

Synthesis and magnetic properties of zinc ferrite from mechanochemical and thermal treatments of Zn–Fe₃O₄ mixtures

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Abstract

The preparation of ZnFe₂O₄ from mechanochemically activated reactive mixtures Zn–Fe₃O₄ is studied. The physicochemical and structural evolution of the system is analyzed by X-ray diffraction, vibrating sample magnetometry, differential thermal analysis and scanning electron microscopy. The activated mixtures reacted towards the formation of ZnFe₂O₄ at lower temperatures than the non-activated ones. In addition, thermal treatments as a function of time revealed a non-expected magnetic behavior of some mixtures. In order to interpret this observation, a qualitative diffusional reaction model is proposed.

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1. Introduction

Soft magnetic ferrites with spinel structure are materials with a large variety of applications in electronic and telecommunication industries [1,2]. Spinel ferrites exhibit a wide range of magnetic properties, according to the variable cation distribution in the crystalline structure and the processing conditions employed [1,3].

In the last decade, high-energy ball-milling or mechanochemical activation has become an increasingly useful technique for synthesizing all kinds of materials [4–6]. Depending on the system and the activation conditions, this processing method may produce a solid-state reaction during the treatment at room temperature [7,8] or induce significant structural changes that can reduce the temperature needed to carry out certain reactions [9,10]. The products obtained

by this technique often present a defective crystalline structure and many of them are metastable phases.

Conventionally prepared franklinite (ZnFe₂O₄) is a normal spinel with tetrahedral sites occupied by Zn²⁺ ions and octahedral sites occupied by Fe³⁺ ions. The conventional route to synthesize franklinite involves a long thermal treatment of a mixture of ZnO and Fe₂O₃ at 1200 K. The obtained material has structural and microstructural features that are critical for its final properties; besides, it is difficult to control them due to the severe processing conditions. Therefore, the development of alternative processing routes is a very important aspect in the synthesis of this ferrite.

The mechanochemical activation of reactive mixtures appears as a method to carry out the solid-state reaction in much more convenient conditions than those required by the traditional technique. In this work, a new route for synthesizing ZnFe₂O₄ starting from Zn–Fe₃O₄ mixtures is proposed, analyzing the effects of the mechanical and thermal treatments on the reaction evolution and the nature and magnetic properties of the obtained products.

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2. Experimental

2.1. Preparation of mixtures

The starting Zn/Fe₃O₄ mixtures were prepared in a molar ratio of 3:2. The reactants used were Zn powder (commercial reagent, 99%) and magnetite (concentrated ore, 97.5%). This mixture was mechanochemically activated in a Herzog HSM100 oscillating mill in air atmosphere. This equipment consists of a 200 cm³ milling chamber, which was charged with a cylinder and a concentric ring (both made of Cr–steel) and 60 g of reactive mixture, reaching a milling media-to-powder mass ratio of about 60. The chamber was put under planetary movement with a frequency of 12.5 Hz during times up to 30 min. Small portions of powder (about 2 g) were withdrawn from the mill every 6 min in order to follow the evolution of the activation process. The samples obtained were labeled ZFx, where *x* is the activation time, in minutes.

Samples ZF0 and ZF30 were thermally treated at 400, 500, 600 and 800 °C for 30 min in air atmosphere. Moreover, thermal treatments of these samples at 400 and 500 °C were performed at different soaking times. All the thermal treatments were made in an electric furnace in air atmosphere. The samples were heated as loose powders and quenched to room temperature after reaching the corresponding time.

The diffraction patterns were obtained using a Philips 1830/00 diffractometer, with Co–K α radiation at 40 kV and 30 mA. The magnetic measurements were carried out in a LakeShore 7300 magnetometer, coupled to an electromagnet, which is able to produce a magnetic field up to 15 kOe. Thermal analyses were performed in a Shimadzu DTA/TG-50H equipment in flowing air, using a heating rate of 10 °C min^{−1} and a sample weight of 40 mg. Micrographs were taken with a Philips 505 scanning electron microscope.

