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INTERACTION OF LITHIUM-TITANIUM CERAMICS WITH AIR DURING SINTERING

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Interaction of lithium-titanium polycrystalline ferrites with ambient air during their sintering is investigated using the methods of electroconductivity and thermal gravimetry within the temperature interval T = 600–1300 K. It is found out that the temperatures exceeding T = 1100 K correspond to effective course of reducing reactions in this material, which results in the formation of an oxygen-deficient ceramic structure in the stage of isothermal tempering (T = 1280 K). It is shown that in the final cooling stage the process of exchange of the ferrite ceramics with the ambient atmosphere exhibits a pronounced oxidative character. The role of these redox processes in the formation of the oxygen non-stoichiometry of the sintered specimen and the depth of its distribution are analyzed.

INTRODUCTION

Ferrites represent composite oxides whose characteristic feature is their tendency to atomic non-stoichiometry. The latter noticeably affects a number of their structure-sensitive properties [1, 2]. The oxygen stoichiometry of oxide materials is primarily determined by the external thermodynamic parameters such as temperature T and partial oxygen pressure P in a gas medium. Variation in these parameters during synthesis, sintering or thermal treatment of ferrite ceramics gives rise to a change in oxygen concentration in the crystal lattice. Note that this is accompanied by generation or disappearance of oxygen vacancies that are electron donors and by a change of charge state of crystal-forming transition metal ions. On the one hand, these peculiarities of the atomic and electronic structure provide tremendous possibilities for purposeful variation of electromagnetic properties of materials, while on the other hand, they lead to additional technological problems due to the difficulty to reproduce structure-sensitive properties of ferrites, which is frequently aggravated by the lack of information on the relationship between oxide composition and their temperature and pressure P. The study of diffusion exchange of ferrite materials with the ambient should, therefore, be in the focus of attention in materials science.

An analysis of the literature made by the authors demonstrated that the data concerning lithium-titanium ferrospinels, very promising for microwave device engineering, are very few.

Considering this circumstance, this work aims at investigation of the character of interaction of lithium-titanium ferrites with ambient air in different stages of a technological sintering cycle.

1. EXPERIMENTAL PROCEDURE

The objects under study were lithium-titanium ferrites whose powders were synthesized under industrial conditions using a commercial technology of ceramic production from a mechanical mixture of oxides and carbonate of the following composition (in wt.%): Li_2CO_3 – 11.2, MnO – 2.7, TiO_2 – 18.65, ZnO – 7.6, and Fe_2O_3 – 59.81.

The ferrite specimens were compacted in the shape of tablets measuring 18 mm in diameter and 3 mm in thickness by cold single-side pressing in a hydraulic press at a constant pressure of 1300 kg/cm^2 for three minutes. The resulting ferrite compacts were subjected to a low-temperature annealing at T = 670 K for one hour in order to remove moisture and the binder.

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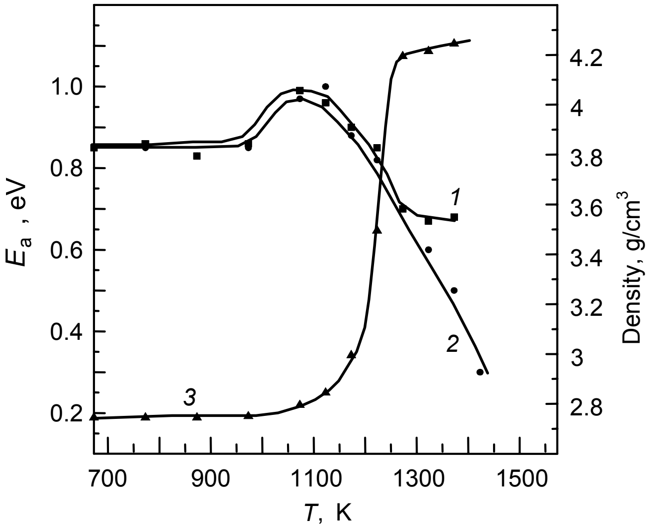

Fig. 1. Dependence of E_a in the compacts at the depths 20 (curve *1*) and 500 μm (curve *2*) and density (curve *3*) on sintering temperature. Time of sintering 2 hours.

A standard laboratory resistance furnace of an MPL-6 type was used for sintering of ferrite compacts. Heating of the specimens to fixed temperatures was done in air at a rate of 8 deg/min. The duration of the subsequent isothermal tempering was 2 hours. The specimens were let to cool down naturally, with the maximum cooling rate being 10 deg/min.

In order to investigate peculiarities of the redox processes in these ferrites, we used an electroconductivity technique [3] and thermogravimetry.

