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SYNTHESIS AND PROPERTIES OF INORGANIC COMPOUNDS

Kinetics of Microwave-Enhanced Solid-Phase Reaction of $NiFe_2O_4$ Formation

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Abstract—Microwave-enhanced solid-phase reaction between iron(III) oxide and nickel(II) oxide has been studied at 850–900°C. The formal-kinetic approach to data processing showed that microwave treatment considerably increases the rate of the solid-phase reactions and changes its rate-controlling stage.

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Microwave heating is a promising way to increase the rates of solid-phase reactions [1, 2]. Microwave heating makes it possible to carry out important physicochemical processes, such as dehydration, decomposition of salt and hydroxide precursors, synthesis of multicomponent compounds, and sintering of ceramics, considerably decreasing time and energy consumption compared to conventional versions of these processes [2]. The amount of literature regarding the chemical applications of microwave heating has grown by several times during the last ten or fifteen years. Among others, it includes numerous works on the microwave-assisted synthesis of individual and multicomponent oxide compounds [3]. Unfortunately, most works are merely experimental: the choice of precursors is not substantiated, and discussion only concerns the microstructure and structure-sensitive properties of products, but not fundamental inferences about the effects of the physical and chemical properties of precursors and the organization of the reaction zone or the mechanism of the interaction of microwaves with test compounds.

In this context, an experimental study of the kinetics and mechanism of solid-phase reactions in powdered reagent mixtures and formal-kinetic analysis are of considerable interest for suggesting a reaction mechanism, at least, its rate-controlling stage.

In this context, this work studies the mechanism of microwave-enhanced solid-phase reactions in the system

$$Fe_2O_3 + NiO \longrightarrow NiFe_2O_4. \qquad (1)$$

In choosing this reaction, we were guided by the considerable experience of our team in studies of ultrasound-enhanced solid-phase reactions in this system Fe_2O_3–NiO [4, 5] and in the presence of salt additives [6]. In addition, the mechanism of nickel ferrite formation can be considered to be reliably determined [7], which makes it possible to consider this reaction as a model one.

EXPERIMENTAL

The starting iron(III) oxide was synthesized by the thermal decomposition of $Fe(NO_3)_3 \cdot 9H_2O$ (pure for analysis grade) in a burner flame. The resulting product was in addition subjected to isothermal annealing at 800°C for 3 h. Nickel oxide was synthesized by an identical procedure with nickel nitrate hexahydrate $Ni(NO_3)_2 \cdot 6H_2O$ (pure for analysis) as the precursor.

Stoichiometric mixtures of the precursor oxides, after being ground with an agate mortar, were homogenized in a laboratory Fritsch Pulverizette 7 planetary mill (agate bowls and milling bodies; heptane). After this, the powders were dried and pelletized on a Carver Model C hydraulic press (120 kg/mm^2). The high-temperature treatment of compacted powders was carried out at 850 and 900°C for 10–60 min in a Linn Therm Multilabor 2.4/2.45 laboratory microwave oven (output power, 2 kW; operation frequency, 2.45 GHz). The heating rate used to bring samples to the isothermal exposure temperature was 50 K/min. After the isothermal exposure was over, samples were quenched in air. References were processed in an ordinary resistor furnace under the same conditions.

X-ray powder diffraction was measured on a DRON-3M diffractometer (CoK_α radiation, 0.03° increments, 5-s exposure). X-ray diffraction patterns were analyzed with reference to the JCPDS-PDF2 database.

The degree of solid-phase reaction (1), α, was determined by quantitative X-ray powder diffraction analysis. The references used were $(1-x)\{NiO + \alpha\text{-}Fe_2O_3\} + xNiFe_2O_4$ mechanical mixtures with various molar ratios between an equimolar NiO + iron(III) oxide mixture and nickel ferrite $NiFe_2O_4$. The single-phase nickel ferrite sample used as a component of reference mixtures was synthesized as follows: after being homogenized in a planetary mill, a stoichiometric iron(III) oxide + nickel oxide mixture was brought to 1000°C,

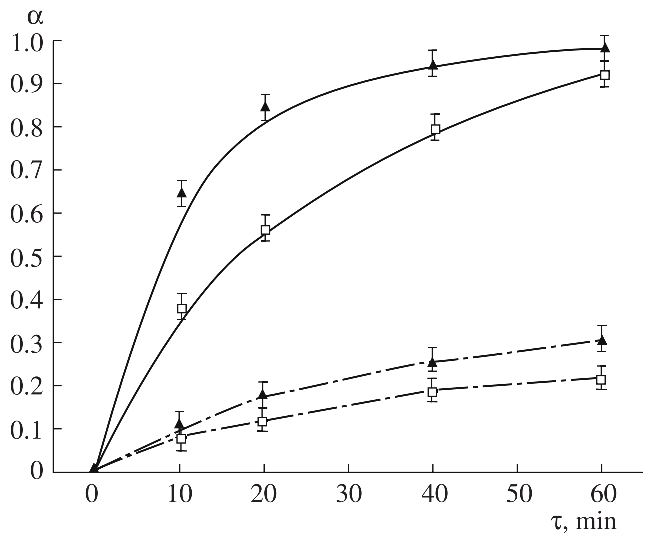

Fig. 1. Rate curves for reaction (1) under microwave heating (solid lines) and thermal heating (dashed-and-dotted lines): ▲ 850 and □ 900°C.

which was followed by isothermal annealing for 10 h at this temperature.

