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Kinetics and mechanism of the high-temperature sonochemical synthesis of spinel-type ferrites

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The mechanism and kinetics of high-temperature sonochemical reactions in the binary oxide systems $LiFeO_2 + Fe_2O_3$, $ZnO + Fe_2O_3$ and $NiO + Fe_2O_3$ were studied.

Sonochemical synthesis is an integral part of contemporary material science because it allows one to obtain a wide range of functional materials including magnetic nanocomposites, catalysts, molecular sieves *etc.*[1] The mechanism of sonochemical reactions in aqueous and non-aqueous solutions is governed by two major effects accompanying ultrasonic action on liquid media, namely, the intensification of mass-transfer processes and cavitation. At the same time, the collapse of cavitation bubbles results in an enormous rise of local temperatures and pressures leading to the decomposition of dissolved volatile compounds and the formation of amorphous and crystalline nanopowders.

Sonochemical reactions in solids proceed in quite a different manner because in this case sonication primarily results in an increase of the concentration of dislocations (up to 10^3 times), an increase in effective diffusion and self-diffusion coefficients (up to 10 times)[2] and the formation of new interphase contacts due to displacement of individual crystallites. Thus, it can be supposed that ultrasonic treatment could give rise to a substantial acceleration of solid-state reactions and, probably, to lower reaction temperatures. For instance, it was shown that the β-PbO → α-PbO phase transition proceeds in an ultrasonic field with a notable rate at ambient temperatures, while without acoustic treatment β-PbO is kinetically stable even at elevated temperatures (up to 500 °C).[3]

Unfortunately, the kinetics and mechanism of ultrasonically assisted solid-state reactions in binary and ternary oxide systems are poorly understood. Thus, the aim of this work was to study the kinetics of the model sonochemical reactions of ferrite formation

$$LiFeO_2 + 2Fe_2O_3 \rightarrow LiFe_5O_8, \qquad (1)$$

$$ZnO + Fe_2O_3 \rightarrow ZnFe_2O_4, \qquad (2)$$

$$NiO + Fe_2O_3 \rightarrow NiFe_2O_4 \qquad (3)$$

and the evolution of the microstructure of reaction mixture components in order to determine the mechanism of diffusion-limited reactions in an ultrasonic field.

Iron(III) and nickel oxides were prepared by thermal decomposition of the corresponding nitrates followed by annealing at 800 °C for 3 h. Commercial ZnO (Aldrich) was used without any additional processing. α-$LiFeO_2$ was synthesised by the solid-state interaction of iron(III) oxide and lithium carbonate at 800 °C for 3 h.

The ultrasonic treatment of homogenised and pelletised oxide mixtures was conducted on a setup shown in Figure 1.[4,5] The ultrasonic frequency was 21.45±0.03 kHz, and the displacement amplitude was 10.0±0.7 μm. Ultrasonic treatment was carried out at 550–900 °C for 0.5–2 h. Reference samples were prepared under

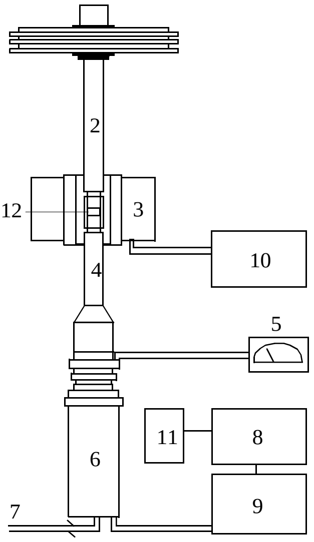

Figure 1 Experimental setup: (1) static load (25 kg), (2) passive waveguide, (3) resistance furnace, (4) active waveguide, (5) ultrasonic amplitude sensor, (6) magnetostriction radiator, (7) water cooling, (8) master oscillator, (9) power amplifier, (10) temperature controller, (11) frequency meter, (12) sample.

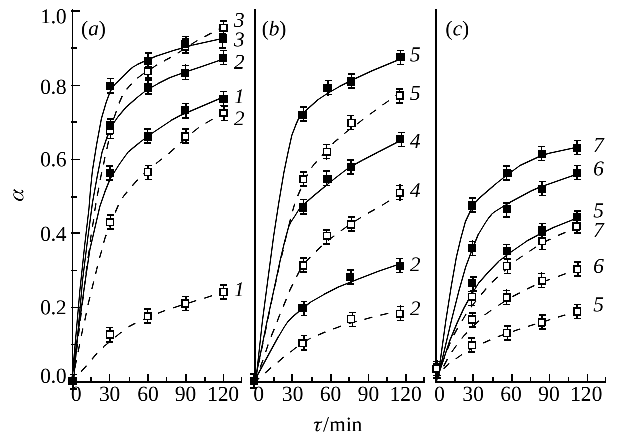

Figure 2 Kinetic curves for solid-state reactions (1) (*a*), (2) (*b*) and (3) (*c*). Open squares correspond to control samples, and filled squares correspond to sonicated reaction mixtures: (*1*) 550; (*2*) 600; (*3*) 650; (*4*) 700; (*5*) 800; (*6*) 850 and (*7*) 900 °C.

