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Section 6: Nano-structured materials

RECRYSTALLISATION PHENOMENA DURING HIGH ENERGY BALL MILLING

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The structural and morphological evolution of the NiZn ferrite during mechanical activation has been investigated using X-ray diffraction (XRD), transmission electron microscopy (TEM) and chemical analysis. During the milling process an important amount of metallic phases due to the vials and balls contaminates the ferrite powder and functions as co-participant to the mechanical activation. The XRD- spectra of the as-milled powders showed the presence of the metallic contribution up to 200 hours of milling. For longer intervals of time the extralines intensities due to the presence of metallic phases decrease and only a spinel phase is observed after 400 hours of total milling. The TEM image revealed, after 200 hours, spheroidal nanometric particles in the range 30-80 nm, alongside of some needle type particles. When the milling time was increased, some big plate monocrystals appear and grow. After 400 hour milling, polyhedral crystals 250÷1000 nm size could be observed in the powder.

Keywords: NiZn ferrite, Ball milling, Recrystallisation, XRD, TEM

1. Introduction

In recent years new methods of materials synthesis have received more attention. Of particular interest are low temperature technique, such as room-temperature ball milling, which offer the possibility of forming the structures exhibiting new and unusual properties [1-5]. High energy ball-milling allows refinement of the microstructure in the nanometer range, alloying between elements with significantly different melting points, initiation of chemical reactions at much lower temperatures than those to which they would normally occur, and also the synthesis of novel crystalline and amorphous phases.

During the milling, the solid grains are liabled to shocks and high pressure due to the ball crushing process. An important amount of vial and ball materials pollutes the sample when milling. The pollution is more or less important depending on many factors such as: the nature of the milling equipment, the milling time, the kind (dry or wet) of the milling, the durrity of the sample powder, etc. The main problem is that pollution exists always. For example, in vial with ball of WC, after 70 hours milling a α-Fe and α–Al_2O_3 mixture, the wolframic carbure is present in amount of 7% (wt) [6]. In most cases the pollution presence is only signaled, but it is rather neglected in the interpretation of materials properties. In some cases, its contribution is considered to be an additive one [7]. Therefore, the two powders are liable together to the same process, and could lead to a new product.

In this paper we investigated the evolution of the morphology of a classical NiZn ferrite during the high- energy ball-milling.

2. Experimental

The initial $Ni_{0.8}Zn_{0.2}Fe_2O_4$ ferrite composition was prepared from p.a. reagents purity (NiO, ZnO, Fe_2O_3 oxides) using the standard ceramic procedure. The sintering treatment was carried out up to 1250 ^{0}C, in oxygen gas-flow, for 24 hours. The resulted powder was wet milled in acetone, using a planetary high-energy ball mill in several stainless steel vials. The ball to powder weight ratio was 15:1 and the total milling time was 400 hours.

The prepared powders were analyzed after various periods of milling time (after 50, 100, 200, 300 and 400 hours respectively) using X-ray diffraction (XRD) by a Philips powder diffractometer employing CuK_α ($\lambda = 1.5406$ Å) radiation. Transmission electron microscopy (TEM) investigations were made using a microscope JEM-200 CX (200kW) on the as-milled powder. Chemical analysis was performed for all the samples.

3. Results and discussion

The XRD patterns for the initial ferrite, after 50, 100, 200, 300 and 400 hours of milling are presented in Fig. 1.

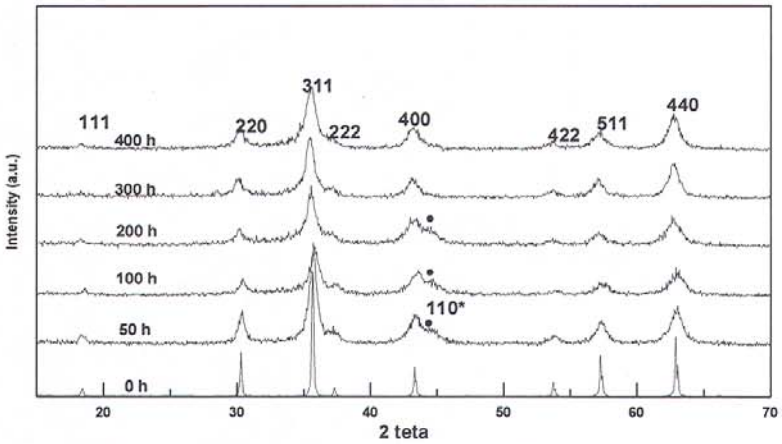

Fig.1. X-ray diffraction patterns of the NiZn ferrite powder after different periods of milling.
● denote peak positions of (Fe,Ni,Cr).

