Composite compacts of Fe/Fe₃O₄ type obtained by mechanical milling-sintering-annealing route

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Abstract. Fe/Fe₂O₃ composite powders were obtained by mechanical milling of iron and hematite up to 120 minutes in a high energy planetary ball mill. The particles size decreases by mechanical milling upon the formation of the Fe/Fe₂O₃ composite particles. After 120 minutes of milling the median particles size is at 7.2 μm. The Fe/Fe₃O₄ type composite were obtained by reactive sintering in argon atmosphere at 1100 °C of the Fe/Fe₂O₃ composite powders milled for 60 and 120 minutes. After sintering a FeO-wüstite residual phase is formed and this phase is eliminated by applying a subsequent annealing at a temperature of 550 °C. The sintered compact before and after annealing is composed by a quasi-continuous iron matrix in which are embedded iron oxides clusters (Fe₃O₄ and FeO before annealing and Fe₃O₄ after annealing). The iron oxide clusters are analogous with the Widmanstätten structure observed in steels before and after annealing. The materials have been investigated using laser particle size analysis, optical microscopy, scanning electron microscopy, energy dispersive X-ray spectrometry and X-ray diffraction.

Introduction

Soft magnetic composite materials are the subject of study for several years. One of the novel classes of soft magnetic composite materials is formed by the ferrite-alloy type composites [1-5]. One of the purposes of producing soft magnetic ferrite-alloy composites is to obtain a material that will possess an electrical resistivity closer to the ones of ferrites and a magnetic induction closer to the one of the alloys. The materials that will possess such type of characteristics should be used in frequencies applications [1, 2, 5]. The ferrites are themselves a large class of magnetic materials that are from many years subject of research and are used in various fields of industry. The soft ferrites (chemical formula MeFe₂O₄, with Me=Fe, Ni, Zn, Cu, etc or a group of these elements) have a characteristic cubic spinel structure from the space group Fd-3m. Their complex cubic spinel structure with 56 sites per unit cell (8 sites for Me²⁺, 16 sites for Fe³⁺ and 32 for O²⁻) dictates, in part, their electric and magnetic characteristics [6, 7]. Among the composites of ferrite-alloy type the iron-iron oxide (iron ferrite – FeFe₂O₄ (Fe₃O₄)) is one of interest [8-11]. Beside its interesting characteristics this type of composite materials it is also attractive due to the low costs of the starting raw materials such as iron and hematite [10, 11].

In this study we present the synthesis of the Fe/Fe₃O₄ sintered composite compacts by an original mechanical milling-sintering-annealing route using as starting materials a mixture of iron and hematite (α-Fe₂O₃).

Experimental

Iron powder (NC 100.24 - Höganäs) and α -Fe₂O₃ (hematite - Alfa-Aesar) were used as starting materials for producing of Fe/Fe₂O₃ composite powder by mechanical milling. A high energy planetary ball mill Fritsch, Pulverisette 4 model was used for mechanically milling of a 100 g of Fe+Fe₂O₃ mixture for up to 120 minutes in air atmosphere. The atomic ratio among the iron and oxygen in the starting mixture was 79/21. A mixture of 75.89 g of Fe and 24.11 g of Fe₂O₃ has been used as starting sample. Composite powder samples of Fe/Fe₂O₃ obtained after 60 minutes and 120 minutes of mechanical milling were subjected to reactive sintering. The sintering procedure was carried out in a furnace under argon atmosphere at a sintering temperature of 1100 °C for 6 hours. After sintering, the samples were subjected to annealing at 550 °C for 4h in argon. The evolution of the phases during mechanical milling, reactive sintering and annealing was investigated by X-ray diffraction technique. A Siemens D5000 diffractometer which operates with CoK α radiation and a Shimadzu 6000 diffractometer which operates with CuK α were used for the X-ray diffraction patterns recording. Both diffractometers work in reflection mode. A Laser Particle Size Analyzer (Fritsch Analysette 22 – Nanotec) with an analysis field of 10 nm to 2000 μ m was used for particles size distribution and d₅₀ median parameter determinations. The optical micrographs were obtained using an Olympus GX51 microscope. The scanning electron micrographs have been obtained using a Jeol-JSM 5600 LV microscope. The Jeol-JSM 5600 LV microscope is equipped by an energy dispersive X-ray spectrometer (Oxford Instruments, INCA 200 software).

