Phase and Structural Transformation in Powders of Lithium Ferrites under Their Heating by an Accelerated Electron Beam

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Abstract – The present paper considers re-search results of kinetic and temperature mechanisms of changes in phase, structural and magnetic characteristics of powders of lithium ferrites under thermal (T) and radiation-thermal (RT) methods of sintering. stresses. On the basis of the presented results it can be concluded that air sintering of lithium-titanium ferrites within the temperature range 970…1270 *K* with the further hardening involves material reconstruction and dissolution of the side phase impurities, contained in the initial powder. Under the conditions of radiation-thermal heating-up rates of phase impurities' dissolution and gas exchange processes with external atmosphere are increasing. This process results in oxygen escape from the ferrite, formation of ions Fe^{2+}, reducing of the average spin of magnetoactive cations and corresponding decease in the magnetic anisotropy effective constant.

According to previously conducted research it was found out that initial heating of compacted powders of lithium-titanium ferrospinel by intense beams of high-energy electrons increases density of ceramic specimens and speeds up formation of hysteresis loop parameters in comparison with thermal sintering conducted under identical temperature-time conditions [1]. However, it remains to be clarified whether high-power radiation impacts influence fundamental characteristics of magnetic materials.

The present paper considers research results of kinetic and temperature mechanisms of changes in phase, structural and magnetic characteristics of powders of lithium ferrites under thermal (T) and radiation-thermal (RT) methods of sintering. RT-sintering was carried out by means of pressing radiation by pulsed electron beam with the energy of 2 MeV with the use of accelerator *ILU-6* (Institute of Nuclear Physics of the Siberian Branch of the Russian Academy of Sciences, Novosibirsk). A beam current in the pulse was 0.4 A, hit duration – 500 μs, pulse frequency – (5–50) Hz. The radiation took place in a light chamotte cell. Heating of specimens under T and RT sintering was carried out at the rate of 130 grad/min, cooling down – at the rate of 150 grad/min. The applied cooling rates provided for keeping of a structural state of specimens, formed during isothermal sintering.

A phase makeup and parameters of a crystal lattice of tested specimens were defined by means of automated X-ray diffractometer *DRON-4-07* on Fe k_α-radiation. A shooting geometry with the Bregg-Brentano focusing with pyrolitic graphite monochromator on a primary beam was used. Received X-rayograms was processed by means of full-profile analysis with the software support *Powder Cell* 2.4.

Measuring of saturation magnetization M_S and effective field of magnetic anisotropy H_A were carried out in high-power pulsed magnetic fields with the use of magnetometer H – 04 of original construction design. An anisotropy field was determined by means of tracing of a singularity point location on the field magnetization dependency. Use of a high-rate ADC (conversion frequency in a single channel is up to 200 kHz) makes possible to estimate a singularity location accurate within 400 A/m. Error of magnetization determination is not over 1%. By magnitudes M_S and H_A an effective constant magnetic anisotropy K_{EF} was determined by a formula (1):

$$K_{EF} = 0.5 \cdot M_S \cdot H_A \qquad (1)$$

X-ray-phase analysis of initial powders has shown that an observed combination of reflexes corresponds to superposition of reflections from a spinel phase and from impurities of gamma-modifications of ferric oxide γ -Fe_2O_3. Calculation of a diffractogram has shown that a magemite phase abundance in the stock is ~ 27%. Initial heating of pressed powders up to 1070 K and above involves an overall elimination of reflections from γ-Fe_2O_3 at a non-isothermal phase irrespective of a heating method and a ferrite crystal structure is a single-phase cubic spinel (S.G. Fd3m). In addition, a parameter of the spinel crystal lattice is increasing while elastic micro-deformations in ceramics grains are decreasing (Table).

