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FABRICATION OF MAGNETIC CERAMIC MATERIALS BASED ON NANOSTRUCTURED HEMATITE POWDER BY SPARK PLASMA SINTERING

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ABSTRACT

High-temperature consolidation of nanostructured hematite (α-Fe_2O_3) powder has been performed using the method of spark plasma sintering (SPS). Magnetic ceramic materials based on individual (α-Fe_2O_3) and composite (α-Fe_2O_3–Fe_3O_4) formulations of high construction strength (fracture strength 249 MPa) have been fabricated. The peculiarities of changes in composite phase composition and microstructure in the SPS temperature range from 700 up to 1100 °C are presented. The materials element composition was studied using the method of energy-dispersive spectroscopy, and the fact of carbon diffusion in the spark plasma current has been corroborated. The ceramic composites magnetic properties have been investigated and the regularities of changes in the values of their magnetization (Ms) and coercive force (Hc) in dependence on the SPS temperature have been described.

Keywords: spark plasma sintering, iron oxides, nanomaterials, ceramics, magnetic properties.

1. INTRODUCTION

Among many magnetic materials applied in different fields of industry, science, and technology, a special focus is associated with ceramic systems based on iron oxides [6]. Magnetic ceramics materials have been developed and are used in most cases as an alternative to metallic magnets to reduce energy loss for remagnetization. Such replacement is possible due to high electrical resistance of oxide ceramics, in particular, ferrites (based on maghemite, magnetite, and, on rarer occasions, hematite) and, therefore, significant reduction of eddy currents and related electromagnetic losses [6].

An additional factor causing intensive replacement of metal alloys consists in low labor and energy consumption of synthesis of ceramic composites (compaction, consolidation, molding etc.), as compared to multi-operation and extremely complex in implementation processes of foundry engineering. However, there exist a number of difficulties at using ceramic materials related, first of all, to phase and structural heterogeneities of the obtained ceramics. Magnetic properties of composites are structurally sensitive [2] and determined not only by the composite phase composition, but also by size and shape of pores and crystallites. Adjustment of these parameters is capable to order/distort magnetic anisotropy, induce/eliminate the emergence of elastic stresses, and, as a result, affect magnetic characteristics [2]. In this regard, the main focus is concerned with synthesis methods, which allow not only efficient reduction of the content of various heterogeneities, but also formation of preset stoichiometry of the material with chemical and structural homogeneity, thus improving the product magnetic properties.

Many researchers mentioned the prospects of application of the technology of spark plasma sintering (SPS) in synthesis of ceramic systems [18], including the development of nanoceramics with good magnetic properties [9]. Specific features of the process of consolidation of nanodispersed magnetic powders by electric current at optimal heating conditions and mechanical loading enable one to obtain high-quality materials with specified and reproducible phase and structural characteristics. High heating rate ensures suppression of the grain growth while preserving its initial microstructure [20]. The magnetic field impact promotes ordering of the spatial positions of magnetic moments of metal ions in the material crystal lattice [8]. The mechanical load at sintering induces transformation of crystalline nanophases of iron oxides, transitions of the type wustite↔magnetite↔maghemite↔hematite, whereas new magnetic phases are formed [11, 19]. All these factors are determining for magnetic properties of composites fabricated using the SPS method. However, understanding of all the mechanisms of the above processes occurring in the spark plasma current at consolidation of magnetic powders, as was described, for example, for maghemite [15], is, in case of a majority most of materials, limited or, as in the case of hematite, absolutely absent.

In view of this, the present work was devoted to SPS synthesis of magnetic ceramic materials based on nanostructured hematite (α-Fe_2O_3) powder. The work objective consisted in studies of the effect of high temperatures of SPS synthesis (700–1100 °C) on the process of consolidation of hematite powder, in particular, studying the powder phase and structural changes at formation of new composites in relation to improvement of its magnetic properties.

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2. EXPERIMENTAL

2.1 Materials

Finely dispersed powder of nanostructured hematite (α-Fe_2O_3) (fraction 0.1-0.5 mm) of a macroporous structure (pore size 100-500 nm) obtained by the template sol-gel synthesis according to the technique described in [14] was used for the synthesis.

