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Effect of milling time on microstructure of cobalt ferrites synthesized by mechanical alloying

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ABSTRACT

Purpose: of this paper is to determine the effect of manufacturing conditions, especially milling time, on the microstructure and phase composition of $CoFe_2O_4$ cobalt ferrite.

Design/methodology/approach: Cobalt ferrite ($CoFe_2O_4$) has been synthesised from a stoichiometric mixture of $CoCo_3$ and α-Fe_2O_3 powders in a high energy planetary mill. Annealing at 1000°C for 6 hours after milling was used to improve the solid-state reaction. Calcinated samples were analysed by X-ray diffraction (XRD), and transmission electron microscopy (TEM). The relationship between the milling time of powders, their microstructure, as well as their properties were evaluated. Particles size distribution and scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDX) examination were also made.

Findings: $CoFe_2O_4$ ferrites were successfully synthesized by mechanical alloying of α-Fe_2O_3 and $CoCO_3$ powders. The powder particles had undergone morphological changes with the increasing milling time. However, the milling time does not affect the ferrite formation rate. It is expected that the improvement of fabrication parameters can further enhance the properties of cobalt ferrite presented in this work.

Research limitations/implications: Contribute to research on the structure and properties of cobalt ferrites manufactured by mechanical alloying.

Practical implications: The reactive milling and subsequently annealing is an efficient route to synthesise cobalt ferrite powder. However, using steel milling equipment risks powder contamination with iron and chromium from the vials and balls.

Originality/value: The results of the experimental research of the developed ferrite materials served as the basis for determining material properties and for further investigation.

Keywords: Magnetic materials, Functional materials, Cobalt ferrite, Mechanical milling

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MATERIALS

1. Introduction

The dynamic rate of technology and the constant searches for new technological solutions broadly apply to materials with unique magnetic properties. The constant striving for the most efficient energy conversion has become the primary factor contributing to the development of magnetostrictive materials. Among them, special attention is paid to ferrites exhibiting giant magnetostriction. The factors influencing the magnetomechanical behaviour of these materials reports in the literature [1-5] are ambiguous. It leads to the search for optional solutions in order to maintain the advantages of using an optimal size distribution of cobalt ferrite particles while ensuring the most efficient energy transformation.

Moreover, although sintered ferrites have several advantages, the presence of residual porosity and non-magnetic impurities cause deterioration of their magnetic and magnetomechanical characteristics. In that case, the accuracy of the technological process is extremely important. Since the undefective crystal structure facilitates the movement of the domain walls under the influence of an external magnetic field, ferrites should be single-phase. Inclusions, impurities and other structural discontinuities make it difficult to migrate the domain walls and thus increase remanence. Due to the hardness and brittleness of ferrite ceramics, the technology of forming and sintering components is multi-stage and energy-consuming. In the ferrite sintering process, in addition to the maximum material density and grain size control, it is crucial to obtain an appropriate structure with evenly distributed ions in the crystal lattice [2, 6-9].

In recent years, there has been growing attention on cobalt ferrite. Due to saturation magnetization, mechanical hardness, high surface area, large positive first-order crystalline anisotropy constant, and relatively high coercivity it is an important spinel ferrite. Hence, it has been extensively used in high-density recording media, ferrofluid technology and medical field [10-12].

Nowadays, metal oxide nanoparticles have attracted more attention than their mass counterparts due to their remarkable optical, electronic and magnetic properties. The increasing interest in ferrite nanoparticles results from the possibility of their application in radio engineering, microwave and HD technologies, computing devices and storage devices [13-15].

Many synthesis strategies for preparing cobalt nanoferrites have been reported, among others: hydrothermal or combustion methods [4,6,16], sol-gel technique [1,14,15], coprecipitation [5,9, 16-18], micro-emulsion [2,8], mechanical alloying [3, 10-12, 19]. The applied production methods determine the final electro-physical properties of materials and their performance parameters.

Mechanical alloying is a high-energy milling process for producing metallic powders with a small scale micro-structure by milling elemental powders for a prolonged time. It is an efficient route for redistribution of cations, lattice strain inducing and grain refinement [20-23].

The aim of this work is to determine the effect of manufacturing conditions, especially milling time, on the microstructure of $CoFe_2O_4$.

The considerations presented in this article are preliminary studies and are part of a larger project, which includes, among others, crystalline size, magnetic properties (saturation magnetization, coercive force, permeability), and degree of inversion.

2. Experimental procedure

2.1. Sample preparation

To fabricate cobalt ferrites, commercial cobalt (II) carbonate ($CoCO_3$) powder with 99.5% purity and iron (III) oxide, α phase (Fe_2O_3) powder, both provided from ThermoFisher Scientific have been used. The morphology and particle size distribution of the base powders are given in Figure 1. The cobalt ferrites have been prepared using the powder metallurgy route. The $CoCO_3$ and Fe_2O_3 powders weighted with the stoichiometric ratios were mixed and milled to form the homogeneous powder mixture according to the formula:

$$Fe_2O_3 + CoCO_3 \rightarrow CoFe_2O_4 + CO_2 \quad (1)$$

A planetary mill Fritsch Pulverisette 5, was used to disperse cobalt carbonate and iron oxide powders. A stainless steel vial (500 cm^3 vol.) was filled with a mixture of powders together with 20mm stainless steel balls as milling media. The ball-to-powder weight ratio (BPR) of 100:1 was used. To verify the effect of milling conditions, different specimens were produced, varied in milling times (1, 2, 3, 4, 5 and 6 hours respectively) with milling speed 300 rpm. Mechanical milling was performed in series of 15 minutes of work and 15 minutes of standstill to allow free cooling of the milling containers. To obtain bulk samples, the ball-milled powder was put into a cylindrical mould