It is obvious that initial powder is well crystallized having a well-formed spinel structure.

After 100 hours of milling the lines are broad, indicating an important decrease of the particle size. Near the (400) spinel peak, a line corresponding to (110) peak of metals with cubic structure (Fe, Cr, Ni) belonging to the vial and balls, can be observed. In fact, after 50 hours of milling the quantity of extra powder due to the milling equipment is about 25% (wt). This quantity is not unusual, some authors [7,8] reporting pollutant additions up to 36% (wt), due to wet milling.

After 200 hours milling, the diffraction lines are more large indicating the continuously diminution of the particle size. The pattern shows, aside from the above-mentioned impurity, the increasing of the disorder degree and of the (400) peak intensity. The augmentation of this line, which was already visible after 100 hours of milling, was assigned to the peak (111) of an austenitic phase of inox steel (ASTM 31-619) resulting from the vial.

After 300 hours, the (100) peak corresponding to the cubic metallic phases couldn't be observed anymore and the (400) peak intensity is decreasing.

The diffraction patterns for the powders milled more than 300 hours revealed the presence of a spinel structure only.

Using TEM we observed the evolution of the powder morphology during the milling.

The powder milled 100 hours presents a pronounced aggregation degree. The aggregates wits dimensions in the range 100÷300 nm presents groups of particles tending to have plate-like form. The dominant structure is spinelic (Fig.2), as electronic diffraction pictures show.

After 200 hours milling the powder has a more heterogeneous character. Uniform spherical particles, having the mean diameter of about 43 nm, are present together with big aggregates (Fig.3) and aggregates of needle-like particles with spinel structure and length between 800 and 1200 nm (Fig.4).

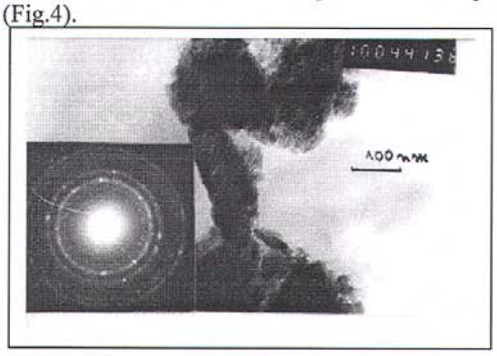

Fig. 2. TEM image of the powder after 100 h milling together with electron diffraction diagram.

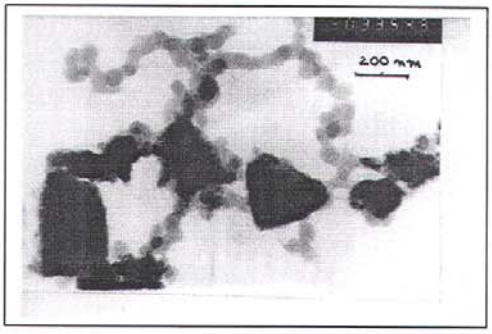

Fig. 3. TEM image of the powder after 200 h milling.

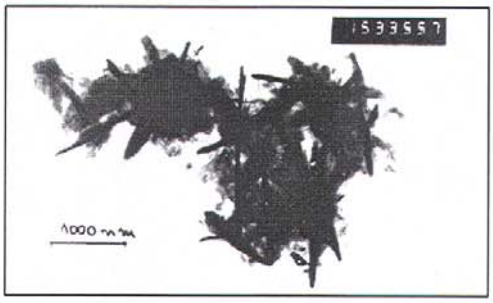

Fig. 4. TEM image of the powder after 200 h milling.

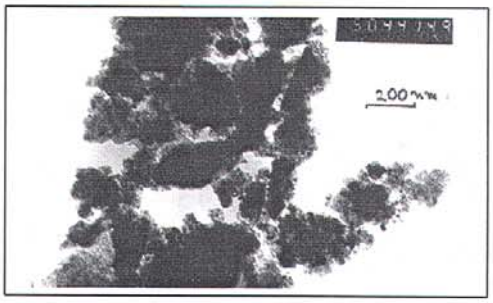

Fig. 5. TEM image of the powder after 300 h milling.

After 300 hours of milling, aside nanometer particles of about 15 nm, more or less aggregated (Fig. 5), are present some monocryatalline plates having spinel structure and different shapes and sizes (Fig.6). The plates are formed from 2 ÷ 5 needle-like particles tending to solder together along their big axes in order to produce big plates of about 4000 ÷ 6000 nm mean size (Fig.7).

