

Letters to the Editor

Influence of an external magnetic field on the dynamics of magnetite reduction by hydrogen

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The influence of weak magnetic fields on the mechanical, thermodynamic, kinetic, and other properties of non-magnetic compounds is a fundamental problem of both condensed matter physics^{1,2} and physical chemistry. A magnetic field is defined as weak when the condition $\mu H \ll kT$ is met, here μ , H , k , and T are the magnetic moment, magnetic field intensity, Boltzmann constant, and temperature, respectively. According to the two-electron concept of spin chemistry,^{3,4} a magnetic field induces a transition between two separate electronic states, namely, the ground singlet state and the excited triplet state with energies E_s and E_t , respectively. The distance between the electrons of a radical pair is denoted by r and is defined as the reaction coordinate. The transition between levels is forbidden in the absence of a magnetic field. The condition

$$|E_s(r) - E_t(r)| \approx \mu_B H,$$

at which the magnetic field induces a transition, is valid for large values of r (equal to several interatomic distances) in the interval of δr . This interval determines the duration of the existence of a radical pair in the reaction zone. This

approach was used for anthracene and tetracene when studying reactions in the solid state.⁵

Earlier⁶ we discovered the effect of the magnetic field on the kinetics of the reduction of bulk cobalt oxide Co_3O_4 . It was shown that the magnetic field affects the effective energy of activation of reduction of bulk oxide and does not affect the energy of activation of reduction of nanoparticles in the $\text{Co}_3\text{O}_4/\text{SiO}_2$ system. It was suggested that the change in kinetic parameters is caused by the influence of an external magnetic field on the structural defects in the solid.

The goal of the present work is to continue the study of the influence of a magnetic field on the reduction of bulk ferromagnetic metal oxides using magnetite as an example.

The object of this study was magnetite powder (VEB LABORCHEMIE APOLDA) with an average particle size of ~ 0.01 mm. The measurements were carried out on a vibratory magnetometer *in situ*.^{7,8} A sample weighing 5 mg was placed in the measuring cell of the magnetometer, secured between two gas-permeable membranes, and heated in a field with an intensity of 60 A m^{-1} under Ar to 600°C with a rate of $10^\circ\text{C min}^{-1}$

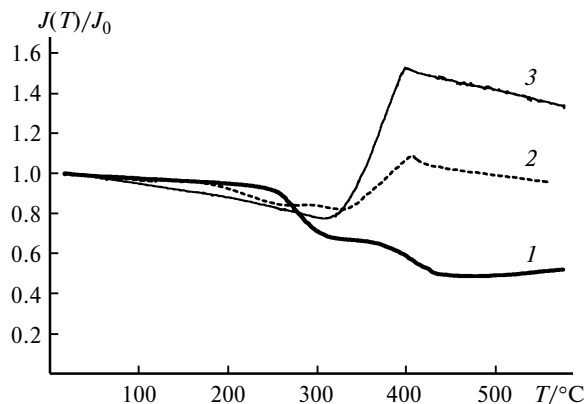
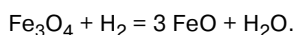


Fig. 1. Temperature dependence of relative magnetization during magnetite reduction in hydrogen in fields with intensities 60 (1), $1 \cdot 10^3$ (2), and $5 \cdot 10^3$ A m⁻¹ (3).

to remove adsorbed water. After cooling, the Ar was replaced with hydrogen (99.997%) at a flow rate of 30 mL min⁻¹. The sample was magnetized to the specified value. The magnetite was reduced in a linear heating mode at a rate of 10 °C min⁻¹ with continuous registration of magnetization with a frequency of 1 Hz; the external field intensity was 60, 500, $1 \cdot 10^3$, $4 \cdot 10^3$, and $5 \cdot 10^3$ A m⁻¹. The reduction was also carried out in an isothermal mode at a temperature of 350 °C by replacing the flow of Ar with H₂.

The obtained temperature dependences of relative magnetization $J(T)/J_0$ ($J(T)$ and J_0 are the magnetizations at temperature T and ~20 °C, respectively) for various external field intensities are shown in Fig. 1.