3. Results

3.1. Mechanochemical activation

Fig. 1 shows the X-ray diffraction (XRD) patterns of the ZFx series. A progressive decrease of the diffracted intensities for both phases can be observed. For magnetite this effect is mainly caused by the loss of the crystallinity, due to the accumulation of defects induced by the mechanical action. Besides, the oxidation of metallic Zn by atmospheric oxygen takes place. The Zn oxidation forms a very poorly crystallized ZnO. In fact, after 18 min of milling only weak intensity peaks corresponding to ZnO can be observed.

Scanning electron microscopy (SEM) micrographs (Fig. 2) of ZF0 and ZF30 reveal a great decrease of

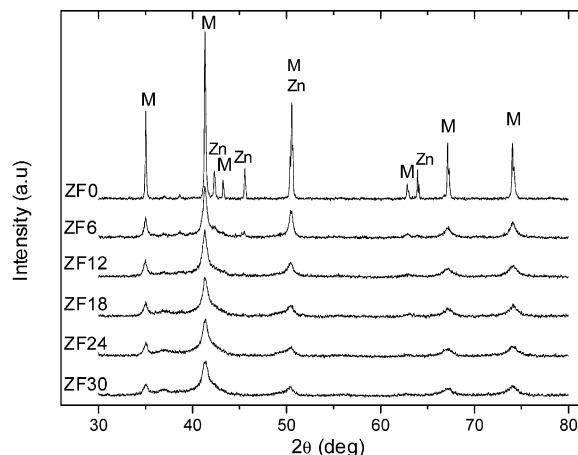


Fig. 1. XRD diagrams of the series of activated samples. M, magnetite (Fe₃O₄).

particle size, and a loss of the original morphology of the particles. In ZF0, Zn and magnetite particles can be clearly differentiated. Zinc particles have a spherical shape, with a mean particle size lower than 5 μm. In contrast, magnetite particles have an irregular shape and they are larger, about 10 μm. After 30 min of mechanochemical treatment, these morphological features completely disappear, and a homogeneous system with agglomerates of submicronic particles is observed.

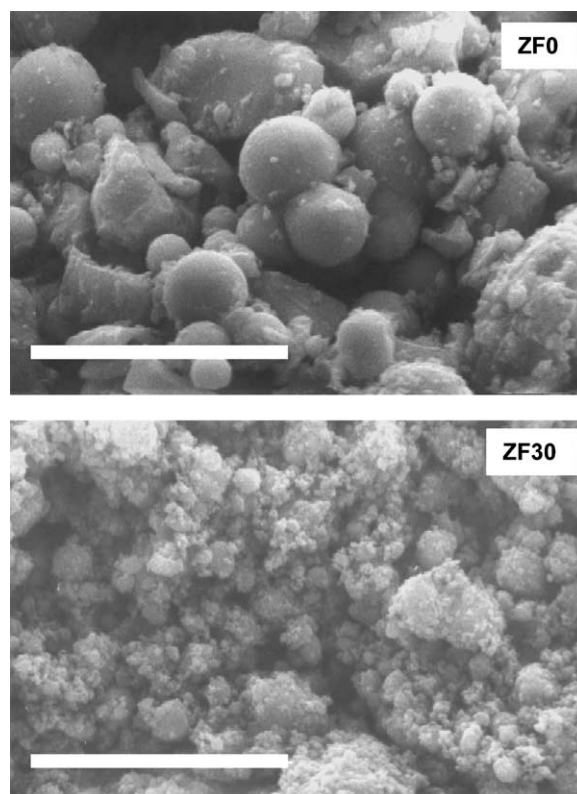


Fig. 2. SEM micrographs of the non-activated and the 30 min-activated mixtures. Bar, 10 μm.

Magnetization measurements as a function of an applied magnetic field reveal a continuous decrease of the saturation magnetization, M_s , with the activation time (Fig. 3). The total drop of M_s from ZF0 to ZF30 was 26%. This is due to the accumulated structural damage of magnetite (which is the only magnetic phase in the system), as it was observed by XRD (Fig. 1). The evolution of coercivity, H_c , with the activation time is also represented in Fig. 3. A steep increase of H_c can be observed up to 12 min of milling, because of the reduction of the particle size, which takes place mainly in the early stages of the mechanochemical process. From 12 min on, the coercivity starts to decrease slightly as a result of the increasing structural disorder.

