Kinetics of Microwave Sintering and Solid State Synthesis in the Microwave Field: Similarities and Differences

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We have investigated the kinetics of solid state synthesis and sintering of $NiFe_2O_4$ and $ZnFe_2O_4$ under microwave treatment. The two studied processes show clearly visible similarities in the influence of microwave irradiation on these processes, as well as some significant differences. Further comparative investigations of synthesis and sintering in microwave field may shed some light on the specific nature of the effects of microwave treatment.

Introduction

In the last ten to twenty years, the number of published works dedicated to microwave synthesis of various compounds, including individual and multicomponent oxides, has increased several times. Unfortunately most of these works are of a purely experimental nature – the authors do not discuss selection of reagents and make no remarks on the processes which take place during chemical transformation [1]; the discussion is almost entirely dedicated to differences in microstructure and functional properties of materials synthesized under microwave and conventional heating, while the influence of starting compounds and organization of the reaction zone is passed over. In this contribution, experimental studies of kinetics and mechanisms of chemical transformation during microwave heating are of great interest. Analysis of kinetics of these processes even when using very simple models may allow scientists to make suggestions concerning at least the limiting stages of reaction.

In the present work we have tried to investigate the kinetics of solid state processes under microwave treatment. In order to eliminate possible interfering factors, we have chosen two processes of "pure" solid state binary interaction without oxidation/reduction processes and/or liberation or consumption of gases. The processes we have chosen are interactions between nickel oxide and iron oxide and between zinc oxide and iron oxide with formation of corresponding spinel ferrites (reactions (1) and (2)). Kinetics and mechanisms of both of these processes under conditional heat treatment are very thoroughly studied elsewhere [2].

$$NiO + Fe_2O_3 \rightarrow NiFe_2O_4 \quad (1)$$

$$ZnO + Fe_2O_3 \rightarrow ZnFe_2O_4 \quad (2)$$

We have also tried to compare kinetic data concerning microwave synthesis of these ferrites with that concerning their microwave sintering to find out the similarities and differences of these processes regarding their influence on kinetics. It is worth mentioning that the presented results should on no account be considered as representing the picture in its entirety – they represent only a first attempt to give a qualitative description of these processes in comparison.

Technique

As starting materials, metal nitrates (reagent grade) were used. Individual nitrates were annealed at 850°C in order to obtain corresponding oxides for microwave *synthesis*. Binary mixtures of nitrates were annealed at 850°C in order to obtain corresponding ferrites for microwave *sintering*. Obtained individual oxides were mixed in stoichiometric quantities and ground for 30 min. at 700 RPM in a planetary mill to obtain homogeneous mixtures of starting reagents for microwave synthesis**,** and then were pressed into pellets of 8 mm diameter and 2 mm height using cold isostatic pressing. Ferrite powders for microwave *sintering* were ground for 30 min. at 700 RPM in a planetary mill, and then were also pressed into pellets of 8 mm diameter and 2 mm height using cold isostatic pressing.

Synthesis was carried out at 850 and 900°C during 10-60 min. in a Linn Therm Multilabor 2.4/2.45 (2 kW, 2.45 GHz) microwave oven. Sintering was carried out at 1,200°C during 60-120 min. in the same oven. The heating rate was approximately 50°/min. After thermal treatment, the samples were quenched in air. Comparison samples were prepared using conventional furnaces under similar conditions.

XRD-analysis of obtained samples was carried out using a Rigaku D/MAX 2500 diffractometer. The degree of transformation (α) in solid state reactions (1) and (2) was determined using qualitative XRD-analysis. Reference samples were mechanical mixtures of $(1-x)\{MO + \alpha\text{-}Fe_2O_3\} + (x)\ MFe_2O_4$ (M = Ni or Zn) with different x values, and were prepared from starting reagents. Using reference samples for both reactions, calibration curves were plotted and the degree of transformation (α) for experimental and comparison samples was determined from these curves.

Results

The kinetic curves for $NiFe_2O_4$ shown in Fig. 1 lead to the assertion that microwave treatment dramatically decreases the time required for solid state synthesis. For example, the degree of transformation in reaction (1) after 1 hour at 900°C reaches the value of 0.98, and at 850°C reaches the value of 0.92, whereas for the same time similar values of the degree of transformation in the reactions involving the comparison samples were only 0.31 and 0.22 respectively. But of more interest is the fact that under microwave treatment, the limiting stage of reaction changes. Analysis of the kinetics of reaction (1) allowed us to establish that during conventional heat treatment in all studied temperature regions, the limiting stage of the solid state reaction is diffusion of ions through a layer of the product (ferrite), as kinetic data shows good agreement with the Jander model:

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

where τ is the duration of synthesis and k_J represents the apparent specific rate of reaction described by the Jander model. It is worth mentioning that the obtained results are in good agreement with information about reaction (1), which can be found in the literature [2].