A noticeable decrease in magnetization is observed at $T > 270$ °C in a field with an intensity of 60 A m⁻¹ (see Fig. 1, curve 1), which is seemingly due to the formation of antiferromagnetic wustite (FeO) by the reaction



A noticeable increase in magnetization caused by the reduction of wustite to iron is observed only at $T > 500$ °C. A considerable change in the behavior of magnetization occurs with an increase in the magnetic field intensity to $1 \cdot 10^3$ A m⁻¹ (see Fig. 1, curve 2). A rapid increase in magnetization is observed above a temperature of 310–320 °C, which ceases at $T = 400$ °C. A sharp termination of the increase in magnetization at 400 °C corresponds to the complete conversion of Fe₃O₄ to Fe, and a further slow drop in J with increasing temperature reflects the thermomagnetic dependence of iron.

The results of the isothermal experiment, in which reduction on a pre-magnetized sample was initiated by replacing the flow of Ar with hydrogen at a temperature of 350 °C, are shown in Fig. 2. The process was carried out at a field intensity of 60, $2 \cdot 10^3$, and $5 \cdot 10^3$ A m⁻¹.

As can be seen from the presented results, reduction in a field with an intensity of 60 A m⁻¹ leads to a decrease

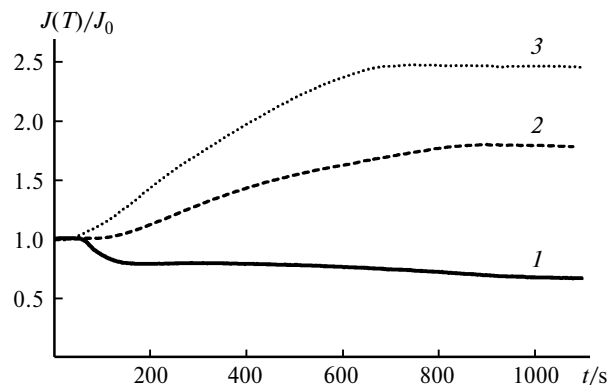


Fig. 2. Time dependent relative magnetization at 350 °C in fields with intensities 60 (1), $2 \cdot 10^3$ (2), and $5 \cdot 10^3$ A m⁻¹ (3).

of the initial magnetization (see Fig. 2, curve 1). At the same time, the magnetization increases when reduction is carried out in a field with an intensity of $2 \cdot 10^3$ and $5 \cdot 10^3$ A m⁻¹ (see Fig. 2, curves 2 and 3). The increase in magnetization is a consequence of the appearance of a magnetic phase in the system, the magnetization of which is greater than that of magnetite at 350 °C. Metallic iron can be such a phase in a Fe–O system. At the same time, a decrease in magnetization during reduction may indicate the transition of a part of magnetite to antiferromagnetic wustite.

In conclusion, in small fields ($H < 1 \cdot 10^3$ A m⁻¹), reduction proceeds through the formation of wustite, while reduction avoids the formation of the wustite phase in fields with an intensity of $> 1 \cdot 10^3$ A m⁻¹. We assume that an external magnetic field can direct magnetite reduction with hydrogen, changing the reaction route from Fe₃O₄–FeO–Fe in low fields or in the absence of a field to Fe₃O₄–Fe in fields with an intensity of $1 \cdot 10^3$ A m⁻¹.

When reducing Fe₃O₄ with hydrogen, the reduction mechanism changes at $T = 390$ °C.⁹ Below this temperature the process follows the contracting sphere mechanism, escaping the formation of wustite,¹⁰ and at $T > 390$ °C reduction proceeds through the formation of FeO in the form of two-dimensional nuclei. The reduction of metal oxides is possible only in the case of dissociative adsorption of hydrogen on active surface sites. It is likely that an external magnetic field leads to a decrease in the temperature of the onset of this process through the generation of these sites and, thus, directs the reaction along the reduction path, avoiding the formation of wustite. At present, we cannot explain these experimental facts; nevertheless, we can assume that the field affects the stage of new phase nucleation.

References

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