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Investigation of oxidation processes in non-stoichiometric lithium–titanium ferrites using TG analysis

A. P. Surzhikov · T. S. Frangulyan · S. A. Ghyngazov · E. N. Lysenko

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Abstract Using non-isothermal thermogravimetry (TG), the oxidation kinetics of oxygen-deficient lithium–titanium ferrospinel, $Li_{0.649}Fe_{1.598}Ti_{0.5}Zn_{0.2}Mn_{0.051}O_{4-\delta}$, manufactured by ceramic engineering is investigated. The oxidation annealing of powder samples is performed in air. According to the X-ray phase analysis, the processes giving rise to variations in oxygen content occur within single-phase spinel structure. The experimental kinetic results are processed using the Netzsch Thermokinetics software. The oxidation rate constants and the effective coefficients of atmospheric oxygen diffusion into the ferrites are determined. The effective activation energy E of oxygen diffusion is found to be 1.95 eV. It is demonstrated that an increase in the oxygen non-stoichiometry parameter δ as a result of recovery annealing of ferrite powders in vacuum at $T = 1{,}070$ K for 2 h gives rise to a slight decrease in E down to 1.89 eV. The activation energy of oxygen grain-boundary diffusion is identified by the electroconduction method. The resulting value 1.93 eV is fairly consistent with that obtained by TG.

Keywords Kinetics · Oxidation of lithium–titanium ferrites · TG · Oxygen diffusion

Introduction

Materials based on lithium ferrospinels involve a wide range of compositions and structural modifications, which predetermines their varied functional properties and quite extensive application areas [1–4]. Most promising for the microwave electronics are those lithium–titanium ferrites that are prepared by the methods of ceramic engineering [1, 2]. The latter techniques are characterized by a considerable influence of the gaseous medium at high temperatures on the defect formation in the oxygen sublattice of ferromagnetic materials [1–5].

When interacting with the surrounding medium, ferrite, depending on such external thermodynamic parameters as temperature (T) and partial oxygen pressure in a gas medium (P), can either absorb oxygen (oxidative reaction) or lose it (reducing reaction). This results in a spontaneous violation of the oxygen stoichiometry of the compound. In many cases, this material might acquire optimal physicochemical properties at quite definite oxygen content. In order to manufacture ferrites with the required characteristics, it is therefore very critical to perform a comprehensive investigation of the diffusion exchange between the complex oxide and the gas medium and to obtain data on the kinetic and diffusion characteristics of this process. An analysis of the literature data has shown that for lithium ferrospinels these data were absolutely lacking until the studies reported in [6, 7]. The latter publications present diffusion characteristics of oxygen measured using the electroconduction method.

Problems of that kind are most efficiently solved using the method of thermogravimetric analysis. The potential of this method has considerably increased due to the advent of advanced supersensitive equipment. Examples of successful application of this approach to the study of

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A. P. Surzhikov · T. S. Frangulyan · S. A. Ghyngazov (✉) · E. N. Lysenko
Tomsk Polytechnic University, pr. Lenina, 30, Tomsk, Russia 634050
e-mail: ghyngazov@tpu.ru

the oxidation kinetics of some types of materials are given in [8–11].

The purpose of this study is to apply thermogravimetric analysis to finding the kinetic parameters of oxidative processes in polycrystalline lithium–titanium ferrites with different degrees of oxygen non-stoichiometry.

The Curie temperature of investigated material is equal 540 K. It is well known that diffusion rate in oxide ceramics under such low temperatures is extremely small. TG researches have shown that the powder ferrite mass remained practically a constant at heating from 300 up to 700 K. Therefore, it is impossible to analyze the influence of magnetic phase transition (ferrimagnetic to paramagnetic) on researched diffusion process. In this connection this study is devoted to investigation of diffusion absorption of oxygen in ferrite in temperature range when the ferrite is in a paramagnetic phase.

Experimental procedures

The material under study was lithium–titanium ceramics, $Li_{0.649}Fe_{1.598}Ti_{0.5}Zn_{0.2}Mn_{0.051}O_{4-\delta}$. Ferrite powders were synthesized under industrial conditions. Their chemical composition is given by the manufacturer. Our independent check by methods of the X-ray fluorescent analysis (device INNOV-X X-50, the USA) and secondary ion-mass spectrometry (device PHI-6300, the USA) has confirmed results of the manufacturer.

