Investigation of the Reactivity of Mechanically Activated Metal Oxides in the Radiation-Thermal Synthesis of Ni-Zn Ferrite*

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Abstract

Radiation-thermal synthesis of ferrite $Ni_{0.75}Zn_{0.25}Fe_2O_4$ was investigated. Comparative analysis of the reactivity of mechanically activated mixtures obtained from commercial oxides and from metal nanooxides was carried out. It was shown that the formation of mechanocomposite was necessary for the efficient reaction.

Key words: radiation-thermal synthesis, ferrites, mechanocomposite

INTRODUCTION

Ferrite ceramics of the nano- and submicron size is usually obtained using methods of coprecipitation and mechanochemical activation of the mixtures of oxides followed by annealing [1]. However, these methods are not always applicable in practice for several reasons: differences in salt solubilities, contamination by admixtures of precipitating agents, low reactivity during mechanochemical synthesis *etc*. In addition, the synthesis of ferrites proceeds intensively at a temperature above the sintering point, sintering unformed particles becomes possible.

A known method to decrease temperature and increase the rate of solid-phase reactions is thorough mixing of reagents, their intense

grinding and an increase in the deficiency of the solid body during the mechanical activation [2]. However, for the classical ceramic synthesis of ferrites, the deficiency generated through the mechanical activation is likely to be unimportant because defect annealing occurs before the start of reaction.

The use of intense electron beams provides new conditions for solid-phase reactions. In spite of annealing of radiation defects at high temperatures, mass transfer in solids accelerates [3, 4]. Passing through the substance, high-energy electrons cause ionization and generate a cascade of secondary electrons with the energy about several ten electron-volts [5]. The latter actively interact with the substance and thus form the non-equilibrium state [6]. Under the excitation of the electron subsystem and subsequent decomposition of nonequilibrium states, defects are formed mainly due to the forma-

tion of vacancy−interstice pairs [7, 8]. It was established that associates of point defects, namely stable double vacancies and unstable short-lived pairs, accelerate substantially the mass transfer in ionic crystals [9−11].

It is known that reactions between two solids are possible only in case of the efficient contact, though its value is very small [12]. One of the methods to increase the efficient area of contact between reagents is their preliminary joint mechanical activation, at which during joint grinding and secondary aggregation, mechanocomposites with a good contact between reagents are formed [13].

Works on the radiation-thermal synthesis (RTS) of nickel-zinc ferrites using pressed tablets were carried out previously. The accelerating effect of ionizing radiation on diffusion rate in the systems Fe_2O_3−ZnO, Fe_2O_3−NiO and $NiFe_2O_4$−$ZnFe_2O_4$ was demonstrated [14, 15]. It is also known that preliminary joint mechanical activation promotes an increase in the rate of radiation thermal synthesis in the system Li_2CO_3−ZnO−Fe_2O_3 [16−19] and homogeneity of resulting ferrite [19].

It is possible to carry out RTS of ferrites with a noticeable rate at a temperature below the point of thermal sintering of oxide powders, it is reasonable to study the properties of composites obtained by the joint mechanical activation of the mixtures of commercial oxides and nanoparticles of oxides as initial reagents.

EXPERIMENTAL

Oxides Fe_2O_3, NiO, ZnO of kh. ch. reagent grade were used after the preliminary thermal treatment at 300 °C for 2 h. Metal nano-oxides obtained by means of evaporation in the set-up based on ELV-6 accelerator (the Institute of Nuclear Physics of the SB RAS, Novosibirsk) were also used [20, 21]. To obtain Fe_2O_3 nanoparticles, the metal was evaporated and then oxidized by oxygen. NiO and ZnO nanoparticles were obtained by means of evaporation of commercial metal oxides.

Reaction mixtures for RTS were prepared by means of the joint mechanical activation. A mixture composed of 6.6 g Fe_2O_3, 2.25 g NiO

and 0.8 g ZnO was placed in a metal reactor 60 mL in volume, then milling bodies were added (steel balls 0.3 cm in diameter with the total mass of 50 g). The mechanical activation was carried out with the help of a Spex-8000 vibratory mill (CertiPrep, the USA) in cycles, 10 min each, to prevent heating of the reaction mixture. The mechanical activation lasted for 20, 40 and 60 min.

The particle size was determined with the help of two methods: 1) optical method using a Microsizer-201A instrument (Russia), with a suspension in water prepared by ultrasonic mixture dispersing; 2) laser ablation at the station of chemical, physical and biological investigations involving the radiation of the free electron laser at the Siberian Centre for Synchrotron and Terahertz Radiation (SCSTR), INP of the SB RAS [22, 23].