Static electrical conductivity was measured in a temperature interval $T = 300–600$ K using the method of spreading resistance [4] accompanied by a layer-by-layer analysis. This method enables analyzing temperature dependences of electrical conductivity in thin subsurface layers at different distances from the surface via their subsequent grinding. The thickness of the layer under examination is about 20 μm.

The electron transfer energy E_a was used as a parameter characterizing electrical conductivity, which most vividly represents the processes of diffuse exchange of ferrite with the ambient. The appropriateness of this approach was validated in earlier works [3, 5]. The value of E_a was determined from the results of processing of the temperature dependences of electrical conductivity measured under continuous current within the temperature $T = 300–550$ K, with thin layers being consecutively removed from the specimen surface.

The thermogravimetric dependences were obtained using an SDT Q600 advanced high-sensitivity analyzer from the scientific-analytical center at the Tomsk Polytechnic University.

2. EXPERIMENTAL RESULTS

The powder compacts prepared for testing had a green density of $\rho = 2.8$ g/cm^3. The electrical conductivity activation energy was $E_a = 0.85$ eV; it was maintained at this value throughout the bulk of the specimens.

Shown in Fig. 1 is the variation in the values of the depicted characteristics upon annealing of the compacts at fixed temperatures for 2 h. It is evident from the graph that at low annealing temperatures $T = 670–1000$ K the density of compacts is virtually unchanged. The value of E_a, in the same temperature interval, remains constant throughout the specimen depth and is equal to that of the activation energy prior to sintering. Subsequent rise of the sintering temperature to $T = 1100$ K results in a pronounced increase in E_a, the latter still being the same throughout the depth of the specimen. After heating involves the region of higher temperatures, beyond $T > 1100$ K, a reverse effect is observed – a decrease in the conductivity activation energy. It is worth mentioning that within the annealing temperature range $T = 1200–1370$ K, wherein the effective densification of the compacts occurs, the behavior of the electron transfer activation energy E_a

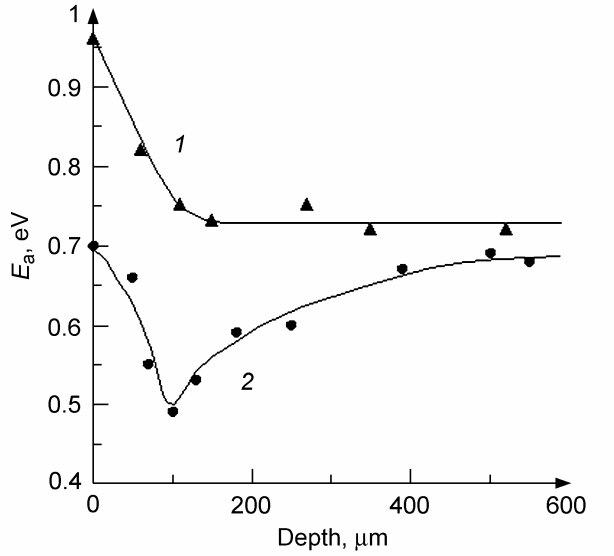

Fig. 2. Distribution of E_a with respect to the depth in a ceramic specimen after sintering at 1280 K for 2 hours under natural cooling (curve *1*) and quenching cooling (curve *2*).

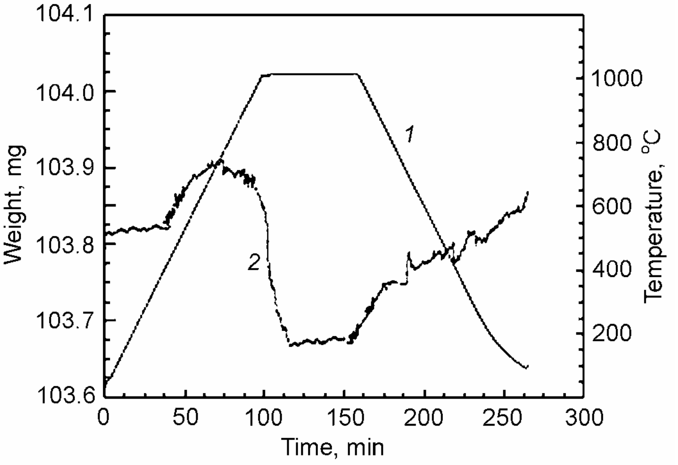

Fig 3. Derivatogram of a ferrite powder specimen.

undergoes a change when we look at the transition from the subsurface layers of the specimen down to the bulk (Fig. 1, curves *1* and *2*). It is this temperature interval shown above that involves the formation of a non-uniform depth profile of $E_a(x)$. As an example, Fig. 2 presents the distribution of $E_a(x)$ with respect to the specimen depth obtained upon sintering at 1280 K for 2 hours under different cooling conditions. It is evident that in the case of natural cooling the value of E_a is monotonously decreased, as the distance from the surface increases, and reaches stationary values in the bulk.

