Advanced Engineering Forum
ISSN: 2234-991X, Vol. 13, pp 3-8
doi:10.4028/www.scientific.net/AEF.13.3

Submitted: 2014-10-07
Revised: 2015-01-05
Accepted: 2015-02-16
Online: 2015-06-22

Composite compacts of Fe/Fe_3O_4 type obtained by mechanical milling-sintering-annealing route

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Keywords: mechanical milling, reactive sintering, magnetite, iron/iron oxide compacts.

Abstract. Fe/Fe_2O_3 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/Fe_2O_3 composite particles. After 120 minutes of milling the median particles size is at 7.2 μm. The Fe/Fe_3O_4 type composite were obtained by reactive sintering in argon atmosphere at 1100 °C of the Fe/Fe_2O_3 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 (Fe_3O_4 and FeO before annealing and Fe_3O_4 after annealing). The iron oxide clusters are analogous with the Widmanstatten 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 $MeFe_2O_4$, 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 Me^{2+}, 16 sites for Fe^{3+} and 32 for O^{2-}) dictates, in part, their electric and magnetic characteristics [6, 7]. Among the composites of ferrite-alloy type the iron-iron oxide (iron ferrite – $FeFe_2O_4$ (Fe_3O_4)) 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/Fe_3O_4 sintered composite compacts by an original mechanical milling-sintering-annealing route using as starting materials a mixture of iron and hematite (α-Fe_2O_3).

Experimental

Iron powder (NC 100.24 - Höganäs) and α-Fe_2O_3 (hematite - Alfa-Aesar) were used as starting materials for producing of Fe/Fe_2O_3 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+Fe_2O_3 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 Fe_2O_3 has been used as starting sample. Composite powder samples of Fe/Fe_2O_3 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 µm was used for particles size distribution and d_{50} 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 d_{50} parameter as a function of the milling time of the Fe+Fe_2O_3 composite powder. In the same figure are given for reference the d_{50} parameter of the Fe and Fe_2O_3 starting powders.

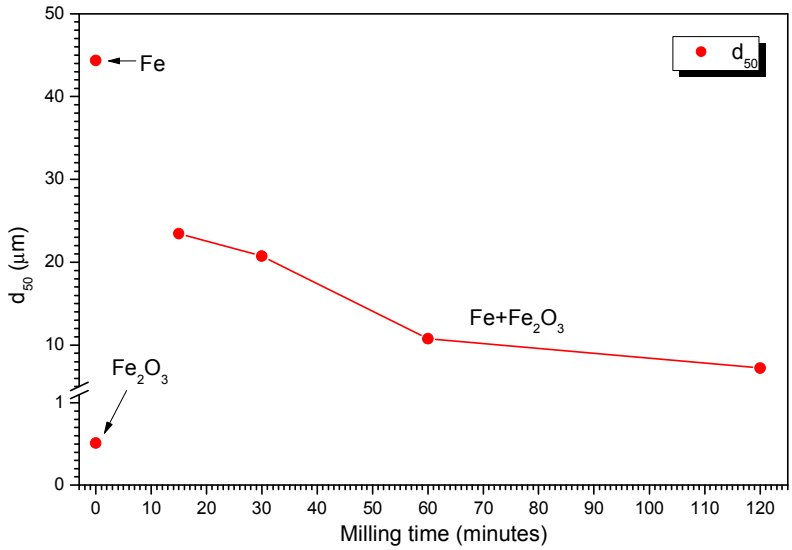


Fig.1. Evolution of the d_{50} parameter as a function of the milling time of the Fe+Fe_2O_3 composite powder. The d_{50} parameter of the Fe and Fe_2O_3 starting powders are given for reference.

It can be remarked the large difference between the iron particles (d_{50}=44.4 µm) and the fine hematite particles (d_{50}=0,2 µm) that have been used at starting materials in the mechanical milling process. One can be observed is that the median diameter of the particles decrease from 23.4 µm up to 7.2 µm upon increasing the milling form for 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/Fe_2O_3 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].