Fig. 4a and b show the differential thermal analysis (DTA) and TG diagrams, respectively. For the non-activated sample, ZF0, two clear thermal events can be observed: the first one, at 420 °C, is an endothermic peak corresponding to the Zn melting; the second one, appearing at near 660 °C corresponds to an exothermic peak. At this temperature, TG analysis shows a mass increase of about 9% for ZF0. This value corresponds to the total oxidation of metallic Zn to ZnO and Fe_3O_4 to Fe_2O_3 . For activated mixtures, the endothermic peak is no longer detectable by DTA and the oxidation peak is widened and shifted towards lower temperatures (between 300 and 400 °C). Moreover, the intensity of this band decreases with the activation time. For activated samples an endothermic effect accompanied by mass loss can also be seen at near 265 °C. This thermal effect is assigned to the decomposition of zinc hydroxycarbonate formed during the milling. In fact, a sample of commercial hydrozincite ($Zn_5(CO_3)_2(OH)_6$) underwent this decomposition reaction at the same temperature [11]. The intensity of the decomposition band decreases from ZF6 to ZF30.

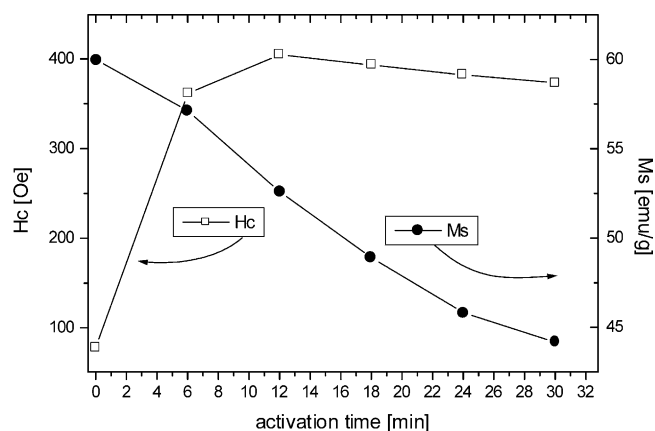


Fig. 3. Saturation magnetization, M_s , and coercivity, H_c , as a function of activation time.

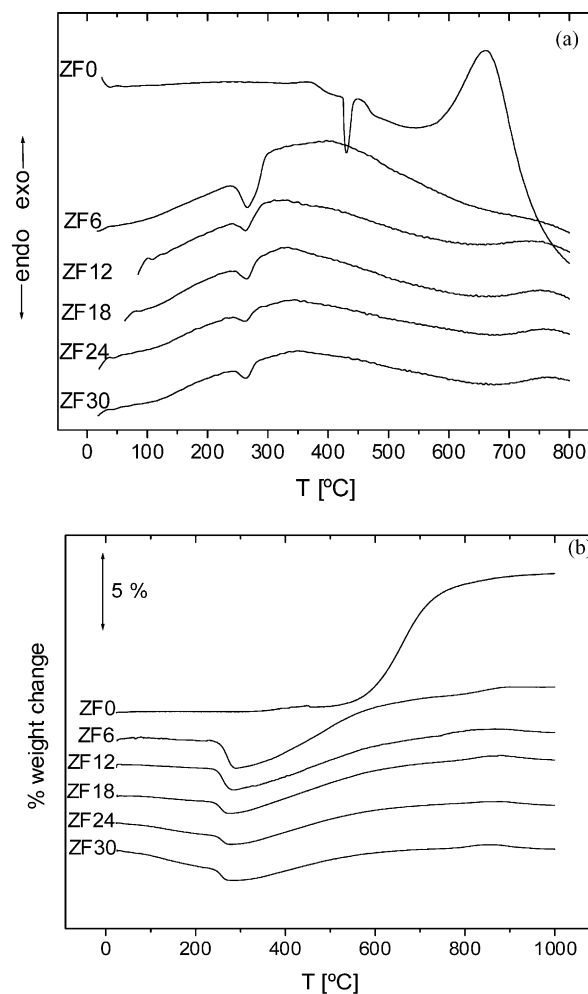


Fig. 4. DTA (a) and TG (b) traces for the series of samples ZFx.