2.2 Synthesis technique

The SPS process was carried out on an SPS-515S unit ("Dr. Sinter*LAB^{TM}", Japan) according to the following scheme: 3 g of the initial finely dispersed hematite powder was placed into a graphite press mold (d=15 mm) and compacted (20.7 MPa). Thereafter, the workpiece was placed into a vacuum chamber (6 Pa) and sintered. A series of several samples were fabricated in experiments performed at different sintering temperatures (700, 800, 900, 1000, and 1100 °C), constant load of 24.5 MPa, heating rate 170 °C/min, and holding time 5 min (Table-1).

2.3 Methods of study

Identification of phases of the fabricated samples was performed on a D8 Advance Bruker AXS multi-purpose X-ray diffractometer (Germany): CuKα-radiation, Ni-filter, average wavelength (λ) 1.5418 Å, registered angles range 10-80°, scanning increment 0.02°, and spectra registering rate 5 °/min. The specific surface area according to the BET method was measured on an ASAP-2020 MP device ("Micromeritics GmbH", USA). The mechanical strength of consolidated samples of a cylindrical shape (d=15 mm, h=2.5-4.5 mm) was determined by crushing on an AUTOGRAPH AG-X plus 50 kN tensile-testing machine ("Shimadzu", Japan), the loading rate was 0.5 mm/min. SEM images of samples were obtained on an S-3400N scanning electron microscope ("Hitachi", Japan) and a Carl Zeiss Crossbeam 1540xb microscope with an Oxford Instruments X-Max 80 energy-dispersive detector ("Carl Zeiss", Germany). Magnetic characteristics were studied on a vibrating sample magnetometer (VSM) included into a physical property measurement system (PPMS) ("Quantum Design", USA).

3. RESULTS AND DISCUSSIONS

Table-1 shows the results of physical-chemical studies of ceramic composites synthesized using the SPS method within the scopes of the present work. Characterization of the specific features of the process of sintering (consolidation) of nanostructured hematite powder and formation of new ceramics was based on revealing peculiarities and regularities of changes in the powder composition, microstructure, and properties (magnetization) upon high-temperature treatment in the spark plasma current.

The data analysis (Table-1) indicates to evident dependence of all parameters of the composites under study on the process temperature conditions. In other words, high-temperature SPS conditions activate all possible physical-chemical processes resulting in irreversible reactions in solid: in particular, they are capable to affect the stable crystalline form of hematite. As was found from XRD results, the crystalline phase of the initial α-Fe_2O_3 remains intact during sintering at 700-900 °C (Figure-1) and at lower temperatures of the SPS process [15]. The hematite stability is deteriorated upon heating above 1000 °C: here, the composition of the formed ceramic composites comprises a mixture of hematite and magnetite (Figure-1).

Table-1. Characteristics of the samples of ceramic composites fabricated through sintering of the nanostructured hematite using the SPS method.

No.	T_s, °C	XRD	S_{spec} (BET), m^2/g	Fracture strength, MPa	M_s, emu/g	H_c, Oe
					300 K	300 K
1	Initial powder	Hematite (α-Fe_2O_3)	6.2	-	0.8	1260
2	700	Hematite(α -Fe_2O_3)	7.5	31	1.2	1130
3	800	Hematite (α-Fe_2O_3) Carbon (C)	4.2	243	2.5	1070
4	900	Hematite (α-Fe_2O_3) Carbon (C)	0.7	249	3.6	990
5	1000	Hematite (α-Fe_2O_3) Magnetite (Fe_3O_4) Carbon (C)	0.1	249	4.8	140
6	1100	Hematite (α-Fe_2O_3) Magnetite (Fe_3O_4) Carbon (C)	0.1	249	10.2	60

Transformation of iron oxide phases in the course of thermal treatment is a well-known process emerging at application of different thermal treatment methods, especially in the absence of oxygen [1]. However, in most cases, it is of importance for nanosized systems, in which the particle sizes are a few dozens of nm [8]. It is evident that under spark plasma conditions (anomalously high temperature in vacuum) the probability of the emergence

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of the α-$Fe_2O_3 \rightarrow Fe_3O_4$ transition is very high. In addition, in our case, the process of partial hematite reduction must be catalyzed by carbon, whose presence was registered in almost all the fabricated samples (Figure-1).