α was calculated from the relationship

$$x = 1.67(2)Y - 0.67(2)Y^2 \ (R^2 = 0.998), \tag{2}$$

where

$$Y = \frac{I_{220}}{I_{220} + I_{104}}. \tag{3}$$

Here, I_{104} is the integrated intensity of the (104) diffraction maximum from the α-Fe_2O_3 phase, I_{220} is the integrated intensity of the (220) diffraction maximum from the $NiFe_2O_4$ phase, and x is the nickel ferrite mole fraction (the degree of reaction).

Mean crystallite sizes for iron(III) oxide and nickel ferrite were estimated as coherence lengths (CLs) from the Selyakov–Scherrer relationship

$$D_{CL} = \frac{\lambda}{B\cos\theta_{hkl}}, \tag{4}$$

where $B = \beta_{hkl} - s$ (β_{hkl} is the overall broadening of the (hkl) diffraction maximum fitted by the Lorentzian, and s is the instrumental broadening (for the diffractometer used, 0.09° ± 0.01° 2θ).

RESULTS AND DISCUSSION

To study the kinetics and mechanisms of microwave-enhanced solid-phase reactions, we carried out a set of experiments on the synthesis of nickel ferrite from oxides with microwave heating. The rate curves in Fig. 1 imply that microwave heating noticeably enhanced the rate of the solid-phase reaction. The degree of reaction α within 1-h exposure in a microwave oven reached 0.98 at 900°C and 0.92 at 850°C; in references, the respective values were 0.31 and 0.22.

Analyzing the degree of reaction as a function of synthesis time in formal kinetic terms, we found that the rate-controlling stage of the reaction changed in a microwave field. In the references, ion diffusion through the product layer was the rate-controlling stage of the solid-phase reaction over the entire range of the temperatures studied. This is proven by the satisfactory goodness of fit provided by the Jander model:

$$(1 - \sqrt[3]{1-\alpha})^2 = k_J\tau, \tag{5}$$

where τ is the reaction time and k_J is the apparent rate constant of the reaction described by the Jander model.

We should note that the above description of experimental data is in good agreement with previous kinetic studies of the solid-phase reaction (1) [5]. The Jander model describes the kinetics of solid-phase reactions controlled by the volume diffusion of one component through the product layer; i.e., this is a diffusion model.

On the other hand, the rate curves for microwave-treated reaction mixtures are best fitted by the soft sphere (ss) equation, which describes a solid-phase reaction controlled by an interfacial chemical reaction:

$$1 - \sqrt[3]{1-\alpha} = k_{ss}\tau. \tag{6}$$

A distinguishing feature of this type of reaction is almost instantaneous nucleation, and the surface of each particle becomes coated with a continuous product layer in short reaction times; the process rate is proportional to the surface area of the unreacted reagent. In the absence of diffusion hindrances and with the provision that iron oxide particles are isotropic, the description in terms of the soft sphere model agrees with the current ideas about the mechanism of this reaction [7]; it is known that, in the reaction of nickel and iron oxides, a ferrite layer forms only on Fe_2O_3 particles.

Regarding the dynamics of alteration of the real structure of reaction components during the reaction (Fig. 2), we note that broadening values for both the starting α-Fe_2O_3 and the reaction product decrease with increasing degree of reaction, indicating an increase in the coherence lengths for these phases. We failed to obtain reliable data on the real structure of iron oxide during 1-h microwave exposure because of the too low intensity of the respective reflections in the X-ray diffraction pattern.

This increase in the coherence length is evidently due to the coherent intergrowth of primary crystallites of the new phase; the coherent intergrowth rate is sufficiently high at high temperatures (commensurate with Tammann's temperature). This behavior of the system agrees with the postulates of the Jander and soft sphere models; these models consider both the starting reagent and the reaction product as compact phases, in which there are all conditions for the coherent intergrowth of crystallites.

The mean crystallite size for the ferrite phase increases far more appreciably with treatment time (from 18–20 nm after 10 min to 40–50 nm after 60 min) than for iron oxide (from 12–15 nm after 10 min to 15–18 nm after 60 min). Most likely, this fact is due to the competition of coherent intergrowth in the iron oxide phase with transformation into $NiFe_2O_4$. The product layer forming on Fe_2O_3 particles creates an additional hindrance to their coarsening.