3.2. Thermal treatments

XRD diagrams of ZF0 and ZF30 thermally treated between 400 and 800 °C are shown in Fig. 5. For ZF0 (Fig. 5a), the increase of temperature causes the formation of ZnO and Fe_2O_3 from the Zn and Fe_3O_4 mixture. The presence of franklinite in this mixture can be clearly detected only at 800 °C, together with much higher concentrations of hematite and zinc oxide. In contrast, for ZF30 the formation of franklinite takes place already from 500 °C on (Fig. 5b). This can be inferred from the shift of the diffraction peaks towards lower diffraction angles, since the crystalline structures of Fe_3O_4 and $ZnFe_2O_4$ are very similar and there is only a very slight difference between their lattice parameters. The hematite and zinc oxide content increases until 600 °C (especially for the former), but at 800 °C the material can be considered as $ZnFe_2O_4$ with very low amounts of Fe_2O_3 and ZnO as impurities.

Magnetic measurements (Fig. 6) show that for ZF0, M_s diminishes from 60 $emu\ g^{-1}$ (at room temperature) to 8 $emu\ g^{-1}$ (at 800 °C). This behavior agrees with the

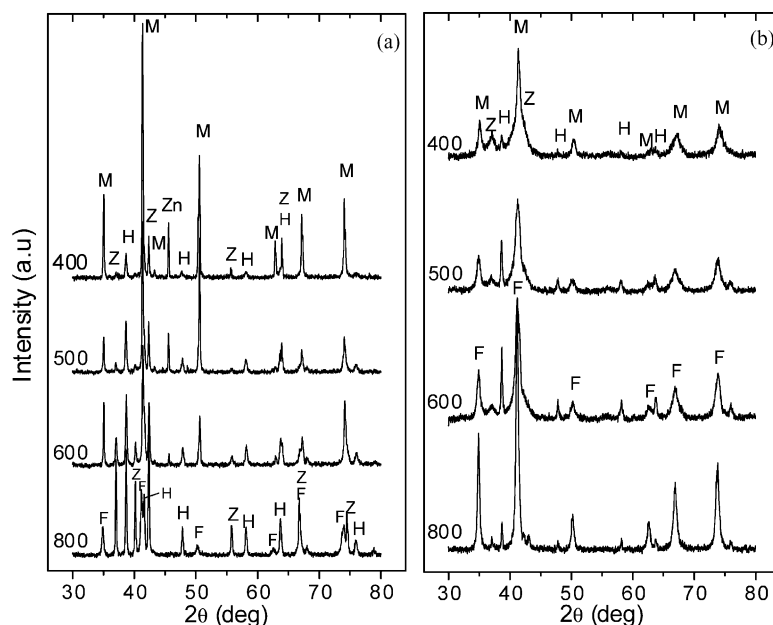


Fig. 5. XRD diagrams of samples ZF0 (a) and ZF30 (b) thermally treated at several temperatures for 30 min. M, magnetite; Z, zincite (ZnO); F, franklinite (ZnFe_2O_4); H, hematite (Fe_2O_3).

continuous formation of hematite observed by XRD and the simultaneous disappearance of the ferrimagnetic phase. However, for ZF30, the formation of franklinite rather than that of hematite can explain the decrease of M_s as function of temperature.

Fig. 7 displays the XRD diagrams of samples ZF0 and ZF30 heated at 400 °C for several soaking times. For ZF0 (Fig. 7a) the intensity of magnetite and zinc peaks decreases very slowly as a function of time. In fact, after 20 h of heat treatment most of the Zn and magnetite are not yet oxidized. Moreover, an increasing content of hematite is observed up to 5 h of thermal treatment. Franklinite is not detected in any of those heat treatments. For ZF30 (Fig. 7b), peaks corresponding to hematite are also observed. From 1.5 h on, a shift

of the diffraction peaks toward lower angles can be seen. This indicates the presence of ZnFe_2O_4 .

The diffractograms of the activated and non-activated samples heated at 500 °C during different times are shown in Fig. 8. For ZF0, a progressive decrease of the intensity of Zn and magnetite peaks is observed, together with the increasing appearance of ZnO and Fe_2O_3 (Fig. 8a). On the other hand, for ZF30, already at 1.5 h of heating it is possible to identify peaks of franklinite, which grow for longer treatment times (Fig. 8b).