Results and discussion

In Fig.1 is presented the evolution of the d₅₀ parameter as a function of the milling time of the Fe+Fe₂O₃ composite powder. In the same figure are given for reference the d₅₀ parameter of the Fe and Fe₂O₃ starting powders.

Fig.1. Evolution of the d₅₀ parameter as a function of the milling time of the Fe+Fe₂O₃ composite powder. The d₅₀ parameter of the Fe and Fe₂O₃ starting powders are given for reference.

It can be remarked the large difference between the iron particles (d₅₀=44.4 μ m) and the fine hematite particles (d₅₀=0.2 μ m) that have been used as starting materials in the mechanical milling process. One can observe that the median diameter of the particles decreases from 23.4 μ m up to 7.2 μ m upon increasing the milling time from 15 minutes up to 120 minutes. The particles median diameter decrease is more accentuated by increasing the milling time from 30 minutes to 60 minutes. This decrease is assigned to the final stage of the formation process of Fe/Fe₂O₃ composite particles. It is assumed that after the formation of composite particles a size reduction of the

particles dimension take place. The iron oxide makes the composite particles more fragile and a more accentuated fragmentation process during milling is expected. A slight decrease of the median diameter can be observed also, during the increase of the milling time from 60 up to 120 minutes of milling. This slight decrease is associated with the quasi-equilibrium between the fragmentation and cold welding process [12].

Fig. 2. X-ray diffraction pattern recorded with $\text{CoK}\alpha$ radiation of the $\text{Fe}/\text{Fe}_3\text{O}_4$ type composite compact obtained by reactive sintering at $1100^\circ\text{C}/6\text{h}$ in argon atmosphere starting from $\text{Fe}+\text{Fe}_2\text{O}_3$ composite milled powder.

The $\text{Fe}/\text{Fe}_2\text{O}_3$ composite powder obtained after 60 and 120 minutes has been used for the synthesis of the sintered compacts. By X-ray diffraction it has checked if the reaction during sintering at 1100°C between hematite and iron has taken place. Fig. 2 presents the X-ray diffraction pattern recorded with $\text{CoK}\alpha$ radiation of the $\text{Fe}/\text{Fe}_3\text{O}_4$ type composite compact obtained by reactive sintering at $1100^\circ\text{C}/6\text{h}$ in argon atmosphere from $\text{Fe}+\text{Fe}_2\text{O}_3$ composite milled powder.

Fig. 3. X-ray diffraction pattern recorded obtained with $\text{CuK}\alpha$ radiation of the $\text{Fe}/\text{Fe}_3\text{O}_4$ type composite compact obtained by reactive sintering at $1100^\circ\text{C}/6\text{h}$ from $\text{Fe}+\text{Fe}_2\text{O}_3$ composite powder after annealing at $550^\circ\text{C}/4\text{h}$ in argon.

In the diffraction pattern are noticed the Bragg reflections of Fe , Fe_3O_4 cubic spinel and FeO - wüstite.

Fig. 4. Optical micrographs of a sintered compact obtained from Fe+Fe₂O₃ powder milled for 60 minutes at a magnification of: **a)** x200 and **b)** x500.

Fig. 5. Scanning electron micrographs of the Fe/Fe₃O₄ type sintered composite compacts obtained at a magnification of x1,000 in BEC mode: **a)** as sintered at 1100 °C for 6 h and **b)** after annealing at 550 °C for 4h