It is well known that the Jander model works for solid state processes, which are limited by diffusion of one of the components through a layer of the product and therefore belong to the group of diffusion-limited models. On the other hand, the most precise description of the kinetic curves for reaction (1) under microwave treatment is given by the shrinking-sphere model with chemical reaction at phase boundaries as a limiting stage:

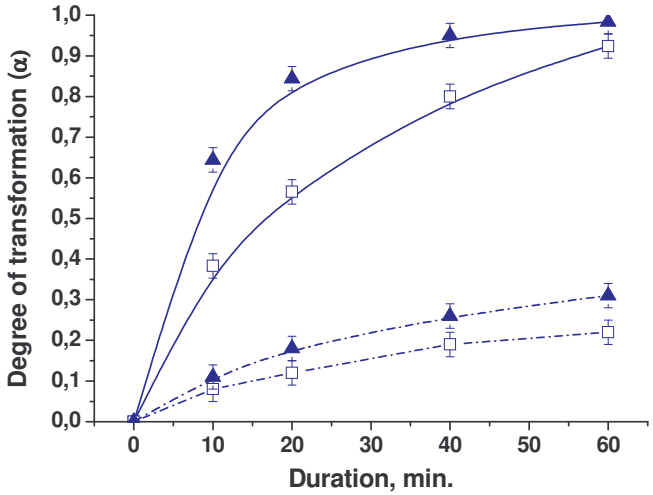

Fig. 1. Kinetic curves for synthesis of $NiFe_2O_4$ under microwave (solid lines) and conventional (dashed lines) heating treatment at 850 (open squares) and 900°C (black triangles).

$$1-\sqrt[3]{1-\alpha}=k_{SS}\cdot\tau \tag{4}$$

A distinctive feature of this type of solid state interaction is that formation of the product nuclei occurs simultaneously in the whole reaction volume, and after a very short time each particle of the reagent is covered with layer of the product. Therefore, the velocity of the reaction is proportional to the surface area of the reagent, which is not transformed yet. Given that all diffusional hindrances are eliminated and Fe_2O_3 particles are more or less isotropic, these results are in good agreement with the current opinion concerning the mechanism of this reaction [2], as it is supposed that during synthesis of $NiFe_2O_4$, a product layer is formed only on Fe_2O_3 particles.

Now if we turn to the kinetic data for reaction of $ZnFe_2O_4$ formation (Fig. 2), we see slightly different picture. As in the case of $NiFe_2O_4$ formation, application of microwave power allows us to speed up the reaction. And again, as in the case of $NiFe_2O_4$ formation, the limiting stage of reaction changes from the diffusion-limited Jander process to the shrinking-sphere process limited by chemical reaction at phase boundaries. But it can be clearly seen that the effect of microwave treatment is far less significant.

There are at least two explanations for the observed effect. First, the mechanisms of formation of zinc and nickel ferrites are significantly different. In both cases formation of the product occurs only at the surface of Fe_2O_3 grains, but synthesis of $NiFe_2O_4$ is hampered by the preliminary formation of a $Ni_{1-x}Fe_xO$ solid solution on the surface of NiO grains. On the other hand, due to the fact that iron oxide is almost insoluble in ZnO during formation of $ZnFe_2O_4$ only diffusion of zinc ions takes place. It is also well-known that the reaction between zinc and iron oxides starts at rather low temperatures (formation of ferrite takes place even at 500-600°C). Therefore the second possible reason for decrease in difference between microwave and conventional heating during zinc ferrite formation may be the fact that velocity of formation of zinc ferrite at these temperatures is already rather high and additional promotion from the microwave field is less evident.

