# Mechanochemical processing of Zn–ferrite powders and their magnetic characterization

J. P. Muñoz Mendoza, O.E. Ayala Valenzuela, V. Corral Flores, J. Matutes Aquino, S. D. de la Torre

## Abstract

Powder mixture of magnetite ($Fe_3O_4$) and elemental zinc (Zn) was high energy ball milled looking forward to synthesize a composite material able to enhance magnetic coercivity ($H_c$). Results revealed up to 449.1 Oe for powder mixture treated for 540 min milling. Specific saturation magnetization ($\sigma_s$) of 50.35 and 43.7 emu/g was respectively reached in samples ball milled for 300 and 540 min. Moreover, specific remanent magnetization ($\sigma_r$) of 3.976 and 9.507 emu/g was respectively obtained for samples ball milled for 60 and 540 min. It is speculated that the degree of magnetization developed on studied samples might be influenced from the metallic-contamination derived from milling wear media such as Fe, Cr and Ni (stainless steel). The Zn–ferrite powder mixture processing and its preliminary magnetization results are discussed.

Keywords: Magnetite; Mechanochemistry; Zinc–ferrites; MA

## Introduction

The mechanical alloying (MA) technique might be understood as a solid state reaction process, by which a powder mixture is alloyed throughout a series of high energy collisions occurring between milling media (balls) and powder particles, under a given atmosphere (usually inert) [9]. During the MA process powder particles are repeatedly deformed, fractured and cold-welded. The sort of milling device used typically depends on the final product features needed. Thus, either high or low energy mills can be used for a variety of precursor and product powders. Parallel to the particle size reduction and therefore creation of new surface area, both the open surface and bulk of the powder particles are mechanically energized up to the point of conferring the powder mixture with a high chemical reactivity apart from an atomic diffusion enhancement. Such phenomena might result in generation of materials, which thermodynamically are found out of equilibrium, such as solid solutions, intermetallics, amorphous, and/or unique composite materials which are difficult to synthesize by using conventional techniques.

The reducing effect of zinc with magnetite, processed using the MA technique has been previously studied by other researchers [1,2]. Apart from understanding the particle size refinement effect of the studied material, in this work it has been verified the reducing effect of Zn on magnetite as a function of the magnetic properties. Thus, the following chemical reaction:

$$Fe_3O_4 + 4Zn \rightarrow 3Fe + 4ZnO$$

proceeds in such a way that the appearance of francolinite ($Fe_3O_4$–Zn) gradually occurs along the MA action, continuing up to the point that iron oxide is finally metal-reduced whereas zinc oxidized. Free energy versus temperature (Ellingham) diagrams [4] indicate that elemental zinc may reduce the iron present in magnetite to fulfill the above reaction from left to right, but not the opposite. The conventional casting routes for inducing the above reaction, however, might lead to a microstructure fairly different from that attainable by mechano-chemical routes. The finally developed microstructure in the material influences its ultimate properties. The aim of this work is to analyze the magnetic behavior of the mechano-chemically processed Zn–ferrite powders.

**Experimental**

Magnetite and zinc powders were processed under inert gas atmosphere (Ar), using a SPEX 8000 mill. Used precursor raw materials were commercial $Fe_3O_4$ (97% pure) and Zn (99.9% pure) powders. The pot mill and the milling balls were made of stainless steel. The material/balls ratio was set to 59, 54/2, 634 and 22.6. This was decided considering that a smaller ratio would cause a less efficient particle diminution as well as an increase of the milling time. Milling times were set to 60, 180, 300 and 540 min from which four samples were eventually selected for analysis. Obtained specimens were characterized using some experimental techniques such as X-ray diffraction (XRD), atomic absorption (AA) and magnetic hysteresis loops. Hysteresis loops were measured using a LDJ vibration magnetometer through a maximum applied field of 16,000 Oe. The real calculus of the specific remanent magnetization was omitted for all hysteresis loops shown in this work. This was due to a mathematical correction done to fit our measuring system involving the specimen holder.

**Results and discussion**

XRD: Figs. 1 and 2 correspond to the XRD patterns of magnetite and zinc precursor powders and its stoichiometric mixture after being treated for several milling times, respectively. These figures reveal that main diffraction peaks of precursors tend to shorten and meld as the milling time rose. Although with some 2θ angle deviation, nearly similar shape of patterns was obtained for the 60–300 min milled specimens.

This suggests the gradual lattice network-combination of reactants to form francolinite. Exception is powder sample obtained after 540 min where the XRD pattern is associated to another unidentified crystalline phase. For this later specimen, two new peaks diffracting at 44° and 61° were visible indicating the presence of elemental Fe, as well as $Fe_3O_4$ [1].