the same conditions without sonication. The degree of conversion (α) was estimated by quantitative X-ray analysis using reference mechanical mixtures of $(1-x)\{\mathrm{ZnO} + \alpha\text{-}\mathrm{Fe_2O_3}\} + x\mathrm{ZnFe_2O_4}$; $(1-x)\{\mathrm{NiO} + \alpha\text{-}\mathrm{Fe_2O_3}\} + (x)\mathrm{NiFe_2O_4}$ and $(1-x)\{2\alpha\text{-}\mathrm{Fe_2O_3} + \alpha\text{-}\mathrm{LiFeO_2}\} + (x)\mathrm{LiFe_5O_8}$ (x is the molar fraction of the corresponding ferrite). Calculated α values were plotted against time (τ) and thus obtained kinetic curves were analysed using conventional kinetic models.[6] Information concerning the influence of ultrasonic treatment on the microstructure of reactants and reaction products was obtained by scanning electron microscopy (SEM) and X-ray diffraction peak broadening analysis. Coherent scattering domain (CSD) size was estimated using the Scherrer equation

$$D_{\mathrm{CSD}} = \frac{\lambda_{\mathrm{CuK\alpha}}}{\beta_{hkl}\cos\theta_{hkl}}. \tag{4}$$

Kinetic curves for solid-state reactions (1)–(3) are depicted in Figure 2. One can see that sonication results in a notable increase of the rate of all of reactions, especially, at the initial stage. A comparison of obtained data allows us to assume that the mechanisms of reactions in these systems in an ultrasonic field and without it markedly differ.

In order to verify this assumption, the results were analysed in terms of a formal kinetic approach. It was shown that all of the reactions proceeding both in an ultrasonic field and without it are diffusion-limited. A further analysis based on the Fisher ratio test demonstrated that, in the absence of ultrasonic activation, solid-state reactions proceed according to the Jander model

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

which describes reactions in spherically shaped particles limited by the diffusion of one of the reactants through the layer of reaction products. On the other hand, the kinetic curves obtained for ultrasonically assisted reactions (1)–(3) can be fitted by the Zhuravlev–Lesokhin–Tempelman (ZLT) model

$$\left(\frac{1}{\sqrt[3]{1-\alpha}} - 1\right)^2 = k_{\mathrm{ZLT}}\tau, \tag{6}$$

which is based on the supposition that the driving force of a reaction decreases as $(1-\alpha)$. The main difference between these two models is as follows: in the Jander model, the reaction zone localizes only on the outer boundaries of reacting aggregates, while in the ZLT model it also penetrates into aggregates and localises on their outer and inner surfaces.

Thus, based on kinetic analysis data, we can conclude that the similar appearance of sonochemical reactions kinetic curves is due to identical mechanisms of solid-state interactions in an ultrasonic field. This is evidenced in a notable growth of reaction rate at the initial stage of interaction, as well as a slight deceleration of reaction at high values of the degree of conversion.

Additional information on the mechanism of the initial and main stages of solid-state sonochemical reactions (1)–(3) was obtained by analysis of $\mathrm{Fe_2O_3}$ (104) and resultant ferrites (220) peaks broadening at various stages of interactions. It was shown that, in control experiments, $\mathrm{Fe_2O_3}$ diffraction peak broadening value (β) does not change during thermal treatment, and in all the cases it is equal to 0.2–0.3 (in °2θ), which corresponds to a CSD size of about 30–45 nm. On the other hand, in an ultrasonic field, an increase in the treatment time up to 2 h results in the growth of $\beta(\mathrm{Fe_2O_3})$ values from 0.2 up to 0.4–0.5, 0.6–0.8 and 0.3 for reaction systems (1), (2) and (3), respectively. The estimation of $\mathrm{Fe_2O_3}$ CSD size using relation (4) gives the following values: ~45; 18–23; 12–15 and 30–35 nm, respectively. We can conclude that the sonication of reaction mixtures (1)–(3) results in a notable decrease in the $\mathrm{Fe_2O_3}$ CSD size.

The plots of $\beta(\mathrm{Fe_2O_3})$ *vs.* α also distinctly reflect the evolution of $\mathrm{Fe_2O_3}$ microstructure. At the beginning of reaction (α = 0–0.4), $\beta(\mathrm{Fe_2O_3})$ values are practically identical (0.2–0.3) for both control and sonicated oxide mixtures. This means that, at the initial stages of interaction, acoustic treatment does not affect significantly the microstructure and reactivity of iron(III) oxide. Therefore, a considerable growth of the reaction rate at the initial stage corresponds to the increase of the quantity of interparticle contacts and the extension of the reaction zone. This supposition was confirmed by additional experiments. Reaction mixture (2) was sonicated at 100–400 °C (these temperatures are too low for this reaction to proceed) for 1 h and then kept at 750 °C for 1 h without acoustic treatment. Further quantitative XRD analysis demonstrated that under these conditions α values for presonicated samples are 0.08–0.15 higher than those for control ones.

Analysis of the CSD size of reaction products ($\mathrm{LiFe_5O_8}$, $\mathrm{ZnFe_2O_4}$ and $\mathrm{NiFe_2O_4}$) as a function of time indicates that without sonication small particles (10–12 nm) of ferrites formed at the initial stage of reaction grow rapidly (within approximately 30 min) to ~20 nm, while the further thermal treatment did not result in a change of the particle size. At the same time, in an ultrasonic field, the CSD size of lithium, zinc and nickel ferrites did not change significantly for about 1 h and then notably increased from 10–12 to ~20 nm.

Thus, based on kinetic, XRD and SEM data, we can propose the following mechanism of the influence of ultrasound treatment on the reactions of spinel ferrite formation. Without sonication, a reaction product forms only on the surface of dense $\mathrm{Fe_2O_3}$ particle aggregates, and their size does not change significantly as the reaction proceeds while ferrite particles grow quickly due to coherent coalescence. On the other hand, a notable decrease of the iron oxide crystallite size, as well as the long-term conservation of the CSD size of resulting ferrites in an ultrasonic field, evidenced that the reaction zone in this case is not smooth due to ultrasound-induced intensification of the diffusive transfer of lithium, zinc and nickel ions through the intergrain boundaries of $\mathrm{Fe_2O_3}$.

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