Figs. 9 and 10 show the evolution of M_s as a function of the soaking time at 400 and 500 °C, for ZF0 and ZF30, respectively. For the non-activated mixture, an abrupt decrease of M_s is observed at short times (up to 1.5 h), which is followed by a slight increase of M_s . Finally, after 5 h of treatment, the saturation magnetization slowly decreases to 39.0 and 19.3 emu g^{-1} , at 400 and 500 °C, respectively. In contrast, ZF30 undergoes a continuous decrease of M_s , which is much more pronounced at 500 °C. In fact, at this temperature, M_s is as low as 6 emu g^{-1} after only 3 h of heating, indicating that the magnetite has almost disappeared from the system.

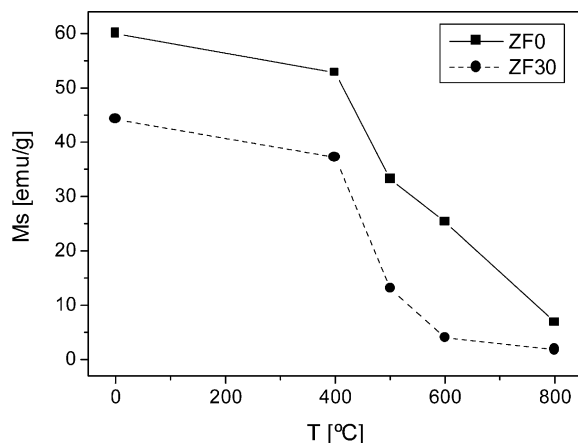


Fig. 6. Saturation magnetization, M_s , as a function of heating temperature for samples ZF0 and ZF30.

4. Discussion

The mechanochemical activation produces both morphological and compositional changes in the Zn– Fe_3O_4 reactive mixtures. However, unlike other studies related to the mechanosynthesis of ZnFe_2O_4 [12,13], the activation is not able to form this ferrite in the studied milling

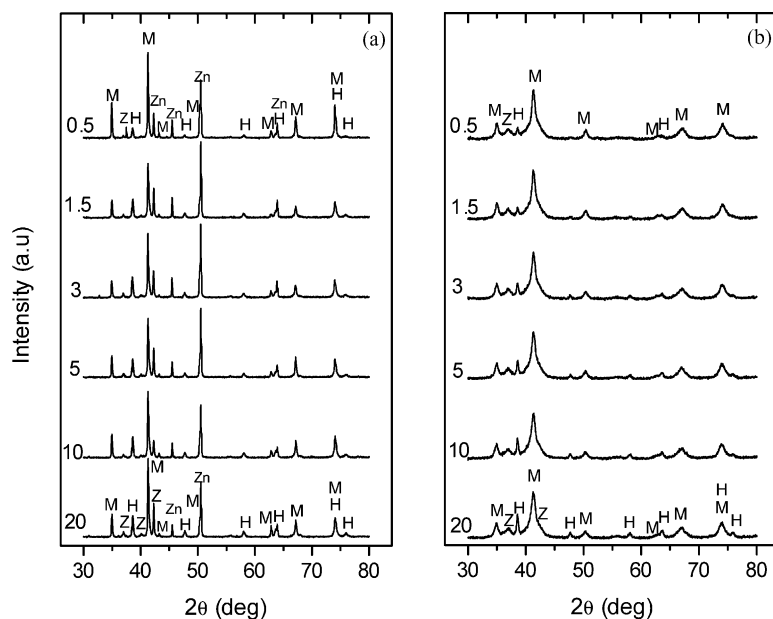


Fig. 7. XRD diagrams of samples ZF0 (a) and ZF30 (b) heated at 400 °C for several soaking times (h). M: magnetite; Z, zincite; H, hematite.

conditions. In our case, the mechanochemical processing induces significant changes in the thermal behavior of the system, as evidenced by the thermal analyses. The oxidation temperature of Zn decreases 250 °C from ZF0 to ZF6, and only 50 °C more from ZF6 to ZF30. This fact is probably related to the dramatic decrease of particle size observed in the early stages of the milling, which involves an increase of the particles' surface area

and an increased reactivity towards the oxidation of Zn. Moreover, the mechanochemical activation of the solid leads to the absorption of atmospheric CO₂ and H₂O, yielding zinc hydroxi-carbonate (about 10 wt.%), which could be a very reactive precursor for the formation of franklinite. The thermal treatments of ZF0 and ZF30 at different temperatures prove the effects of the mechanical treatment on the formation of ZnFe₂O₄ at low