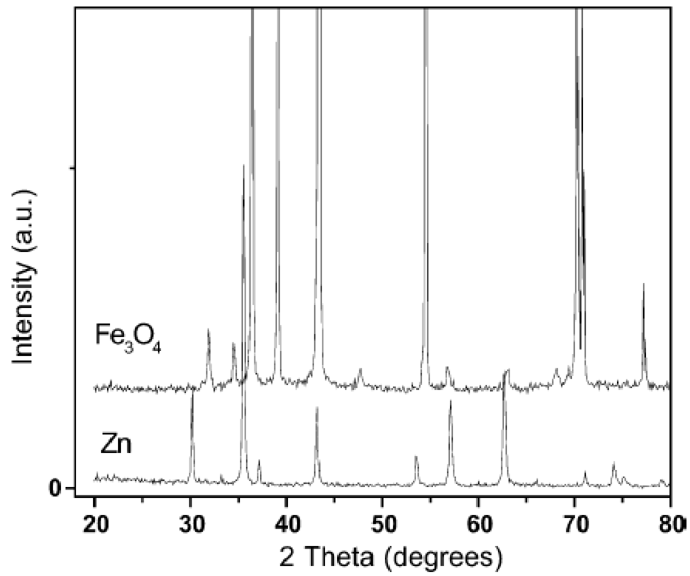


Fig. 1. XRD patterns of original precursor powders.

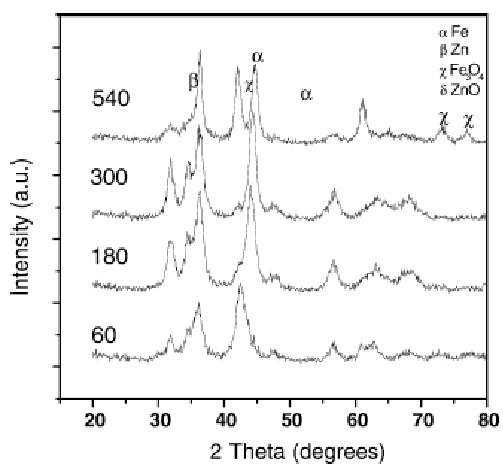


Fig. 2. XRD patterns of powder mixture in Fig. 1 after being milled at indicated times (min).

Similarly, two other peaks found at 73° and 76° indicate that $Fe_3O_4$ is left in the powder product. Elemental Zn is revealed from reduction of the peaks intensity at 31.5° and 56° ZnO is also evident from its main diffraction peak occurred at around 36.5°.

Metallic contamination of studied powder mixture: The milling action of the precursor powders, carried out using stainless steel media ended up with a sort of elemental-metallic contamination, which was monitored using atomic absorption analysis is reported in Fig. 3.

Not only the concentration of iron but also that of chromium was found to rise as the milling time increased. For magnetic effect purposes, however, Fe plays a stronger effect. The reduction of zinc, on the other hand, is due to the fact that it oxidizes as ZnO.

Magnetic analysis: Hysteresis loops shown Fig. 4 corresponds to the obtained from powder samples milled for 540, 300, 180 and 60 min and the original mixture of zinc and magnetite before the milling operations. In this figure, both the coercitivity rise and hysteresis loop area are seen to enlarge as the milling time rose. The appearance of hysteresis loops lightly tilted to the x-axis is due to the omission in calculating specific remanent magnetization. It is highly probable that the gradual incorporation of Fe into the powder product due to erosion of the milling media has enhanced Hc making the material harder magnetically speaking.

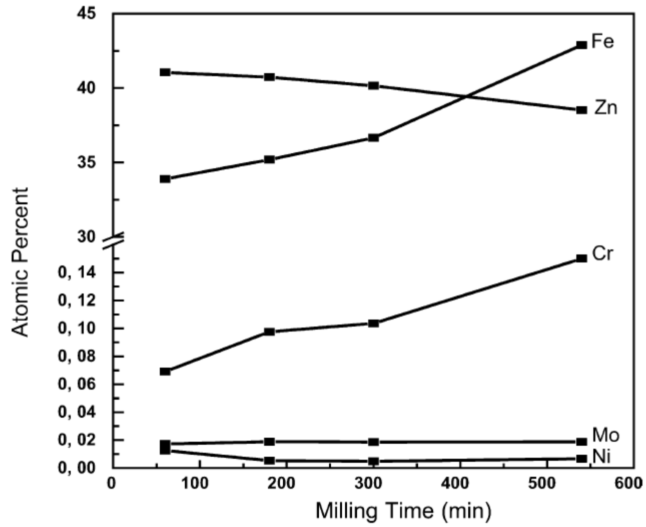


Fig. 3. Atomic percentage of metallic traces monitored as a function of milling time. These metals were incorporated into the precursor powder mixture of magnetite and elemental zinc.

However, it is evident from Table 1 that the specific magnetization saturation keeps on rising up to 300 min milling before dropping at 540 min. This magnetization enhancement is associated to the gradual increase of metallic Fe, whereas the final drop concerns formation of non-magnetic ZnO.

