

Influence of metallic additives on manganese ferrites sintering

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Abstract. Influence of cuprum nanopowder additive received by electric explosion on the process of manganese ferrites MgFe₂O₄ consolidating at thermal sintering was researched by dilatometry method. Cuprum nanopowder at a rate of 5 mass % was added into the original commercial-grade powder of manganese ferrite MgFe₂O₄. Powder mixture was numerously blended with screening for better blending before pressing. Powder compacts were formed by cold one-axle static pressing. It was proved that introduction of cuprum additive caused shrinkage increase at final heating stage. There was abnormal compact enlarging at sintering in the air at isothermal stage; the specified process was not observed in vacuum. This difference can be explained by changes in conditions of gaseous discharge from volume of pores.

1. Introduction

Ceramic materials are widely used for both functional and instrumental purpose. Ceramic materials on the base of zirconium dioxide [1–4] and lithium ferrite [5, 6] stand apart. The main technological stage [7] of ceramic production is powder compact burning, its sintering [8, 9], and also modification [10, 11]. As for ferrites, process of their sintering was mostly determined by interaction of sintered material with surrounding gaseous atmosphere [12, 13]. Moreover, diffusion processes have a great importance and secondary ion mass spectroscopy method is effectively used to study it [14, 15]. Dilatometry method [16–19] and thermal gravimetric analysis [5], grapho-analytical method [20], are widely used to study ceramic materials sintering. Both conventional methods of thermal processing in resistance furnaces and nonconventional methods based on radioactive action of accelerated beam [6, 18], laser and other types of light stimulus can be used for sintering and processing of ceramic materials [21–23]. Method of sintering in resistance furnace is most suitable for manufacturing of ferrites. Furthermore, considerable attention is paid to sintering temperature decrease to reduce final products cost. In this respect blending method proved to be effective [24–27]. Polymers [27], oxides [26] and metals [25] were used as additives. For instance, work [23] presents information about introduction of zinc and niobium into barium hexaferrite formulation which has strong impact on morphology and size of grains.

Providing conditions of uniform diffusion of additive on volume basis of original powder is important at introduction of additives in small amounts in relation to original powder. It means that amount of particles of additive should be compared with amount of particles of original powder ranged from 20–50 micrometers in size. Nanopowders of metals meet the conditions, as they have very high specific surface area and at the same time they have small weight. As a result of it even if they have small weight percent they uniformly diffuse on volume basis of powder.



The present work presents the results of research of influence of additive of nanodisperse powder of cuprum (Cu), made by electric explosion method on the process of consolidating at manganese ferrites sintering MgFe_2O_4 made by dilatometry method.

2. Experimental part

Manganese ferrite samples MgFe_2O_4 , made from original commercial-grade powders according to ceramic processing technology were studied. Nanodisperse powder of cuprum was received by electric explosion method. Average size of particles ranges from 20...60 nm. Specific surface area of nanopowder of cuprum, determined by BET method, was not less than $15 \text{ m}^2/\text{g}$.

Influence of cuprum additive on the processes of compacting and sintering of ferrite MgFe_2O_4 was carried out. Introduction of additive in number of 5 mass % in original powder was made by multiple blending with screening to provide uniform diffusion of additive on volume basis of original powder.

Samples for sintering were compacted by cold one-axle static pressing in press-form at laboratory hydraulic press PGR-10 (ИГР-10) under a pressure of pressing 155 MPa. Compacts had cylindrical form of 9 mm in diameter and about 3 mm thick.

Research of kinetics of compression of test samples was conducted at highly-sensitive dilatometer DIL402C, company NETZSCH (Germany). Heating and cooling rate was 10 degrees/min.

Research of kinetics of compression by dilatometry method was conducted for compacts, received from original powder without additives at sintering in the air (sample of type A), samples with adding Cu at sintering in the air (sample of type B) and in vacuum (sample of type C).

3. Results

Figure 1 shows kinetic connection of linear shrinkage of all test sample types.

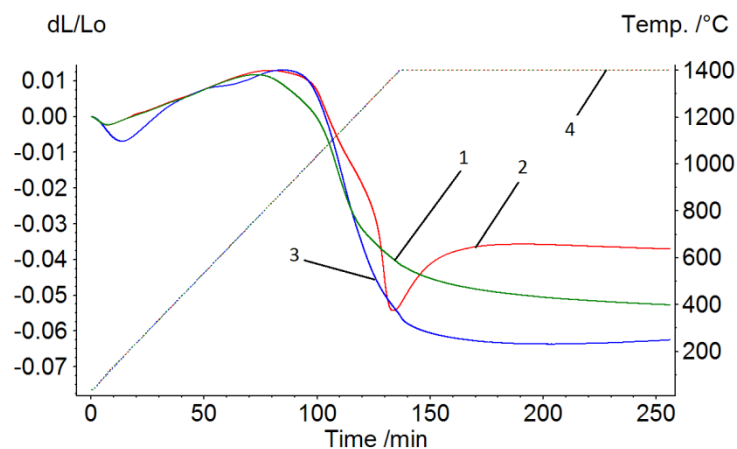


Figure 1. Kinetic connection of linear shrinkage $\Delta L/L_0$: 1, 2, 3 – samples of types A, B and C, correspondingly; 4 – temperature conditions of burning.

According to analysis of connections in Figure 1 it follows that introduction of Cu causes shrinkage increase at heating stage in comparison with samples of type A, as at sintering in the air (curve 2), and in vacuum (curve 3). Determined by first derivative curves (Figure 1), shrinkage of samples of types A, B and C, temperatures corresponding to maximum shrinkage rate are equal to $T_m = 1126.1; 1330.5; 1145.3^\circ\text{C}$, correspondingly.

Change of T_m can be explained in the following way. There is oxidizing of Cu with oxide of CuO formation at heating of samples of type B, which causes its enlargement in relation to samples of type A. Liquid phase formation occurs at melting temperature CuO equal to 1242°C , resulting in $T_m = 1330.5^\circ\text{C}$. At heating stage of samples of type C there is melting of Cu without oxide formation. As melting temperature of Cu is lower than CuO and is equal to 1085°C , T_m of samples of type C is

also lower and is equal to $T_m=1145.3^{\circ}\text{C}$. Presence of liquid phase in samples of types B and C leads to friction decrease between particles at consolidating.

In accordance with work [17] there are two simultaneous processes at thermal sintering liable for change of linear sizes of a sample. The first process was specified by interparticle interaction, the second process was conditioned by changes of volume of gaseous pores. Presence of liquid phase in samples of types B and C at their sintering prevents from gaseous discharge from volume of pores, which causes their enlargement at the stage of isothermal time. As it can be seen from Figure 1, the process of enlargement mostly occurs at sintering in the air (samples of type B), which causes abrupt enlargement at isothermal time. Gaseous discharge from pores is more effective at sintering in vacuum (samples of type C) because of larger gradient of pressure which causes shrinkage enlargement in comparison with samples of type B.

4. Summary

It was established that consolidating of ferrite compacts MgFe_2O_4 with 5 mass% additive of nanopowder Cu, received by electric explosion method, strongly depends on ambient air environment pressure. Gaseous discharge from volume of pore space of a compact is difficult at atmospheric pressure because of blockout of pores of liquid phase of additive. At sintering in vacuum decrease of pores volume and their quantity is more effective, which finally leads to considerable increase of compacts shrinkage. Introduction of low-melting metallic nanopowders should be preferably made at sintering of manganese ferrites in vacuum to obtain nonporous ceramics.

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