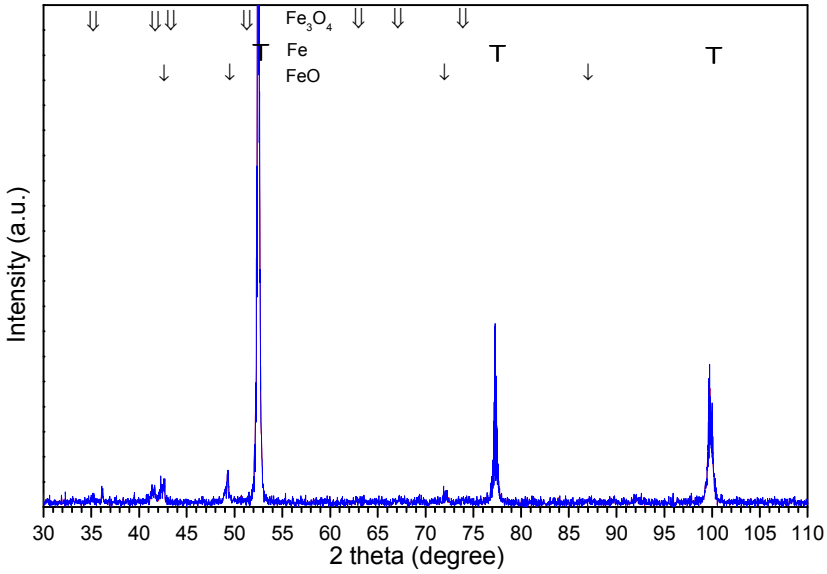


Fig. 2. X-ray diffraction pattern recorded with CoK_{α} radiation of the Fe/Fe_3O_4 type composite compact obtained by reactive sintering at 1100°C/6h in argon atmosphere starting from $Fe+Fe_2O_3$ composite milled powder.

The Fe/Fe_2O_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 CoKα radiation of the Fe/Fe_3O_4 type composite compact obtained by reactive sintering at 1100 °C/6h in argon atmosphere from $Fe+Fe_2O_3$ composite milled powder.