The exception here is the sample obtained at 700 °C, for which the absence of carbon on the X-ray image is, probably, related to its low content and highly dispersed state. The emergence of free carbon in SPS-composites was registered by many researchers and is caused by its presence in the composition of electrodes, molds, insulation paper, and other articles [5, 4]. Thus, carbon removed by spark plasma from the surface of working elements diffuses as over the surface as within the whole bulk of the consolidated material. Here, in the range of high temperatures of heating in vacuum, carbon, first of all, reduces hematite until magnetite over the whole accessible surface of the sintered powder.

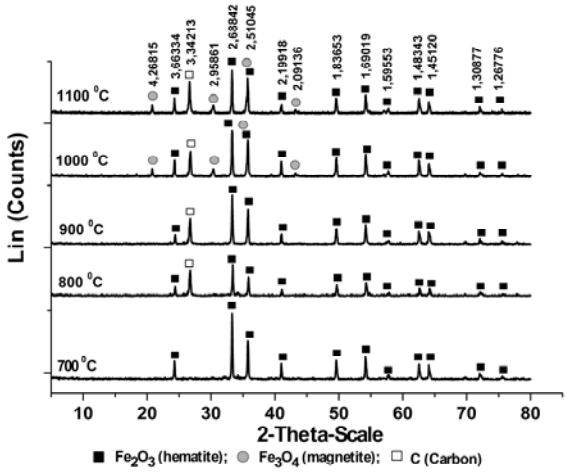

Figure-1. XRD analysis data for the samples of ceramic composites obtained by SPS consolidation of the nanostructured hematite powder at different temperatures

Carbon monoxide formed in this reaction diffuses deep into the bulk of the powder consolidated particles at the expense of initial internal macrostructure and various defects resulting from deformation and solid-phase processes at sintering. At this stage, hematite is reduced in the material and CO is oxidized until CO_2. The rate and depth of the described processes of diffusion and, therefore, reduction is different, which was revealed by the element analysis: in the defect area, the oxygen content is twofold lower, while the carbon content is several-fold higher than these values respective general quantitative distribution of main elements over the composite surface (Table-2). The EDS analysis results will be examined in detail below.

This fact was registered in more expressed way at studies of the surface section of the sample obtained at 900 °C (Figure-3, area 1). The volume of such pores depends directly on the degree of particles binding, changes in their shapes, and the density of their packing relatively to each other.

Hematite spark powder sintering at temperatures above 900 °C is accompanied with the decrease of the value of specific surface area until minimal values (0.1 m^2/g), but yields significant strengthening of the synthesized composites, whose elasticity modulus increases from 31 to 249 MPs (Table-1). It is evident that the temperature increase intensifies the processes of diffusion in solid and plastic deformation with attainment of creep threshold stress, and, therefore, of the material yield [12]. In this case, the whole free volume in solid is filled with the material, pore disappear, and a compressed (monolith) compound is formed (Figures 2ef).

Detailed microscopic studies of the microsection of the sample 4 (Table-1, Figure-3) synthesized at 900 °C enabled us to reveal defect areas (area 2) in a densely packed structural network formed, as was mentioned above, by particles sintered along contact boundaries and external pores bound to each other (area 1).

Formation of spontaneous defect areas is a negative feature of all synthesized composites. The peculiarity of their microstructure consists in substantial grains enlargement over cracks boundaries (area 2). Formation of the observed defects can be logically explained by agglomerated character of the initial powder. Under SPS process conditions, the electric current density increases in the bulk of the most densely compacted agglomerates. There emerge foci of the increased temperature producing local overheating and, finally, particle fusion (area 3). Elimination of the formation of 'focus' defects is possible through deagglomeration of initial powders, as was achieved in synthesis of titanium composites (Sivkov *et al*., 2012) by the methods of mechanochemical treatment and thorough fractioning of dispersed materials prior to their consolidation.