So, according to the X-ray diffraction, the sintered composite compacts consist in a mixture of Fe, Fe₃O₄ and FeO phases. In the diffraction pattern it is no evidence of hematite peak and the reaction between iron and hematite precursors is considered as being complete. During sintering, although the reaction among Fe and Fe₂O₃ is complete, an undesired FeO phase was formed. Therefore, a subsequent annealing treatment was applied in order to eliminate the FeO residual phase. The temperature of the annealing was chosen in agreement with the Fe-O phase diagram which indicated that at a temperature that do not exceed 570 °C and for oxygen content less than 57 at. % a composite consisting in Fe and Fe₃O₄ can be obtained [13]. X-ray diffraction pattern recorded obtained with CuK_α radiation of the Fe/Fe₃O₄ type composite compact obtained by reactive sintering at 1100 °C/6h from Fe+Fe₂O₃ composite powder after annealing at 550 °C/4h in argon is presented in the Fig. 3. In the diffraction pattern are observed the Bragg reflections of Fe and Fe₃O₄. There is no trace of FeO phase after annealing at 550 °C/4h, thus indicating that the wüstite phase was transformed into magnetite during heat treatment. The general reaction obtained among the processing of the powder via milling-sintering-annealing route can be written as:

The undesired FeO phase was eliminated, but a very small amount of Fe₂O₃ is noticed. In the diffraction patterns can be identified a weak reflection of the hematite. This is assigned to the supplementary oxidation of the sample at the surface, the transformation of a part of the magnetite into hematite. As reference JCPDS files no. 06-0696 for Fe, 06-0615 for FeO, 33-0664 for Fe₂O₃ and 19-0629 for Fe₃O₄ were used.

In fig. 4 are presented the optical micrographs obtained for the Fe/Fe₃O₄ type sintered composite compacts after sintering at 1100 °C for 6 h at two magnifications: a) x200 and b) x500. One can observe is that the material consists in two zones: a light one and a dark one. The light one is the expected to be the metallic one consisting in iron and the dark one is the iron oxides (magnetite-Fe₃O₄ and wüstite-FeO) zone [11]. In the micrographs can also be observed some pores ranging from a few micrometers up to tens of micrometers. It can notice that the dark zone, the iron one, is a pseudo-continuous matrix. The composite compact consist in a pseudo-continuous iron matrix and oxides clusters.

Fig. 5 shows the scanning electron micrographs obtained for the Fe/Fe₃O₄ type sintered composite compacts after sintering at 1100 °C for 6 h (a) and after sintering at 1100 °C for 6 h and subsequent annealing at 550 °C for 4h (b). The SEM analysis comes to confirm the optical microscopy investigations which showed that the material consists in two types of zone: a quasi-continuous iron matrix – lighter zone and iron oxides clusters - darker zone. The iron oxide zones are similar with the Widmanstatten structure observed in steels. The sintered compacts microstructure is similar after the annealing treatment although the dark zone is formed by a single iron oxide type: Fe₃O₄.

Fig. 6. Distribution maps of the Fe and O chemical elements on a microzone of the compact sintered at 1100°C and annealed at 550°C obtained by X-ray microanalysis.

The distribution maps of the Fe and O chemical elements on a microzone of the compact sintered at 1100 °C and annealed at 550 °C obtained by X-ray microanalysis is displayed in Fig. 6. The iron element is distributed in the whole microzone that has been analyzed as expected; the iron is present, according to X-ray diffraction, as elemental iron and also in magnetite. It can be observed that in the lighter zone the iron concentration is larger as compared to the darker one as it was expected. The oxygen is uniformly distributed in the darker zones where the magnetite phase is present and is missing in the lighter zone.

Summary

Starting from Fe and Fe₂O₃ commercial powders Fe/Fe₂O₃ composite powder has been successfully obtained by mechanical milling. The milling time was up to 120 minutes and the median diameter of the particles decrease upon increasing the milling time. At the final of mechanical milling process the median particles size is at 7.2 μm. The Fe/Fe₃O₄ type composite was successfully synthesized by reactive sintering of the Fe/Fe₂O₃ composite powders obtained by milling for 60 and 120 minutes. After sintering a FeO-wüstite residual phase is also formed. This undesired FeO-wüstite phase was eliminated by applying annealing. The sintered composite materials of Fe/Fe₃O₄ type consists in a

quasi-continuous iron matrix in which iron oxides clusters are embedded. The iron clusters have two phases before annealing, Fe_3O_4 and FeO , and a single phase, Fe_3O_4 , after annealing. The microstructure of the sintered composite compacts have a structure that is like the Widmanstätten structure observed in steels. The same structure for the iron oxide cluster is mentioned also after the annealing.

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