgO} = \text{Mg}^{2+} + 2e^- + \frac{1}{2} \text{O}_2 \]  

is unlikely to be operative in this case owing to the low concentration of free electrons in the lattice.

When the oxygen partial pressure is lowered (curves 2 and 3), additional effects appear, which are attributable primarily to the thermodynamic instability of hematite at the hematite/ferrite interface and of ferrite at the ferrite/pure magnesium oxide interface. From the MgO–FeO–Fe$_2$O$_3$ equilibrium diagram [9] it is evident that lowering the oxygen pressure increases the activity of hematite in the boundary ferrite layer as a result of the dissociation

\[ 3 \text{Fe}_2\text{O}_3 = 2 \text{Fe}_3\text{O}_4 + \frac{1}{2} \text{O}_2 \]  

The Fe$^{2+}$ ions being formed act as free electrons and promote transport by the mechanism described in Eq. (1). If under these conditions the oxygen pressure is still sufficiently high, the Schmalzried mechanism may become dominant. In addition to this, lowering the oxygen partial pressure at the same time leads to spinel dissociation according to the reaction

\[ (\text{Fe}_2\text{O}_3)_{\text{ferrite}} = 2\text{FeO}^- + \frac{1}{2} \text{O}_2 \]  

as a result of which the activity of the "FeO" rises in the coexisting wüstite and spinel phases. Magnesium oxide, which has a virtually defect-free structure at high P$_{\text{O}_2}$, on dissolving wüstite sharply increases the concentration of vacancies, which greatly facilitates the process of diffusion with the formation of new portions of ferrite. It should be noted that, with change in oxygen partial pressure, the composition of the ferrite phase in equilibrium with magnesium oxide also changes (although to a much smaller extent) as a result of substitution of Fe$^{2+}$, with the formation of solid solutions of ferrite and magnetite. This may facilitate the process of transport through the spinel by the mechanism

\[ \text{Fe}_2\text{O}_3 = 2\text{Fe}^{3+} + 6e^- + \frac{3}{2} \text{O}_2 \]  

It is difficult to ascertain which of the pressure reduction effects is the decisive one, but with any of them one would expect spinel formation to become intensified with decrease in oxygen partial pressure. This was, in fact, observed in our experiments (see curves 1, 2, and 3). It is possible that, under static conditions, an appreciable contribution to ferritization comes from the volatility of Fe$_2$O$_3$. However, no direct information is available upon the role of such transport.

For a mixture treated in nitrogen, the degree of ferritization under both static and dynamic conditions is similar. This may be ascribed to the fact that the beneficial effect of volatility for a specimen heated in a closed system is commensurable with the beneficial effect of dissociation of ferric oxide in a stream of