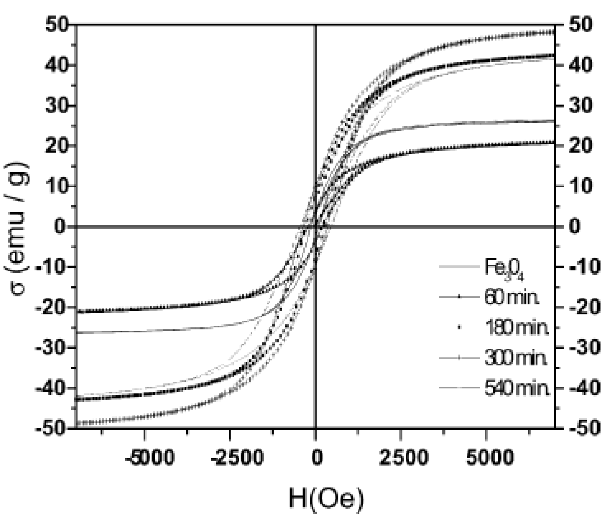


Fig. 4. Magnetization curves of powder mixture in Fig. 3 after being milled at indicated times, and the curve of the original powder mixture of zinc and magnetite.

Coercitivity $H_c$ reached its maximum value at 540 min milling, whereas $\sigma_s$ did at 300 min. In order to obtain the real $\sigma_r$ data, however, an intrinsic de-magnetization factor must be considered since the studied material is one of the medium-soft types. At the moment of writing this report no correction has been performed on the data listed in Table 1, nor in the hysteresis loops of this work figures. Literature suggests that this sort of ferrites might have $\sigma_r$ values equivalents to 80% of the specific saturation magnetization [3].

The atomic diffusion rate of metallic elements and oxides in most solids is a function of several factors [5], including working temperature and pressure, microstructural and crystalline defects [6], reactivity (nature) of materials, among other possible experimental parameters [7]. It has long be known that activating metallic and/or oxide systems through the usage of the mechanical alloying technique, also called mechanochemistry (depending on the sort of solid reactions occurring) might substantially enhance atomic diffusion after a given time of mechanical energization [2]. Thus, due to larger surface area and promotion of more grain boundaries thermodynamic barriers can be overcome [8].

Table 1
Magnetic parameters measured from $Fe_2O_3$ and Zn powder mixture milled at indicated times

| Sample (min) | $H_c$ (Oe) | $\sigma_r$ (emu/g) | $\sigma_s$ (emu/g) |
|---|---|---|---|
| $Fe_3O_4$ + Zn | 115.8 | 3.06 | 27.07 |
| 60 | 204.7 | 4.483 | 22.12 |
| 180 | 272.6 | 8.318 | 44.19 |
| 300 | 354 | 12.314 | 50.35 |
| 540 | 449.1 | 11.46 | 43.7 |

The studied system is energetically favored so that it is not surprising to form a magnetic-properties disclosing zinc–ferrite. Once the proposed reaction starts taking place upon milling and either elemental traces of Fe increase, enhancing magnetization of the system and parallel making Zn to oxidize reducing magnetization, the finally attained $H_c$ increases because the number of magnetic domains was also increased. Although not shown here, it was found by SEM microscopy that sub-micrometer sized clusters develop as the milling time increases. Once oriented due to the magnetic field applied these clusters, in turn, acting as tiny magnetic domains tend to rise $H_c$. After the magnetic field is removed such clusters might retain its orientation such that coercitivity remained risen.

$Fe_3O_4 + 4Zn \rightarrow 3Fe + 4ZnO$ containing francolinite.

Apparently, the above reaction might be fully completed providing that the milling time was allowed to extend. This, however, might not be the case since the formation of a metastable phase called francolinite temporarily tricked the system's thermodynamic. Francolinite might be used in applications such that magnetization is required to occur at intermediate times demanded by soft and hard materials, such as videotape recording ribbons.

**Conclusions**

A powder mixture of magnetite ($Fe_3O_4$) and elemental zinc (Zn) was high energy ball milled and its magnetic coercivity ($H_c$) was enhanced. It is speculated that the degree of magnetization developed on studied samples might be influenced from the presence of metallic-traces such as Fe and Cr.

**Acknowledgements**

This work was partially supported by Conacyt through the project no. 37507-U.

**References**

[1] L. Takacs, Nanocomposite formation and combustion induced by reaction milling, in: S. Komarnemi, J.C. Parker, G.J. Thomas (Eds.), Nanophase and Nanocomposite Materials, MRS Symposium Proceedings, vol. 286, 1993, pp. 215–220.

[2] L. Takacs, On the mechanism of displacement reactions initiated by ball milling, in: Proceedings of the 123rd TMS Annual Conference, San Francisco CA, 1994, p. 26.

[3] G. Bertotti, Hysteresis in Magnetism, Academic Press, New York, 2001.

[4] J.J. Moore, Chemical Metallurgy, Butterworth, Heinemann, 1990.

[5] G.E. Mursh, Atomic Diffusion in Defective Solids, Trans Tech Publications Limited, 1980.

[6] Y. Ming Chiang et al., Physical Ceramics Principles for Ceramic Science and Engineering, Wiley & Sons, 1996.

[7] S. Mitura, Nanomaterials, Elsevier, Amsterdam, 2002.

[8] E. Metcalfe, Microstructural Characterization: Characterization of High Temperature Materials, vol. 1, STS Press, McLean, 1989.

[9] P.R. Soni, Mechanical Alloying, Cambridge International Science Publishing, 1999.