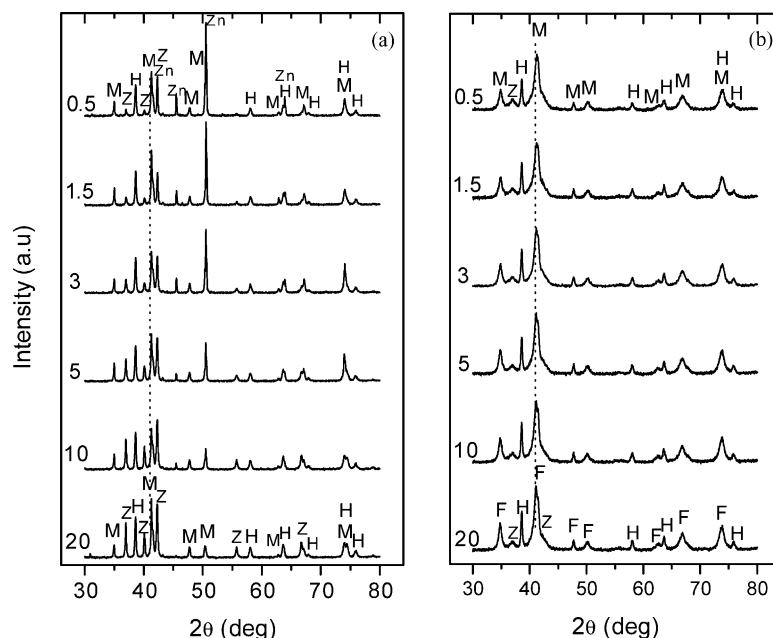


Fig. 8. XRD diagrams of samples ZF0 (a) and ZF30 (b) heated at 500 °C for several soaking times (h). The dotted line indicates the position of the maximum intensity peak of franklinite. M, magnetite; Z, zincite; H, hematite; F, franklinite.

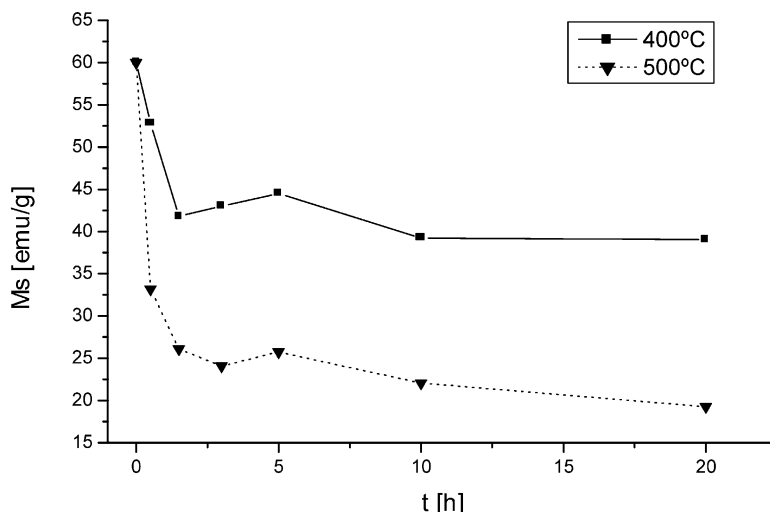


Fig. 9. Ms as a function of soaking time for sample ZF0 heated at 400 and 500 °C.

temperatures. In fact, for ZF30 the reaction starts already at 500 °C, and after 30 min at 600 °C the reaction is almost completed.

The thermal treatments performed at 400 and 500 °C as a function of heating time show a marked difference of reactivity between the activated and the non-activated mixtures.

As it was mentioned before, hematite begins to form immediately, and for that reason Ms decreases right after. Hematite most probably appears on the surface of magnetite particles when magnetite partially oxidizes.