Another interesting feature of microwave treatment is as follows: in spite of the considerable difference between the rates of the solid-phase reaction under microwave heating and thermal heating, the dynamics of alteration of the real structure is virtually the same in both cases. The difference between the coherence lengths determined in the reference and microwave experiments is in most cases within the measurement error limits (Fig. 2). In other words, microwave treatment does not additionally enhance grain coarsening. This result agrees with numerous studies of microwave-enhanced sintering [1, 3, 8, 9], where grain coarsening was virtually unobserved in a microwave field despite the considerable increase in the ceramic compaction rate. Likely, this effect is due to the fact that microwave treatment stimulates intercrystallite diffusion more than volume diffusion.

Thus, we can conclude that the rate-controlling stage of the process changes as a result of diffusion enhancement in a microwave field. Comparing the results of the experiments we carried out in this work with nickel ferrite synthesis in salt matrices [6], we state that the microwave effect consists in releasing diffusion hindrances. In all probability, the reaction mechanism does not change upon release. These data are in good agreement with the currently dominating model of nonthermal effects of microwaves [10]. This model postulates that a high-frequency electromagnetic field should generate fluxes of charged species (ions or vacancies) in the substance; the intensity of these fluxes changes symbatically with the intensity of the external electromagnetic field. As a result, unbalanced fluxes of charged species appear along any extended crystal defect (free surfaces, interfaces, or grain boundaries) and an additional driving force of diffusion is created. Not influencing the mechanism of the chemical reaction, microwaves intensify diffusion; this means that the greatest effect of microwaves is expected in diffusion-hindered processes.

The release of diffusion limitations should most likely considerably decrease the activation energy of the reaction. Unfortunately, the data obtained in this work do not make it possible to calculate the effective activation energy of the reaction in a microwave field; this value is estimated at 60–70 kJ/mol, i.e., 2.5–3 times lower than the activation energy of the process with ordinary thermal heating [4]. Analogous results were obtained in the kinetic study of the reaction between titanium dioxide and barium carbonate [11]. The activation energy of this process in a microwave field was near one-fourth that during ordinary heating.

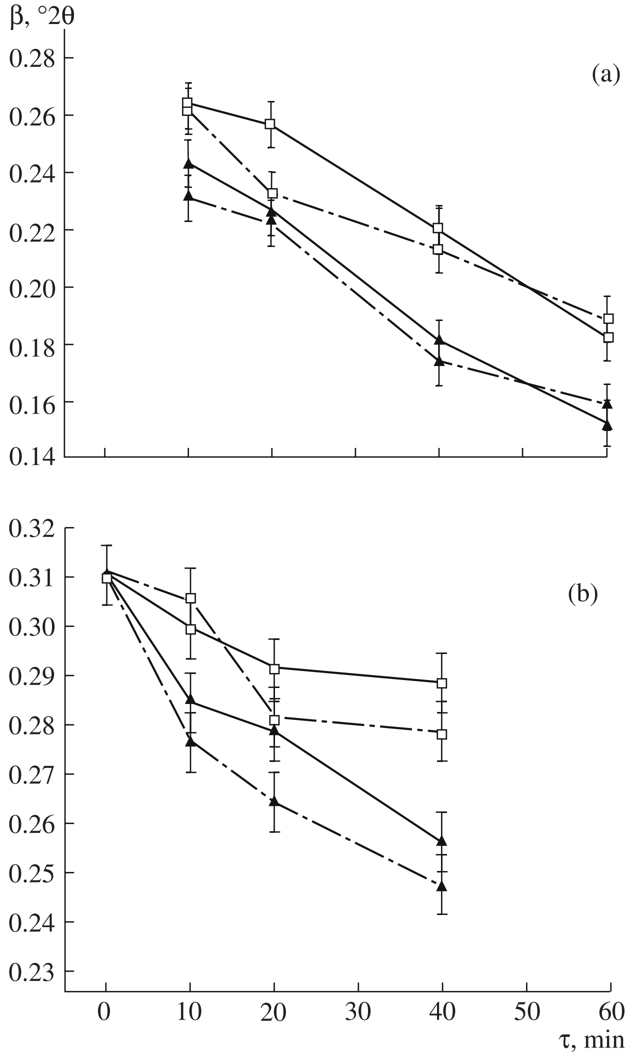

Fig. 2. Physical broadening of (a) (104) α-Fe_2O_3 and (b) (220) $NiFe_2O_4$ diffraction peaks vs. time of microwave heating (solid lines) and thermal heating (dashed-and-dotted lines): ▲ 850 and □ 900°C.

In summary, we have shown that the use of microwave fields is an efficient approach to considerably increasing the rate of a solid-phase reaction at high temperatures. Having studied the kinetics of the solid-phase reaction between iron oxide and nickel oxide, we determined that microwave treatment releases diffusion hindrances, thus changing the rate-controlling stage of the reaction.

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