Table. Structural parameters of isochronous sintered ferrites (τ=60min)

T_{sint}, K	a, Å		$\Delta d/d \cdot 10^3$	
	T	RT	T	RT
Stock	8.355		1.7	
970	8.360	8.361	8.360	8.361
1070	8.364	8.365	8.364	8.365
1270	8.370	8.372	8.370	8.372

It was succeeded to trace a change kinetics of magemite phase content only under the temperature of isothermal sintering of 970 K. The data presented in Fig. 1 indicate that an electron beam impact intensifies magemite phase dissolution. This process within radiation-thermal sintering is accompanied by a high-rate growth of parameters of the spinel phase crystal lattice (Fig. 2) and by a more intense decrease of elastic micro-deformations in ferrite powders (Fig. 3).

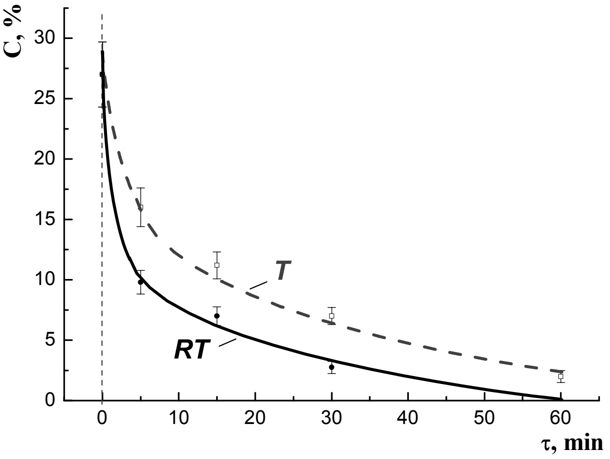

Fig. 1. Kinetics of magemite phase dissolution in ferrospinel under T_{sint}=970 K

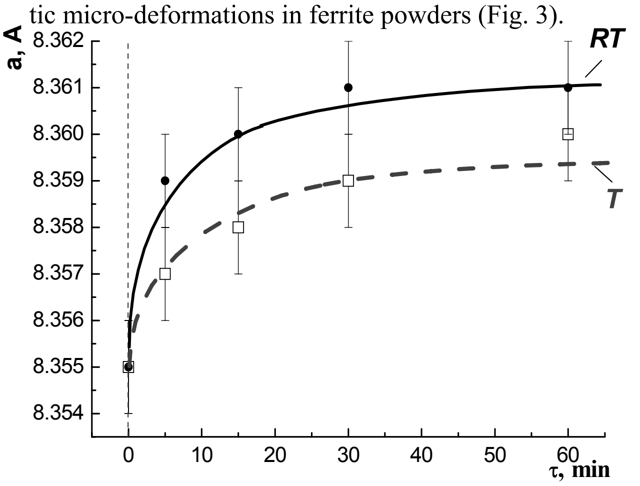

Fig. 2. Kinetic dependencies of change in crystal lattice parameter of the spinel phase under T_{sint}=970 *K*

Though the presented kinetic dependencies within the sintering period of ~60 min verge towards saturation and a process of magemite phase dissolution is almost finished, a sintering temperature rise involves further increase of the spinel lattice parameter and a more deep reducing of the grade of elastic micro-deformations (Table). Consequently, magemite dissolution in the spinel is not a single cause of change in ferrite structural characteristics. In our opinion, the above mentioned changes in structural parameters might be explained by rise of cation concentrations with large ionic radius under the sintering temperature. Cooling rates, close to a quenching load, used in this research are most likely to ensure keeping of the amount of cooled-down cations practically unchanged. It might also be assumed that formation of cations with large radii within the isothermal sintering is stipulated by change in charge state of cations of variable valency – iron ions. Since the radius of ions Fe^{3+} is 0.67 Å, and of the ions Fe^{2+} is 0.83 Å, a partial replacement of relatively small ions Fe^{3+} by large ions Fe^{2+} causes an observable rise of the lattice parameters. Thus, sintering of lithium-titanium ferrites within the temperature interval 970…1270 *K* under atmospheric pressure (Po_2 =0.21 *atm*) is accompanied by material reconstruction.