Pellets measuring 18 mm in diameter and 3 mm in thickness were prepared by single-action cold compaction of synthesized ferrite powders, followed by roast-sintering in air (partial oxygen pressure $P = 0.21$ atm.) at $T = 1{,}370$ K for 2 h. The heating and cooling rate was 10 K/min. Upon sintering, thin near-surface layers, possessing a higher oxidative degree with respect to the bulk, were mechanically ground off both sides of the pellet. The thickness of the layer to be removed with non-uniform oxygen distribution over the depth was determined from the layer-by-layer measurement of electric conductivity of the ceramic samples. It was found to be about 500 μm. The remaining internal volume of the ceramic pellet was ground in an agate mortar to yield powder. The freshly prepared powder was then screened through a series of sieves to separate a fraction with an average grain size of 20 μm. The volume of the resulting fraction was divided into two halves. The first half was left as-sieved (Type A) without any thermal treatment, while the powder in the second half was subjected to recovery annealing in vacuum (residual gas pressure $P = 3 \times 10^{-4}$ mm mercury column) at $T = 1{,}070$ K for 2 h. This treatment yielded ferrite powder (Type B) with high oxygen deficit as compared to Type A powder.

The X-ray diffraction analysis was performed in an ARL X'TRA diffractometer (Thermo Electron ARL Products, USA-Switzerland) using CuK_{α} emission. Changes in mass of the samples due to their interaction with the gas medium were registered directly in the course of thermal treatment using an STA 449 C Jupiter Analyzer (Netzsch-Geratebau GmbH, Germany) with the sensitivity of balance 0.1 μg.

Oxidation kinetics under isothermal conditions presents certain difficulties associated with inevitable influence of the heating stage on the results obtained. In order to study the oxidation kinetics of Type A and B powders we, therefore, used a combination of non-isothermal and isothermal TG. Note that the non-isothermal heating was performed in a linear mode with the rates 0.5, 1.0, 3.0, and 8.0 K/min.

For the TG measurements, the lithium–titanium powder was put into an Al_2O_3 crucible shaped as a cup. To ensure accurate baseline measurements, the crucible was loaded with inert powdered Al_2O_3, whose mass was equal to that of the powder under study.

Experimental results and discussion

According to the X-ray diffraction data, the powdered lithium–titanium samples of Types A and B consisted of single-phase spinel. In the initial state their lattice parameters were $a = 8.368$ Å and $a = 8.370$ Å, respectively. This implies that vacuum annealing of the powder is followed by an increase in the lattice parameter. According to the data reported in [12], lattice parameter variation is due to the $Fe^{+3} \rightarrow Fe^{+2}$ transition resulting in increased concentration of crystal-forming Fe^{+2} cations, whose ionic radius is larger than that of Fe^{+3} cations. There is a certain interrelation between the Fe^{+3}/Fe^{+2} concentration ratio and the deviation of the oxygen sublattice of ferrite from stoichiometry. The higher is this ratio, the smaller is the lattice parameter and the smaller is non-stoichiometry of ferrite with respect to oxygen.

The above considerations imply that oxygen deficit in powder B is higher than that in powder A.

Shown in Fig. 1 are the TG curves for the Type A ceramic powder during the first (curve *a*) and repeated (curve *b*) heating. The TG curves for the Type B powder sample are not qualitatively different from those for the Type A sample. It is also evident from Fig. 1 that during the first heating with increasing the temperature, the mass of the analyzed sample increases up to the temperature $T \approx 1{,}000$ K (see "Introduction" section).

This result testifies to the fact that the Type A material in the initial state exhibits deviation from non-stoichiometry of oxygen toward its deficit. Within the specified temperature range, the content of oxygen does not

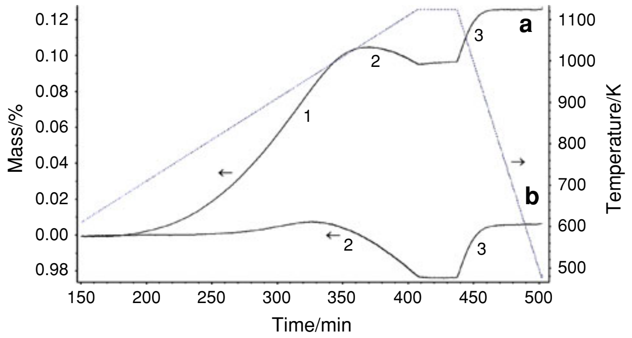

Fig. 1 Changes in mass of powdered ferrite in Type A sample during the first (curve *a*) and repeated (curve *b*) heating. Heating rate 2 K/min. Cooling rate 10 K/min

correspond to the equilibrium state of the condensed phase with the gas medium. That is why an additional non-isothermal heating gives rise to oxidation of the sample under study.