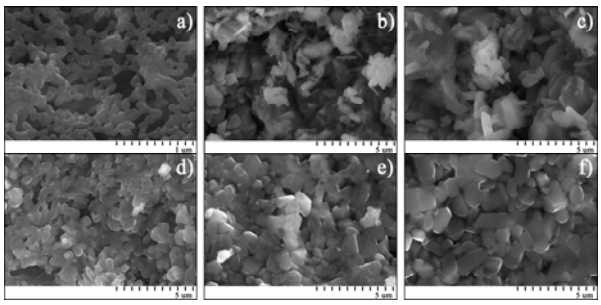

Figure-2. SEM images of nanostructured hematite (initial powder) (a) and its forms consolidated by the SPS method at different temperatures: 700 (b), 800 (c), 900 (d), 1000 (e), 1100 °C (f).

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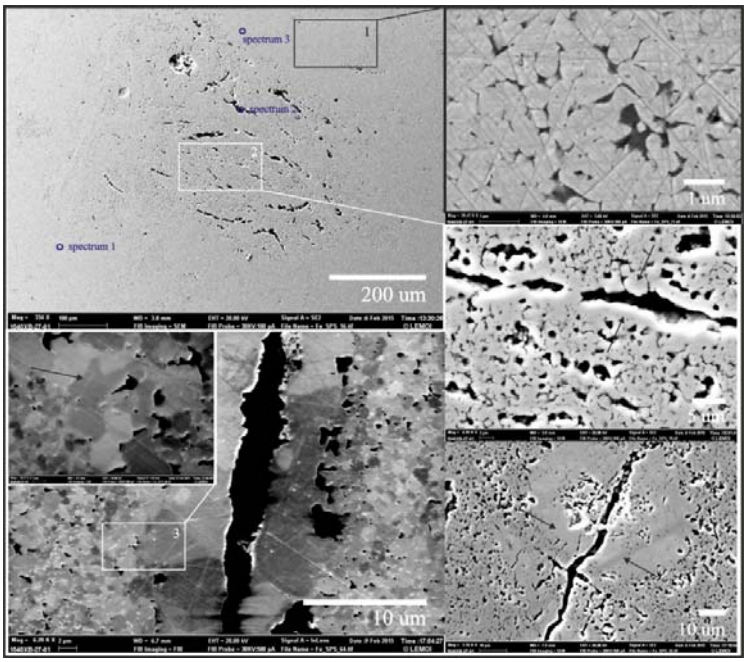

Figure-3. SEM images of the surface (microsection) of the sample of ceramic composite based on iron oxide fabricated by the SPS method at 900 °C: areas without (1) and with (2) defects.

As was revealed by the method of energy-dispersive spectroscopy, structural defects constituted the reason of local heterogeneities of the element composition in the ceramic composites under study. It was established from the data of 3 EDS spectra (Table-2) recorded on different parts of the sample 4 (Figure-3) that the composite contained, aside from main components (Fe and O), the residual products of synthesis of the initial hematite powder (Si). The minor Cr impurity is caused by the sample surface contamination during microsection preparation (polish). The presence of carbon was grounded earlier and is related to its diffusion from working and auxiliary equipment parts. The maximal carbon content (28.76 at. %) is observed for the spectra 2 (Table-2) recorded on the local defect (pore) area, which indicates to the intensity of its very surface transition during SPS. In average, the element composition over the whole sample surface (from edge to edge) measured over 73 points (6 points per slide) at an increment of μm was homogeneous (Table-2).

Table-2. Element composition of the surface of ceramic composite based on iron oxide and synthesized by the SPS method at 900 °C (at. %).

Element / Spectrum	C	O	Si	Cr	Fe
Spectrum 1	8.24	61.34	1.03	0.28	29.11
Spectrum 2	28.76	32.09	7.06	0.34	31.74
Spectrum 3	8.03	60.64	1.09	0.24	30.00
Max	28.76	*61.34*	*7.06*	*0.34*	*31.74*
Min	*8.03*	*32.09*	*1.03*	*0.24*	*29.11*
Average over the whole surface	6.58	62.34	1.69	0.25	29.13