Of special interest for the analysis of ferrite interaction with the ambient are the data from thermogravimetric measurements. Figure 3 presents a typical derivatogram from ferrite powder. Curve *1* illustrates the annealing temperature conditions that included heating at the rate 10 deg/min to $T = 1280$ K, isothermal tempering at this temperature for 1 hour, and subsequent cooling at the rate 10 deg/min. Curve *2* depicts the accompanying variation in ferrite mass.

The dependence shown in this figure is of complex character and consists of several temperature sections, within which considerable changes in the powder mass are observed. In the stage of heating from $T = 870$ K up to $T = 1070$ K, the ferrite mass is increased, while a further increase of the temperature up to temperature of isothermal exposure gives rise to a loss of mass of the analyzed probe. This tendency also persists during the stage of isothermal tempering of the specimen at $T = 1280$ K. One cannon but notice a good coincidence of the temperature intervals within which an increase or decrease in the sample mass is observed (Fig.3) with those temperature regions where the ferrite conductivity activation energy is increased or decreased (Fig. 1).

According to the data presented in Fig. 3, upon switching to the cooling regime, the analyzed probe mass is increased again. Thus, as the temperature is decreased the powder mass begins to actively compensate for the loss of oxygen, which took place earlier.

3. DISCUSSION OF RESULTS

When discussing the results obtained, we relied on common physical concepts of the nature of the processes occurring in ferrospinels under temperature variations [1, 2]. Concerning the problem addressed here, the following considerations are relevant.

1.Interaction of ferrites with the ambient in the course of sintering or subsequent thermal treatment invariably gives rise to spontaneous distortion of stoichiometry. Note that only one value of oxygen pressure corresponds to each temperature value, at which a composition of ferrite stoichiometric with respect to oxygen is formed. If thermal treatment of ferrite occurs under unchanged partial oxygen pressure, the character of ferrite interaction with the ambient can change from oxidative to reducing and vice versa. This would result in the formation of ceramic structures with differing level of deviation of the metal to oxygen ratio from that of stoichiometric one.

2.The major pathway via which the exchange of the oxygen ferrite matrix with a gas medium occurs is grain-boundary diffusion (GBD). Oxygen diffusion along grain boundaries (GBs) proceeds by a few orders of magnitude faster than that in the bulk [5, 6]. This circumstance gives rise to the fact that oxygen concentration in the region of GBs appears to be higher than in the bulk of the grain. Oxygen atoms exhibit strong acceptor properties. When they capture electrons, the concentration of charge carriers is decreased and a negative surface charge is formed, which causes an increased electrostatic potential at a GB and a formation of an intergrain potential barrier. In [5], it was clearly shown by measuring the static conductance that the value of E_a in Li–Ti-ferrite ceramic is nearly equal to the height of this barrier. Thus, we might suggest that there is a certain correlation between the value of E_a and the content of oxygen in grain interlayers in polycrystalline ferrite. According to the data reported in [5–7], this value increases as ferrite gets oxidized and, conversely, decreases in the case of a reducing reaction.

The above initial arguments allowed us to detail the character of the interactions of lithium-titanium ferrites with the ambient air in different stages of their burning.

The invariance of the activation energy of electrical conductance (Fig. 1, curve *2*) and the mass of the investigated ferrites (Fig. 3, curve *2*) is indicative of the fact that the air medium is quite passive with respect to the ferrites during their sintering to $T = 850$ K. This result is accounted for by a significantly difficult course of diffusion processes at comparatively low temperatures

The reason for this high value $E_a = 0.85$ eV is a higher degree of oxidation of surface layers of the compact particles compared to the bulk. This is due to the presence of adsorbed oxygen on the surface of powder particles, which under heating is embedded into the crystal lattice of ferrospinel, favoring oxygenation of these layers. A uniform distribution of E_a over the bulk of the specimen is to be expected, which was observed in the experiments.

An increase in the values of E_a, falling within the annealing temperature range $T = 850$–1070 K, is indicative of the effective course of oxidation processes due to oxygen diffusion into the material. This is supported by the gravimetry data indicating an increase in the mass of the analyzed probe. It is very likely that under the above-mentioned conditions the content of oxygen in ferrite does not correspond to the state of equilibrium between the condensed phase and the air medium. Hence, for the chemical potential of gas- and solid-phase oxygen potentials to be equalized, there should be a process that would give rise to oxygen absorption by the ferrite. Since the compact density in this temperature range is quite low and hardly varies, diffusion along GBs occurs easily, which results in nearly uniform distribution of E_a over the specimen depth.