Upon reaching the temperature $T \approx 1{,}000$ K, the ferrite mass begins to decrease (see "Experimental procedures" section, curve *a* in Fig. 1). That means that oxygen escapes from ferrite powder into the surrounding atmosphere. This occurs due to a shift of the oxygen equilibrium toward its excess, when this temperature is increased while the partial oxygen pressure in the surrounding medium is retained constant. Thus, the interaction of ferrite powder with the medium above 1,000 K transits into the reduction regime. It should be noted that the oxidation stage is hardly present in the process after repeated heating of the powder, and the mass loss in the course of heating is compensated for by its increase during the cooling stage (Fig. 1, curve *b*). Reversibility of these processes is indicative of the fact that ferrite composition changes only with respect to oxygen.

The results of the TG analysis allowed us to identify the temperature interval for heating this material $T = 670$–920 K, within which one can correctly analyze the kinetics of oxygen absorption in non-stoichiometric ferrite powders. The kinetic analysis was carried out using a combined heating mode involving both non-isothermal and isothermal stages. The analyzed sample was heated at a certain rate from $T = 670$ K to $T = 920$ K. This was followed by a comparatively long isothermal tempering at this temperature until equilibrium with the surrounding medium was reached, which was indicated by the conservation of constancy of the sample mass. The kinetic behavior of mass variation in Type A powder is presented in Fig. 2. Arrows show the points of time of transitions from non-isothermal heating to isothermal tempering.

The X-ray diffraction studies demonstrated that after oxidative annealing the lattice parameter in Type A and B ferrite powders decreased down to $a = 8.360$ Å. It appears quite reliable that the resulting lattice parameter is consistent with the stoichiometry of the ferrite under study.

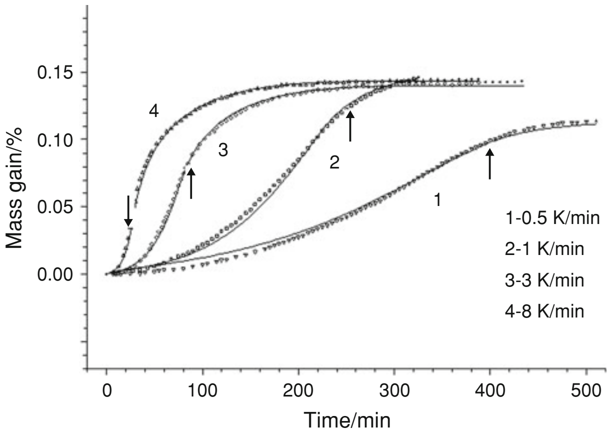

Fig. 2 Oxidation kinetics of Type A Li–Ti ferrites. Experimental TG measurements (*dots*) and calculated curves (*solid lines*)

The relative mass gain for the Type A powder as a result of annealing was found to be $\Delta m/m = 0.14\%$, which was smaller than for the Type B powder, with the mass gain for the latter being $\Delta m/m = 0.25\%$. The respective variations in non-stoichiometry parameter $\Delta\delta$ were calculated from the formula $\Delta\delta = (\Delta m/m)\cdot(M/M_o)$, where Δm is the mass change in transition from the initial conditions toward the equilibrium with the surrounding medium, m is the oxide mass under the initial conditions, M is the molecular mass of the oxide under study, and M_o is the atomic mass of oxygen. The values of $\Delta\delta$ for Type A and B powders were found to be 0.017 and 0.030, respectively. According to the X-ray phase analysis, the processes resulting in oxygen content variation in ferrites occurred within single-phase spinel structure. The data obtained allow one to analyze the revealed kinetic behavior within the framework of a single-phase oxidation mechanism of ferrite.

The kinetic results were processed using a license software program Netzsch Thermokinetics developed for those who use devices manufactured by Netzsch-Geratebau GmbH. The calculations relied on the method of multivariate nonlinear regression involving solution of a system of differential equations associated with a particular type of reaction. This software program is basically described in [13].

The analysis performed has demonstrated that it is the D_{3F} model (three-dimensional diffusion model according to Fick's diffusion law) which provides a most satisfactory description of the kinetic dependences obtained. The calculated kinetic parameters are summarized in Table 1, and the curves constructed using these parameters are plotted in Fig. 2.

It is clear from the data presented in Table 1 that there is a slight decrease in the activation energy of oxidation when the degree of oxygen non-stoichiometry of ferrite increases.