The transitory and slight rise of Ms for ZF0 between 1.5 and 3 h indicates the presence of an intermediate stage between magnetite and franklinite. In order to observe an increase in Ms, at least part of the intermediate layer must have higher magnetization than magnetite. This intermediate composition layer will have the composition $(\text{Zn}_x\text{Fe}_{1-x})\text{Fe}_2\text{O}_4$ with $0 < x < 1$. In order to form franklinite Zn^{2+} ions must

diffuse through hematite replacing Fe^{2+} ions in the magnetite structure. This can be accomplished by a gradual replacement of Fe^{3+} ions in A sites by Zn^{2+} ions, those Fe^{3+} going into B sites replacing Fe^{2+} ions. In this way, the presence of non-magnetic Zn^{2+} ions breaks the balance between the magnetic moments of tetrahedral and octahedral Fe^{3+} ions, increasing the net magnetization. As the Zn^{2+} diffusion proceeds, the replacement of Fe^{2+} cations in the magnetite structure and the enhancement of magnetization occur. The intermediate structure forms with rising x (and Ms) up to about $x = 0.5$. Afterwards, as $x > 0.5$, Ms decreases until stoichiometric franklinite is formed ($x = 1$). However, at long soaking times (up to 5 h) the oxidation of magnetite becomes prevalent and the Ms of the system gradually decreases. For ZF30 the evolution of the reaction is completely different and both at 400 °C and 500 °C the magnetization continuously decreases because of the transformation to franklinite. This remark-

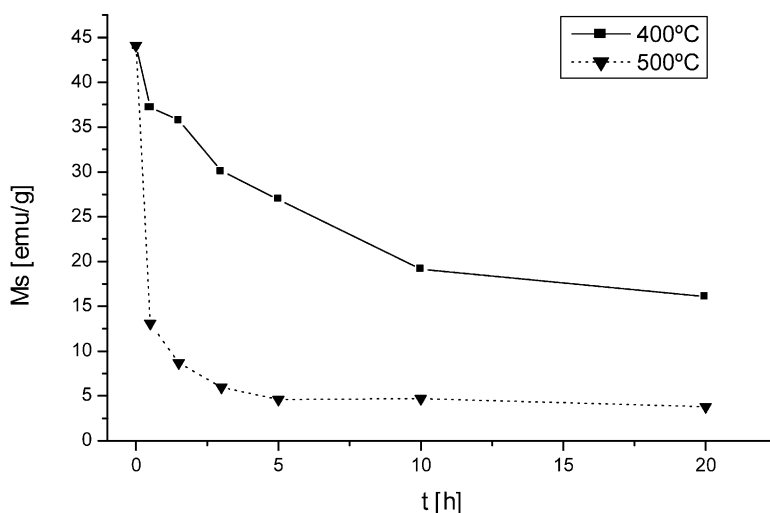


Fig. 10. Ms as a function of soaking time for sample ZF30 heated at 400 and 500 °C.

able difference can be understood taking into account the new diffusion paths and interfacial contacts provided by the mechanochemical treatment, leading the reaction to the direct formation of ZnFe_2O_4 .

5. Conclusions

The mechanochemical activation of $\text{Zn-Fe}_3\text{O}_4$ mixtures produced morphological, structural and compositional changes. In the early stages of treatment, the main observable effect was a significant decrease of particle size, which was followed by the oxidation of Zn, the absorption of CO_2 and H_2O , and the amorphization of the crystalline structures. The presence of franklinite was not detected during milling in the time range examined.

Marked differences of thermal behavior between the non-activated and the 30 min-activated mixtures were found. For this last sample, a reduction of about 200 °C in the temperature of ZnFe_2O_4 formation was observed.

During the thermal treatments at 400 and 500 °C, a solid solution $(\text{Zn}_x\text{Fe}_{1-x})\text{Fe}_2\text{O}_4$ was formed from the non-activated mixture. The magnetic properties of this phase allowed us to conclude that its formation is based on the replacement of Fe^{3+} by Zn^{2+} cations. This phenomenon was a consequence of the slow solid-state diffusion existing in the solid without activation. The formation of this solid solution did not take place in

conditions in which the diffusion is favored, e.g. longer thermal treatment and/or mechanochemical activation times.

The suitable combination of mechanical and thermal treatments made it possible to obtain ZnFe_2O_4 in much less extreme conditions than those used by the conventional method.

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