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The important result of the present study consists in the establishment of the dependence of magnetic properties of the synthesized ceramic composites on the SPS process temperature. As was shown in [15], even at low-temperature SPS of α-Fe_2O_3 (up to 350 °C), magnetization of composites based on it was higher and directly proportional to the sintering temperature. Similar regularity was revealed in the present study as well. According to field dependencies of the magnetization of the samples (Figure-4) synthesized by the SPS method on the basis of antiferromagnetic hematite (0.8 emu/g), magnetization of their consolidated forms increases along with the sintering temperature increase and is not limited by the value of 10 emu/g (Table-2). This effect is explained, to a greater extent, by changes in the crystalline phase of the initial hematite powder, in which magnetite is formed (Figure-1); i.e., a new magnetic phase is formed: Fe_3O_4–α-Fe_2O_3 or γ-Fe_2O_3 [10]. Additional reason could be related to the revealed grain growth (dispersity changes) in the initial hematite during the SPS process (Figure-2), which also affects the system magnetization (Berkowitz *et al*., 1968). Also, taking into account the appearance of hysteresis loops (Figure-4), one can unambiguously state on the effect of continuous pulse current on the magnetic susceptibility of the composites under study. Constricted (perminvar-like) hysteresis loops result from stabilization of the domain structure ('perminvar' effect) (Stöhr and Siegmann, 2006): at this effect, the magnetization direction is stabilized in both domains and domain walls due to exchange or unidirectional magnetic anisotropy. In case of strong stabilization of magnetization directions in domains and domain walls, the latter are located in deep potential energy wells, whereas superposition of the external magnetic field does not yield their shift. As late as upon attainment of the field critical magnitude, domain boundaries are disrupted, and shifts are developed. At cyclic field changes, one observes perminvar-like or double hysteresis loop. This effect weakens along with the SPS temperature increase, and the coercive force value decreases significantly (from 1130 до 60 Oe, Table-1).

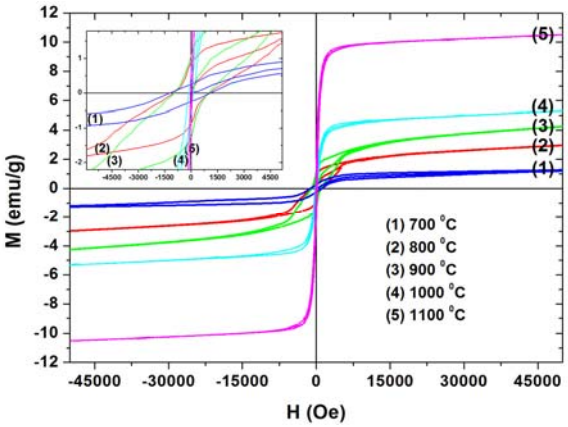

Figure-4. Field dependencies of magnetization (at 300 K) of the samples of ceramic composites fabricated by SPS consolidation of nanostructured hematite at different temperatures. Insert: dependence of the coercive force on the SPS temperature.

4. CONCLUSIONS

Nanostructured hematite powders were successfully consolidated using the SPS method at high temperatures (700-1100 °C). As was revealed by the XRD method, the phase composition and microstructure of high-temperature composites were heterogeneous. The crystalline α-Fe_2O_3 is unstable and partially reduced in the spark plasma current until Fe_3O_4 at temperatures above 900 °C. As was found using the microscopy method, the mentioned sintering conditions activated solid-phase processes, whereas the temperature increase yields substantial grain growth and particle reorientation and deformation, which results in destruction of the material internal and external porous structures. The ceramics strength attains 249 MPa at the specific surface area equal to 0.7-0.1 m^2/g. The energy-dispersive spectroscopy was used to determine the composite element composition (for the sample fabricated at 900 °C, the main components are Fe (29.13 at. %) and O (62.34 at. %), average values) and to establish the fact of carbon diffusion from the working parts surface (admixture of C 6.58 at. %). The ceramic composites magnetic properties were investigated, and it was demonstrated that the value of magnetization of antiferromagnetic hematite powder (0.8 emu/g) changed substantially during the SPS treatment and increased along with the increase of the sintering temperature, thus attaining 10.2 emu/g at 1100 °C. However, the coercive force is in inverse proportional dependence on the SPS temperature and decreases down to the minimal value of 66 Oe. The performed studies confirm high potential of the SPS technology as a promising approach to development of magnetic ceramics of individual and composite systems based on Fe_xO_y. The obtained results are of importance in understanding specific features of SPS for consolidating α-Fe_2O_3 powder and require further study.

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