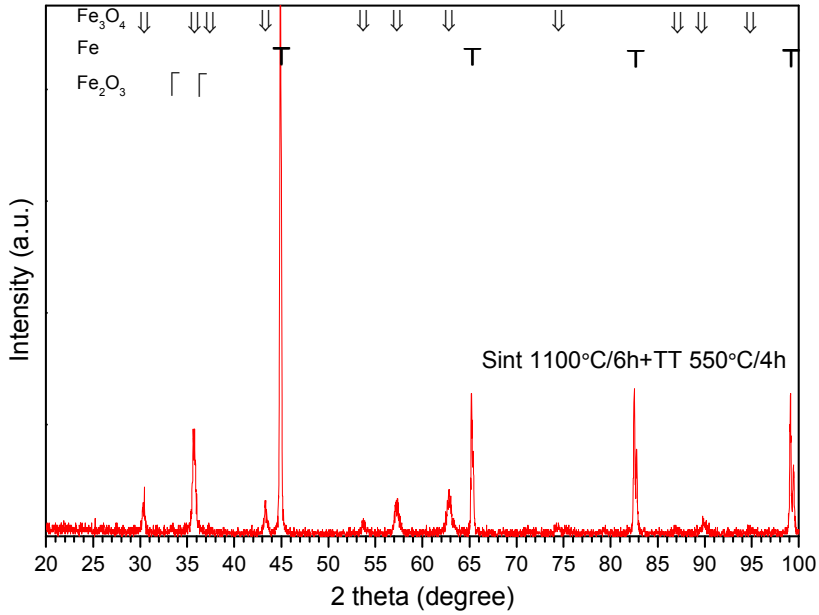
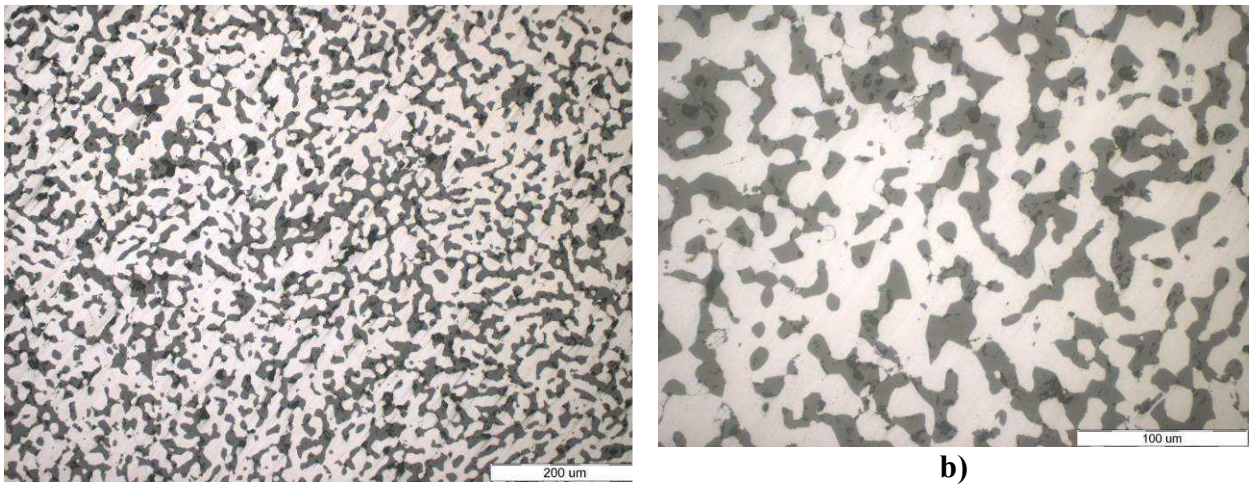


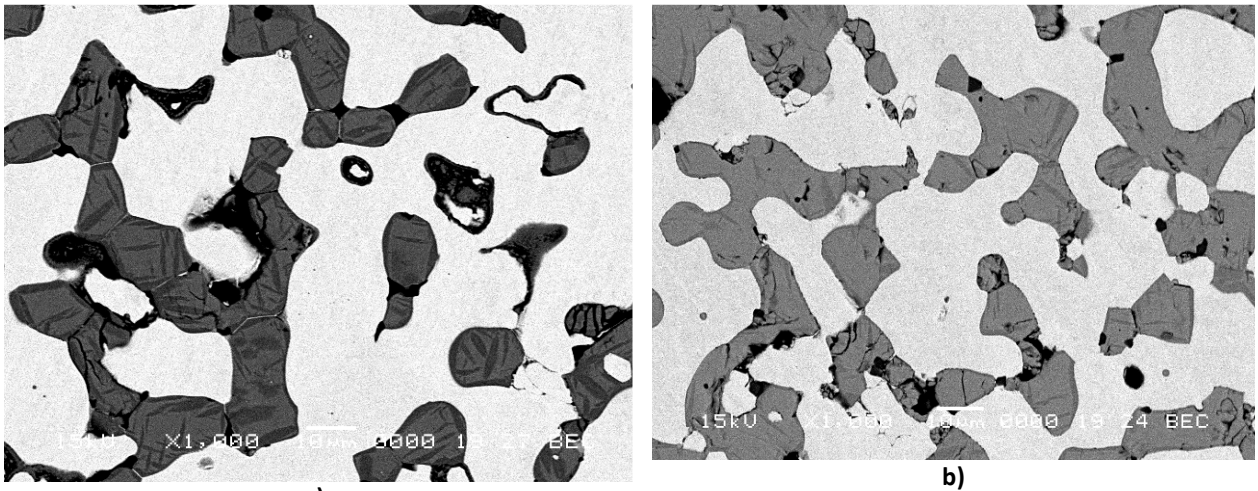
Fig. 3. X-ray diffraction pattern recorded obtained with CuK_{α} radiation of the Fe/Fe_3O_4 type composite compact obtained by reactive sintering at 1100°C/6h from $Fe+Fe_2O_3$ composite powder after annealing at 550°C/4h in argon.