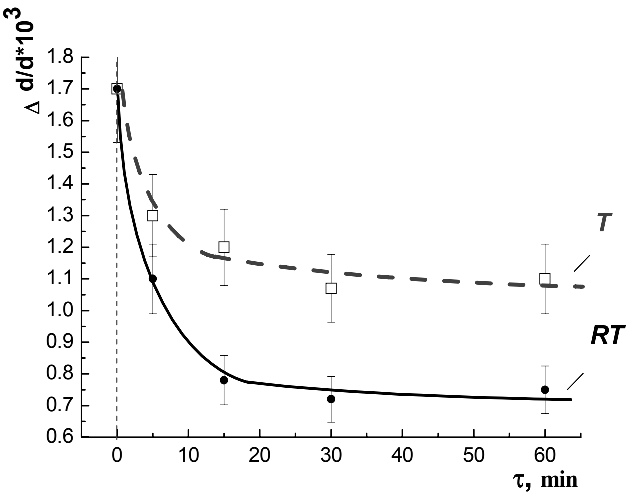

Fig.3. Kinetic dependencies of the magnitude of elastic stresses **Δd/d** of the spinel phase under T_{sint}=970 *K*

shown that the magemite phase dissolution is accompanied by reducing of the saturation magnetization and increasing in magnetic anisotropy effective field. The magnitudes of an effective constant of magnetic anisotropy after isochronous sintering (τ=60 min) within the temperature range 970…1270 *K*, calculated according to these data, are given in Fig. 4. It can be seen that changes in the value K_{EF} first of all, correlate with changes in the spinel phase lattice parameter. Secondly, *RT* sintering creates conditions under which activity of the processes, causing reduction of K_{EF} is significantly increasing. It is also possible to explain such behavior of K_{EF} n the framework of a hypothesis of restoring character of the processes taking place under high-temperature sintering of ferrites. It is known that in contrast to the majority of ferrites with a negative constant of magnetostriction λ_s, a magnetite has got a positive constant λ_s. Considering ferrospinel containing ions Fe^{2+} as a solid solution of magnetite in the spinel, it is easy to demonstrate that in the framework of a single-ion model reduction of a resultant magnetostriction constant will correspond to accumulation of ions Fe^{2+}. However, this will involve reducing of a magnetoelastic component of the magnetic anisotropy effective constant K_{EF}, that can be presented in the form (2):

$$K_{EF} = K_1+\lambda_s\cdot\sigma \qquad (2),$$

where K_1 – crystallographic magnetic anisotropy; λ_s – magnetostriction constant; σ – value of elastic stresses.

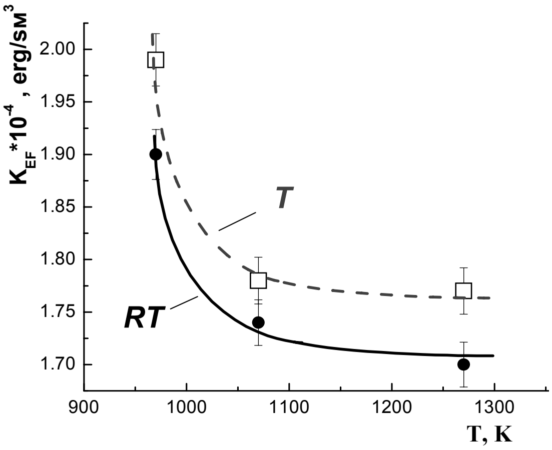

Fig. 4. Dependencies K_{EF} on the temperature of isothermal sintering

On the basis of the presented results it can be concluded that air sintering of lithium-titanium ferrites within the temperature range 970…1270 *K* with the further hardening involves material reconstruction and dissolution of the side phase impurities, contained in the initial powder. Under the conditions of radiation-thermal heating-up rates of phase impurities' dissolution and gas exchange processes with external atmosphere are increasing. This process results in oxygen escape from the ferrite, formation of ions Fe^{2+}, reducing of the average spin of magnetoactive cations and corresponding decease in the magnetic anisotropy effective constant.

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References

[1] A.P. Surzhikov, A.M. Pritulov, *Radiation-thermal sintering of Ferrite Ceramics*, Moscow, Energoatomizdat, 1998, p. 217.