The Netzsch Thermokinetics software makes it possible to calculate the kinetic dependences of the degree of

Table 1 Kinetic characteristics of ferrite oxidation calculated from TG data

Powder sample	Kinetic model	Parameter $\log A/s^{-1}$	Parameter $E/\mathrm{kJ\ mol}^{-1}$	Parameter E/eV
A	D_{3F}	5.75	181	1.88
B	D_{3F}	4.79	166	1.72

transformation (α) for isothermal conditions from the known constants of the reaction rate (Fig. 3). Parameter α represents a ratio of the current mass gain values to the maximum possible gain, which corresponded to the oxidation of lithium–titanium spinel to stoichiometric state.

Since the oxidative reaction proceeds in a diffusion regime, so from the calculated dependences of α on time we can estimate the effective coefficients of oxygen diffusion in ferrite for different temperatures of oxidative annealing. Processing of the kinetic results relied on the solution of the second Fick's law [14]

$$\alpha = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left\{-[n\pi]^2\frac{D}{R^2}t\right\} \qquad (1)$$

where D is the diffusion coefficient, R is the particle radius, and t is the annealing time.

The calculations have revealed that for Type A and B powders the temperature dependences of the effective diffusion coefficient are described by the expressions $D(\mathrm{cm^2/s}) = 6.38\ \mathrm{e}^{-1.95/kT}$ and $D(\mathrm{cm^2/s}) = 2.25\ \mathrm{e}^{-1.89/kT}$, respectively. It is clear that the values of E_D for both A and B powder systems are virtually the same. The resulting activation energy E_D tends to be lower than the activation energy of bulk oxygen diffusion typical for ferrites ($E = 2.5$–3 eV) [15]. This discrepancy could have been caused by a considerable role of grain boundaries in the oxidative process. This point of view is favored by the following experimental findings.

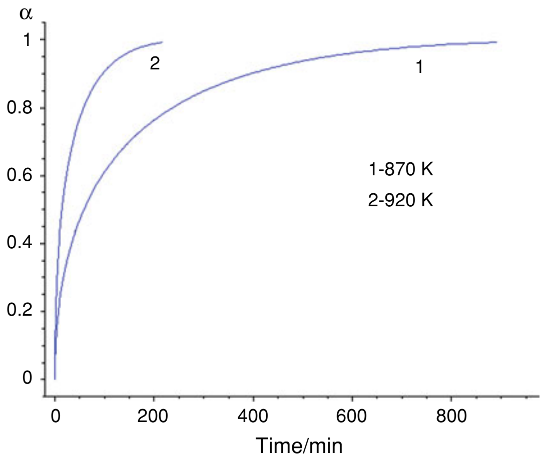

Fig. 3 Isothermal behavior of degree of transformation α in the oxidative reaction of Type A ferrites calculated for different temperatures

Grain-boundary diffusion in polycrystalline Li–Ti ferrites sintered at $T = 1{,}380$ K for 2 h was investigated by the method of layer-by-layer measurement of the activation energy of electrical conduction E_σ. This technique is detailed in [16, 17]. Samples shaped as ceramic pellets with uniform distribution of E_σ over the depth were subjected to oxidative annealing (in air at an oxygen pressure of $P = 0.21$ atm.). In the course of oxidative annealing, as a result of grain-boundary oxygen diffusion a depth profile of $E_\sigma(x)$ was observed to form, which reflected the diffusant distribution over the depth. The $E_\sigma(x)$ profiles were approximated by the formula reported in [16], which analytically related the value of $E_\sigma(x)$ to the oxygen ion concentration $N(x)$ in point x. In so doing, $N(x)$ was prescribed as a respective solution to the Fisher's diffusion equation [18].

Since the grain-boundary width δ is unknown, it was not the coefficient of grain-boundary diffusion D_b but rather the product $\delta \cdot D_\mathrm{b}$ entering the analytical expression for the Fisher's model. We derived the following expression for the grain-boundary temperature dependence:

$$\delta D_b = 6.8 \cdot 10^{-5} \cdot \exp(-1.93/kT)$$

It is evident that the resulting values of the activation energy are close to those obtained using TG. This fact supports the assumption that during oxidation of non-stoichiometric ferrites grain-boundary diffusion is the predominant diffusion mechanism.

Conclusions

We have identified kinetic characteristics of oxidation of lithium–titanium polycrystalline ferrites and oxygen diffusion coefficients controlling this process.

It has been shown that the activation energy of oxidation coincides with the activation energy of grain-boundary oxygen diffusion. The results obtained indicate that absorption of oxygen in ferrite is predominantly controlled by grain-boundary diffusion.

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