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



a) b)

Fig. 4. Optical micrographs of a sintered compact obtained from $Fe+Fe_2O_3$ powder milled for 60 minutes at a magnification of: **a)** x200 and **b)** x500.



a) b)

Fig. 5. Scanning electron micrographs of the Fe/Fe_3O_4 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, Fe_3O_4 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 Fe_2O_3 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 Fe_3O_4 can be obtained [13]. X-ray diffraction pattern recorded obtained with CuK_α radiation of the Fe/Fe_3O_4 type composite compact obtained by reactive sintering at 1100 °C/6h from $Fe+Fe_2O_3$ 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 Fe_3O_4. 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:

$$0.1 \cdot Fe_2O_3 + 0.9 \cdot Fe \rightarrow 0.075 \cdot FeFe_2O_4 + 0.875 \cdot Fe \qquad (1)$$

The undesired FeO phase was eliminated, but a very small amount of Fe_2O_3 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 Fe_2O_3 and 19-0629 for Fe_3O_4 were used.

In fig. 4 are presented the optical micrographs obtained for the Fe/Fe_3O_4 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-Fe_3O_4 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/Fe_3O_4 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: Fe_3O_4.

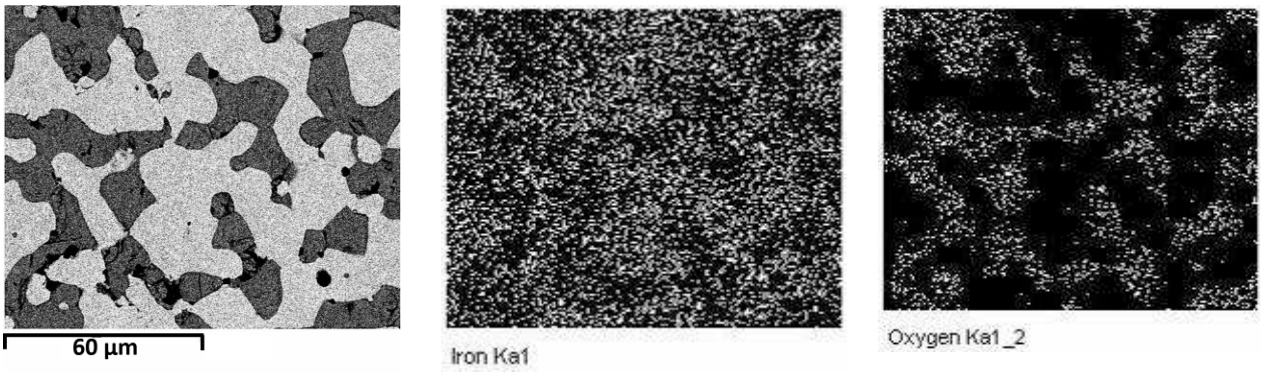


Fig. 6. Distribution maps of the Fe and O chemical elements on a microzone of the compact sintered at 1100°C and annealed at 550°C obtained by X-ray microanalysis.

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 were the magnetite phase is present and is missing in the lighter zone.

Summary

Starting form Fe and Fe_2O_3 commercial powders Fe/Fe_2O_3 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/Fe_3O_4 type composite was successfully synthesized by reactive sintering of the Fe/Fe_2O_3 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/Fe_3O_4 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 Widmanstatten structure observed in steels. The same structure for the iron oxide cluster is mentioned also after the annealing.

Acknowledgment - This work was supported by a grant of the Romanian National Authority for Scientific Research, CNCS – UEFISCDI, project number PN-II-RU-TE-2012-3-378.

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