Radiation thermal synthesis of the samples was carried out using ILU-6 accelerator (INP SB RAS): electron energy 2.5 MeV, current density up to 1 $\mu A/cm^2$ without reaction mixture compacting. The mass of weighted portion was calculated so that the surface density did not exceed 0.69 g/cm^2. (This value provides maximally uniform energy absorption by the sample). The RTS was carried out as follows. The samples of reaction mixture were placed in a corundum crucible which was put into the reactor. Mixture temperature was controlled with the help of a thermocouple (Pt−Pt-Rd) directly immersed into the sample (maximal possible measurable temperature during short-term heating was 1200−1300 °C). The rate of heating and thermal stabilization of the reaction mixtures was adjusted with the help of the program controlling the parameters of accelerator operation; temperature and connection with the PC were recorded with the help of FP-TC-120 unit (National Instruments, the USA).

Synthesis was carried out under the following conditions:

1. Heating of the reaction mixture to the given temperature during 20 min, subsequent thermostating for 20 min. After cessation of the electron beam treatment, the mixture was cooled in the natural way; at the initial stage, the cooling rate was 150−200 °C/min.

2. Heating of the reaction mixture at the rate of 20 °C/min to 1200 °C, subsequent cooling under the action of the electron beam at the rate of 20 °C/min to 300–400 °C.

The transformation degree a in reaction mixtures was determined from the ratio of integral intensities of the reflections of ferrite ceramic phase and iron oxide, as the least reactive component. Diffraction studies were carried out at the channel No. 4 of the VEPP-3 storage ring (SCSTR, INP of the SB RAS) [24].

Microscopic studies were carried out using the scanning electron microscopy (S-3400N with the attached detector of backscattered electron diffraction HKL Channel-5, HITACHI) and transmission electron microscopy (JEM-2000 FX II, Jeol).

RESULTS AND DISCUSSION

Mechanical activation of commercial metal oxides leads to the formation of the composite that is not destroyed during ultrasonic treatment. According to light scattering data, the size of agglomerates does not exceed 50 µm. The size

distribution curve has three maxima at 1, 2.5 and 10 µm. With an increase in the time of mechanical activation, particles become larger, which is the evidence of secondary aggregation.

Analysis of the size of separate particles of mechanocomposites was carried out using the terahertz radiation, which allows ablation without destruction, additional grinding and activation of chemical processes. It was established that the maximum of particle size distribution in the samples after treatment for 20, 40 and 60 min falls within the range 30–100 nm (Fig. 1).

After mechanical activation for 40 min, the most uniform mixture was obtained. A sample of the mixture treated for 60 min contains particles smaller than 30 nm, while the particles prevailing in the sample after mechanical activation for 20 min have the size more than 100 nm. Recalculation of particle size distribution for their mass fraction shows that 20 min of mechanical activation is insufficient for efficient sample grinding. For this reason, experiments on RTS of ferrite involving reaction mixtures obtained by the joint mechanical activation of commercial metal oxides for 20 min were not carried out.

Mixtures obtained after the treatment of initial reagents for 40 and 60 min demonstrate a different reactivity during RTS. The data on transformation degree in the coordinates $\ln (\alpha/(1 - \alpha)) - 1000/T$

are presented in Fig. 2. One can see that this dependence is linear for the mixtures of com-
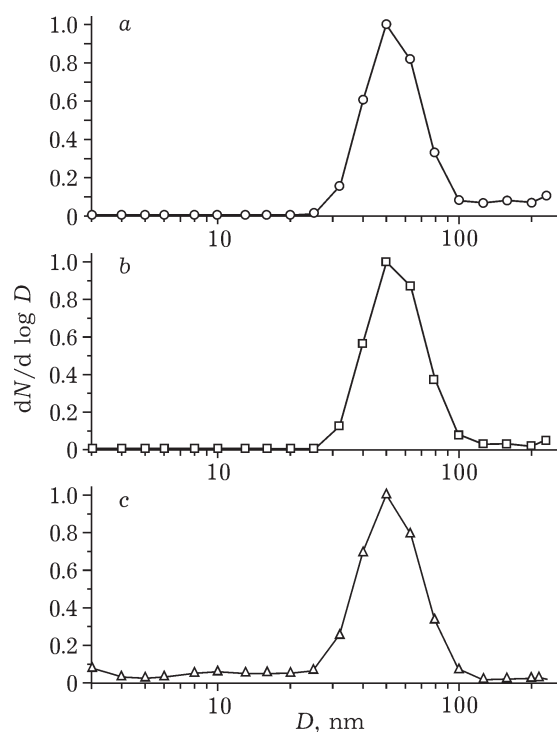