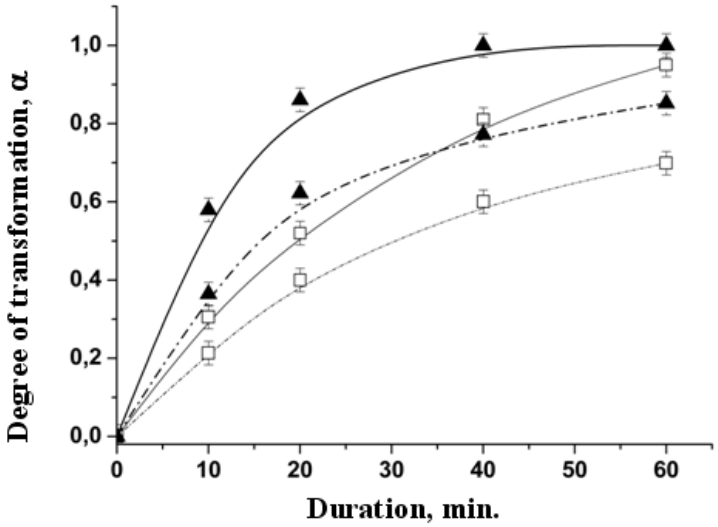

Fig. 2. Kinetic curves for synthesis of $ZnFe_2O_4$ under microwave (solid lines) and conventional (dashed lines) heating treatment at 850 (open squares) and 900°C (black triangles).

Therefore the second possible reason for decrease in difference between microwave and conventional heating during zinc ferrite formation may be the fact that velocity of formation of zinc ferrite at these temperatures is already rather high and additional promotion from the microwave field is less evident.

On this stage we can establish that microwave treatment significantly affects the velocity of diffusion-controlled reactions; and further that the more a reaction is inhibited by diffusion of ions, the stronger the effects of microwave treatment will be.

The second stage of the presented work consists of the study of sintering of $NiFe_2O_4$ and $ZnFe_2O_4$ powders. Densification curves for samples treated by microwave and conventional heating are presented in Fig. 3. It can be clearly seen that microwave treatment allows us to speed up sintering of both ferrites but, unlike in the case of synthesis of these ferrites, there is no noticeable difference between $NiFe_2O_4$ and $ZnFe_2O_4$. As it was already shown in very thorough work [3] on zinc oxide powder sintering, microwave irradiation has the most significant impact on the intermediate stage of sintering, which mostly corresponds with grains gliding and elimination of open porosity. Deeper theoretical and experimental investigation of this effect has still not been carried out, and at the present time, taking into account [4], we can only suggest that this effect may be somehow related to intensification of grain boundary diffusion by microwave irradiation.

If we now try to compare the densification and kinetic curves for both ferrites, we find that the processes of synthesis and sintering are in a way similar: in both cases, microwave irradiation allows us to increase the velocity of the intermediate stage. As a result, dependences for processes under microwave irradiation quickly achieve near maximum value, while on the other hand, dependences for conventional heating show almost linear behavior.

There is also a significant difference between synthesis and sintering, in that the final state of samples after microwave and conventional sintering is almost the same while, final degrees of conversion during synthesis of $NiFe_2O_4$ under microwave and conventional heat treatment are very different. It is very unlikely that increasing the duration of synthesis will

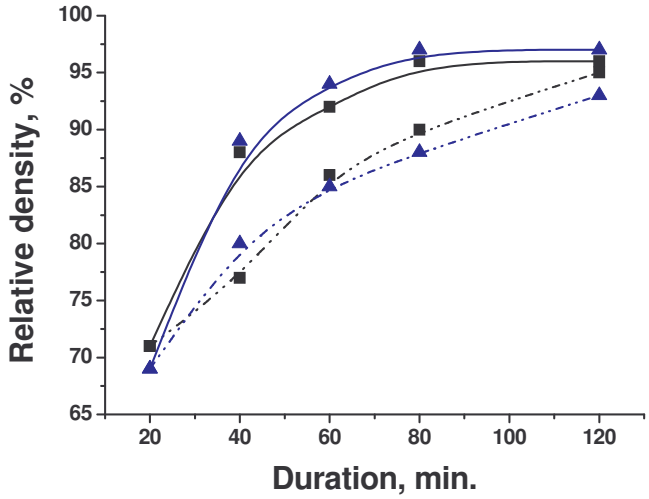

Fig. 3. Densification curves for sintering of $NiFe_2O_4$ (blue triangles) and $ZnFe_2O_4$ (black squares) under microwave (solid lines) and conventional (dashed lines) heating treatment at 1200°C.

change the situation significantly as curves corresponding to conventional synthesis are nearly constant. At the present time we do not have sufficient experimental data to draw any conclusions from these visible similarities and differences between microwave synthesis and sintering processes, but it is reasonable to suggest that such comparative studies may be very helpful for determining the nature of specific effects of microwave irradiation on various solid state processes.

Conclusion

The studied processes of solid state synthesis and sintering of nickel and zinc spinel ferrites under microwave and conventional heat treatment show clearly visible similarities in the influence of microwave irradiation on these processes, as well as some significant differences. Further comparative investigations of synthesis and sintering in microwave field may shed light on the specific nature of the effects of microwave treatment.

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