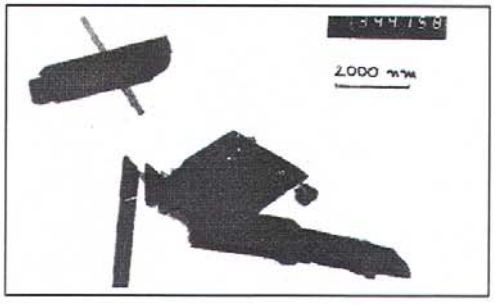

Fig. 6. TEM image of the powder after 300 h milling.

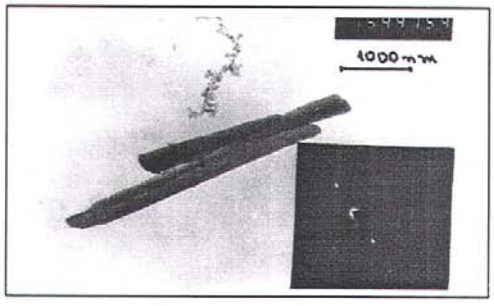

Fig. 7. TEM image of the powder after 300 h milling.

After 400 hours of total milling there could be observed big polycrystalline aggregates (about 2000 nm) aside big monocrystalline plates. Unlike the other samples, after 400 hours milling there is a

tendency of the spinel nanometric particles to reorganize by forming new aggregates (Fig.8). In the mean time there were observed some needle-like particles and thin plate polyhedral particles with rounded borders (Fig.9).

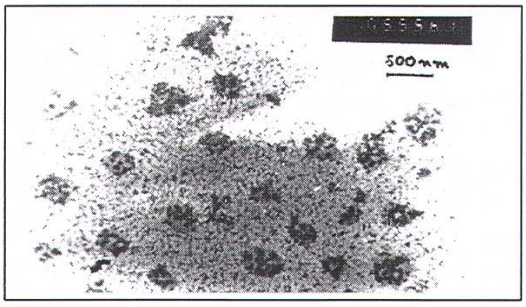

Fig. 8. TEM image of the powder after 400 h milling.

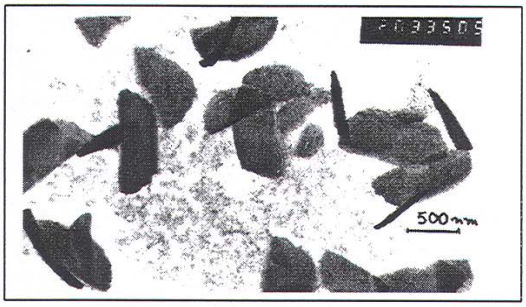

Fig. 9. TEM image of the powder after 400 h milling.

When interpreting the experimental results, one must take into consideration the fact that the ferrite and the pollution metallic powder are milled together. According to the chemical analysis, after 50 hours of milling the chemical elements content of the powders is quite unchanged.

It is known [9] that on the iron particles at high temperature anodic and cathodic reactions may start at distinct points situated on the metallic surface.

Owing to the very low solubility of magnetite, it should become the stable solid phase as soon as the $Fe3^{+}$ concentration exceeds a certain low value. Therefore, the films formed on iron are magnetite rather than ferrous oxide or hydroxide, which are relatively soluble. However, in the presence of oxygen, the dissolved ferrous hydroxide may be converted to magnetite at a distance from surface, where it cannot act as protective layer, so that the corrosive attack continues.

In the presence of the nanometric ferrite particles with very defected surfaces the metallic nanometric particles tend to form at first needle-like monocrystals having spinel structure. It is more probably that the chemical composition of the needles is different from the initial ferrite one and the presence of the large diffraction lines doesn't allow the observation of the two shifted spinelic structures.

By increasing the milling time, the morphology of the powder changes. The needle-like particles well formed after 200 hours begin to grow along the axis at first, and then they tend to solder together producing big plates of different shapes.

The disappearance of the diffraction peaks corresponding to metallic phases at the same time with the appearance of the monocrystalline particles having plates forms, indicates the fact that the metallic powders had an important role in the recrystallisation phenomena.

If the milling procedure continues, a new morphological changing process was present. The nanometer particles, with spinel structure tend to reorganize themselves by forming successive aggregates, leading to some thin plate polyhedral particles with rounded borders.

4. Conclusions

The experimental data revealed that, during the long high-energy ball-milling processes, the NiZn ferrite powder suffer a morphological evolution. This evolution is hardly influenced by the presence of metallic pollution phase due to the milling vials and balls and most probably by the nature of the solvent [10].

Generally, at least two morphological phases are always present in the powders. One of them-nanometric spheroidal particles –originated from the initial ferrite powder and the other one consisting of monocrystalline particles (needle like and plates). The latest was formed as the result of the

metallic particles function as a sort of crystallization seed. The interpretation of the properties of such a powder must be done carefully, taking into account the influence of the morphological aspect on the studied properties.

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