Fig. 1. Size of particles in reaction mixtures obtained by joint mechanical activation of commercial oxides, determined by means of laser ablation. Treatment time, min: 20 (a), 40 (b), 60 (c).
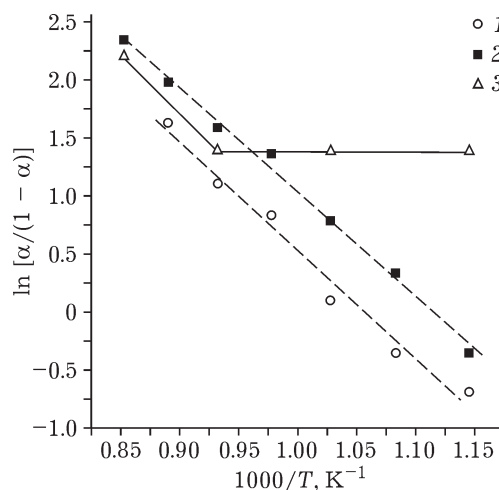

Fig. 2. Temperature dependences of the transformations of reaction mixtures after mechanical activation of commercial oxides (1, 2) and metal nanooxides (3). Activation time (min): 40 (1), 60 (2), 20 (3).
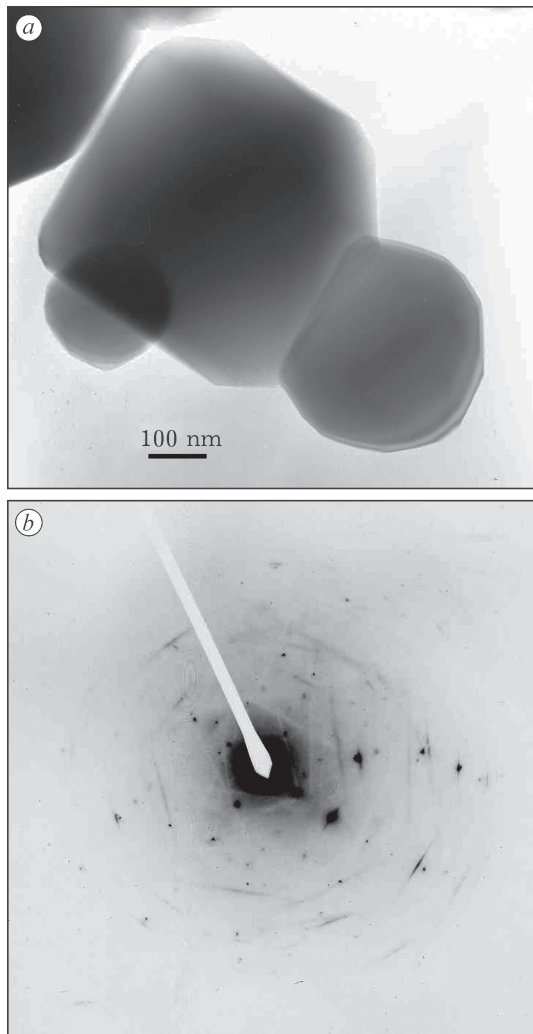
Fig. 3. Electron micrograph of the particles of ferrite $Ni_{0.75}Zn_{0.25}Fe_2O_4$ (*a*) and electron diffraction (*b*) after the synthesis in the slow cooling mode to 1200 °C.

mercial oxides after joint mechanical activation for 40 and 60 min (experimental points *1*, *2* and dash straight lines obtained by approximation of these data). The values of activation energy of the process are close to each other and equal to 8 kJ/(mol · K). The additional acceleration of the process is not observed after the achievement of 800 °C, when the most intense shrinkage of the samples occurs due to the start of sintering of reaction mixtures.

We carried out a comparative experiment with the use of nanoparticles of oxides obtained by means of evaporation as the initial components for the formation of the composite were. The size of initial metal nano-oxide particles is smaller than the size of particles in

reaction mixtures after mechanical activation (see Fig. 1), so the formation of composites becomes possible with a decrease in the time of the joint mechanical treatment (20 min). It was discovered that ferrite synthesis proceeds intensively during mechanochemical activation (transformation degree ~50 %), even at a temperature of 600 °C the transformation degree reached 80 % and remained almost unchanged till the RTS temperature of 800 °C (see Fig. 2, experimental points *3* and a continuous line). With an increase in temperature to 900 °C, transformation degree is close to that for the mixture obtained by longterm joint mechanochemical activation of commercial oxides (60 min). So, short-time mechanochemical activation, even with the use of oxide nanoparticles as initial reagents, does not provide the formation of mechanocomposite with efficient contact between particles.

The size of agglomerates with developed zone of contact between the particles may be assessed on the basis of the size of ferrite particles synthesized from the mixtures that were obtained by long-term joint mechanical treatment. During RTS in the mode of slow heating to 1200 °C, crystallites 100−500 nm in size with clear faceting and the structure close to perfect are formed (Fig. 3). The unit cell parameter is $a = 8.3666$ Å, microdeformation value $e = 0.01$ %. RTS at temperatures substantially higher than the temperature of oxide sintering does not lead to active accretion of crystallites in the samples with high transformation degree.