A comparison of the dependences presented in Figs. 1 and 3 evidences of a cardinal change in the character of interaction of ferrite with the surrounding medium at $T > 1090$ K. A decrease in the mass of the analyzed probe and in the value of GB potential barrier with temperature clearly points to a loss of oxygen by ferrite due to reducing reactions. This result can be interpreted as follows. It is well known that only one value of oxygen pressure in a gas medium corresponds to each temperature value at which a ferrite composition stoichiometric with respect to oxygen is formed. An increase in temperature requires that the equilibrium gas pressure satisfying the stoichiometric condition be increased. Otherwise stoichiometry of the ceramic would be distorted. Under the conditions used in our experiment the oxygen pressure was constant, therefore, in the region of elevated temperatures $T = 1090–1370$ K the partial oxygen pressure in air was found to be lower than equilibrium one at which the stoichiometric composition of ferrite with respect to oxygen can be maintained. This factor causes activation of the reducing processes, resulting in the loss of oxygen and formation of non-stoichiometric ceramic structure.

According to the gravimetric analysis (Fig. 3), the process of exchange of ferrite with the ambient atmosphere under cooling conditions changes its pathway, acquiring oxidative character. This is unambiguously indicated by the fact that when the temperature is decreased the mass of the material is naturally increased due to diffusion.

It is significant that no significant differences in the conduction activation energies between the surface and deep-lying layers of the sintered compacts are observed up to the annealing temperature $T = 1220$ K. This is due to still low density of the sintered compacts, which considerably favors the loss of oxygen from the porous ceramic material according to the mechanism of GB diffusion. Non-uniformity in the distribution of E_a is observed at the temperatures corresponding to the effective densification of the compacts. An increase in the ceramic density is generally accompanied by a smaller number of GB defects, which would therefore deteriorate diffusion transparency of GBs. In view of this fact, interaction of deep layers of the specimen with the atmosphere tends to be retarded. In subsurface layers this process is more effective. This results in a considerable non-uniformity of the structure state and electrical properties of ferrite ceramics.

When viewed together, the aforementioned results imply that the degree of oxygen non-stoichiometry, the shape of the depth profile, and the values of E_a after sintering of lithium-titanium ferrites are controlled by the occurrence of two oppositely directed processes: reduction, dominating in the stage of isothermal exposure, and oxidation, prevailing during transition into a cooling mode. The former would result in lower values of E_a. Note that the higher the sintering temperature, the lower E_a is to be expected. In the course of transition into the cooling mode, the distribution of $E_a(x)$ formed during isothermal exposure is overlaid by a profile resulting from the oxidation process. It is most unfortunate that this circumstance interferes into a clear experimental identification of the type of distribution of $E_a(x)$ that would be observed in the course of isothermal burning of polycrystalline ferrite. Nevertheless, it is possible to perform model experiments simulating the conditions under which the contribution from oxidation processes during cooling could be minimized. Their essence consists in the use of a quenching mode allowing one to maintain the structural state of deep layers of ceramics, which they had by the end of an isothermal stage of burning.

The results of these experiments are given in Fig. 2, where the distribution profiles of $E_a(x)$ in the deep layers of ferrite ceramics sintered at $T = 1280$ K and cooled at the rate 10 deg/min and in a quenching mode are depicted. It is evident that the deep layers of quenched and slowly cooled specimens are characterized by quite close values of E_a. The distributions of $E_a(x)$ formed in the subsurface layers were, however, very different. Upon quenching, the dependence of $E_a(x)$ exhibits a complicated character and consists of two sections. In the first section, E_a is decreasing as we move from the surface, while in the second one it behaves in a contrary fashion. This behavior is completely consistent with the above-mentioned considerations. The presence of the second section in the curve is indicative of the fact that it is immediately in the course of isothermal exposure that a distribution profile typical of the reducing process of ferrite interaction with the atmosphere is formed. This profile is overlaid by a section of the curve near the surface resulting from diffusion-controlled oxidation processes taking place in the stage of cooling. Under very fast dropping of temperature (quenching), diffusion interaction of ferrite with the ambient is retarded. Thus, the degree of oxidation of subsurface layers turns out to be much lower than that of the mode of slow cooling of the specimens.

SUMMARY

Based on a series of investigations, we have identified the character of interaction of lithium-titanium polycrystalline ferrites with the ambient air at normal atmospheric pressure within the temperature range $T = 600–1300$ K. It has been shown that the temperatures exceeding $T = 1100$ K correspond to an effective course of reducing reactions in this material, which results in the formation of an oxygen-deficient ceramic structure in the stage of isothermal exposure.

In the stage of cooling, the prevailing role belongs to the oxidation processes. It is these processes that finally determine the level of achieved stoichiometry of subsurface layers of the final product and the character of its non-uniform distribution with respect to the depth.

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