CONCLUSION

Thus, the possibility to obtain submicron ferrite crystals through RTS using reaction mixtures prepared by long-term joint mechanical treatment was demonstrated. The role of the mechanical activation is an additional decrease of the synthesis temperature and the formation of the composite with the developed zone of contact between reagents. The use of oxide nanoparticles as initial reagents for the purpose of decreasing the time of treatment for RTS of ferrites does not give a positive result: mechanocomposites with a developed zone of the contact between reagents are not formed.

REFERENCES

1 Levin B. E., Tret′yakov Yu. D., Letyuk L. M., Fiziko-Khimicheskiye Osnovy Polucheniya, Svoystva i Primeneniye Ferritov, Khimiya, Leningrad, 1987.

2 Avvakumov E. G., Mekhanicheskiye Metody Aktivatsii Khimicheskikh Protsessov, Novosibirsk, 1986.

3 Lyakhov N. Z., Boldyrev V. V., Voronin A. P., Gribkov O. S., Bochkarev I. G., Rusakov S. V., Auslender V. L., *J. Therm. Anal.*, 43, 1 (1995) 21.

4 Boldyrev V. V., Voronin A. P., Gribkov O. S., Tkachenko E. V., Karagedov G. R., Yakobson B. I., Auslender V. L., *Solid State Ionics,* 36, 1 (1989) 1.

5 Pikaev A. K., Sovremennaya Radiatsionnaya Khimiya. Osnovnye Polozheniya. Eksperimentalnaya Tekhnika i Metody, Nauka, Moscow, 1985.

6 Stepanov V. A., *Zh. Tekhn. Fiz.*, 68, 8 (1998) 67.

7 Lushchik Ch. B., Lushchik A. Ch., Raspad Elektronnykh Vozbuzhdeniy s Obrazovaniyem Defektov v Tverdykh Telakh, Nauka, Moscow, 1989.

8 Klinger M. I., Lushchik Ch. B., Mashovets T. V., Kholodar' G. A., Sheinkman M. K., Elango M. A., *Usp. Fiz. Nauk,* 147, 11 (1985) 523.

9 Annenkov Yu. M., *Izv. TPU*, 309, 3 (2006) 46.

10 Indenbom V. L., *Pis'ma v ZhTF,* 5, 8 (1979) 489.

11 Dienes G. I., Damask A., *J. Appl. Phys.,* 29, 12 (1958) 1713.

12 Boldyrev V. V. (Ed.), Reactivity of Solids: Past, Present and Future, Blackwell Sci. Ltd., Oxford, 1996.

13 Boldyrev V. V. and Boldyreva E. V. (Eds.), Reactivity of Molecular Solids, John Wiley & Sons, New York, 1999.

14 Bochkarev I. G., Voronin A. P., Boldyrev V. V., *Dokl. AN SSSR*, 303, 1 (1988) 122.

15 Auslender V. L., Bochkarev I. G., Lyakhov N. Z., Voronin A. P., Boldyrev V. V., *J. Solid State Ionics*, 101−103, 2 (1997) 489.

16 Surzhikov A. P., Vasendina E. A., Lysenko E. N., Vlasov V. A., *Izv. Vuzov. Fizika,* 56, 1−2 (2013) 155.

17 Surzhikov A. P., Pritulov A. M., Lysenko E. N., Sokolovskii A. N., Vlasov V. A., Vasendina E. A., *J. Therm. Anal. Calorim.*, 109, 1 (2012) 63.

18 Surzhikov A. P., Pritulov A. M., Shabardina N. V., Shabardin R. S., Usmanov R. U., *Izv. Vuzov. Fizika,* 48, 2 (2005) 184.

19 Surzhikov A. P., Lysenko E. N., Vlasov V. A., Malyshev A. V., Nikolaev E. V., *Izv. Vuzov. Fizika,* 56, 6 (2013) 681.

20 RU Pat. No. 2426625, 2011.

21 Fadeev S. N., Golkovski M. G., Korchagin A. I. Kuksanov N. K., Lavrukhin A. V., Petrov S. E., Salimov R. A., Vaisman A. F., *Rad. Phys. Chem.,* 57, 3−6 (2000) 653.

22 Petrov A. K., Kozlov A. S., Taraban M. B., Goryachkovskaya T. N., Malyshkin S. B., Popik V. M., Peltek S. E., *Dokl. AN,* 404, 5 (2005) 698.

23 Petrov A. K., Kozlov A. S., Malyshkin S. B., Taraban M. B., Popik V. M., Scheglov M. A., Goryachkovskaya T. N., Peltek S. E., *Nucl. Inst. Phys. Res. Sect. A.*, 575, 1 (2007) 68.

24 URL: http://ssrc.inp.nsk.su/CKP/stations/passport/4/.