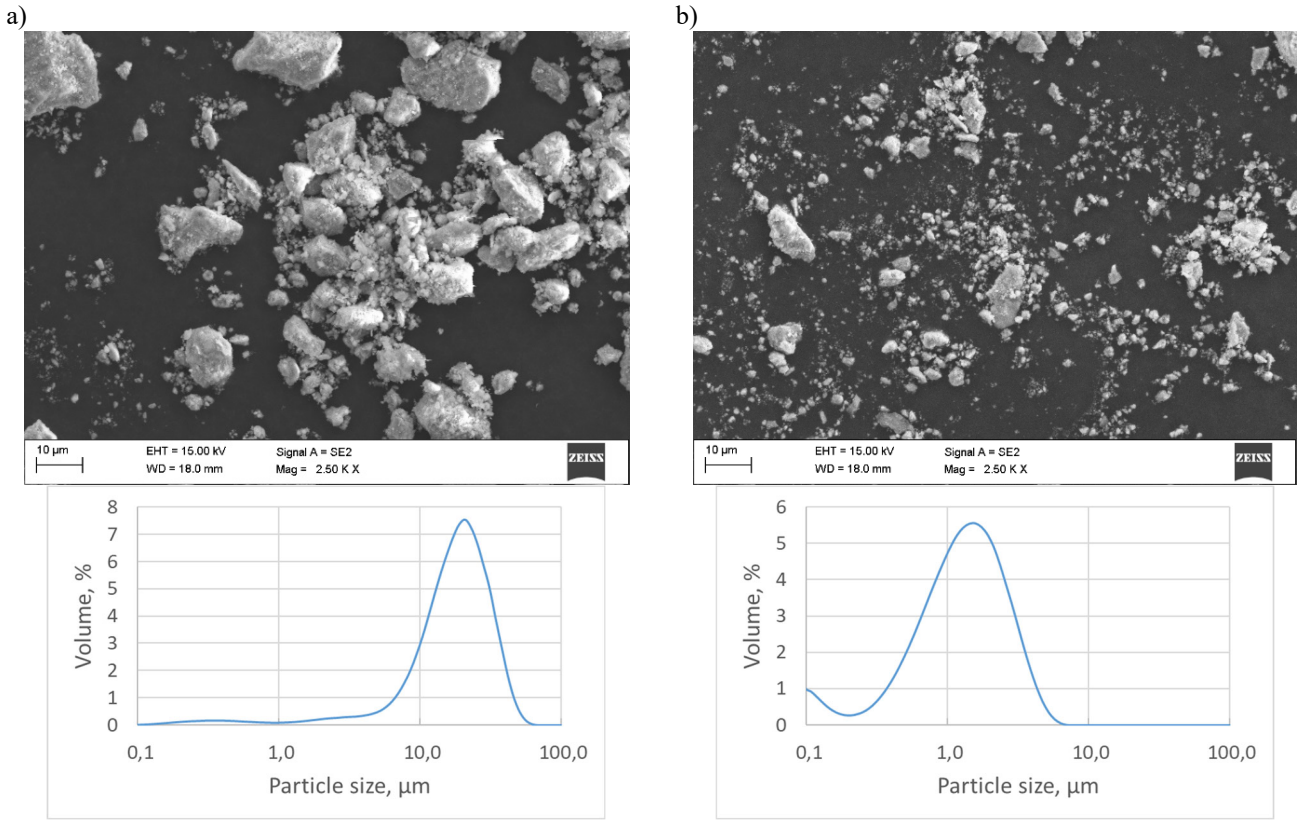

Fig. 1. Morphology and particle size distribution of: a) $CoCO_3$ and b) Fe_2O_3 powders in as-received state

11 mm in diameter, compressed using a hydraulic press with 500 MPa pressure and then calcinated in temperature at 1000°C for 6 hours in the air using a high-temperature chamber furnace (Czylok). No milling was performed after calcination.

2.2. Characterization

Investigation of particles size distribution has been realised on laser particle size analyser (Analysette 22 MicroTec Plus, Fritsch Gmbh), based on dual laser diffraction particle sizing system. Microstructural and morphological powder characterization were made in scanning electron microscope ZEISS SUPRA 35 (SEM) with Energy-Dispersive X-ray Spectroscopy (EDX) and by using the detection of secondary electrons at an accelerating voltage of 20 kV and a maximum magnification of 50000x. In order to determine the phase composition of the calcinated ferrite samples, X-ray diffraction analyses were carried out. An X-ray diffractometer X'Pert Pro MPD by Panalytical was used, which was equipped with a copper anode lamp, as well as a PIXcel 3D detector on the diffracted beam axis. The diffraction lines were recorded in the Bragg-Brentano geometry in the angular scope of 10-120° [2θ], with the step of 0.03° and the step time of 80s. The obtained diffraction patterns were analysed in the Panalytical High Score Plus software, containing a PAN-ICSD identification data. Microstructural analysis of calcinated ferrite was done using FEI S/TEM TITAN 80-300 electron microscope with HAADF and BF/DF detectors and energy dispersion spectrometer (EDS) from EDAX.

3. Results and discussion

Figure 1 shows SEM micrographs and particle size distribution of the $CoCO_3$ and Fe_2O_3 powders in the as-received state. The SEM studies show that $CoCO_3$ powder has an irregular shape and different particles size, mainly below 20 µm. It can also be seen that iron oxide powder is much smaller and formed in agglomerations of nanometric particles alongside micrometric size particles. It is clear from Figure 2 that powder particles had undergone morphological changes with the increasing milling time.

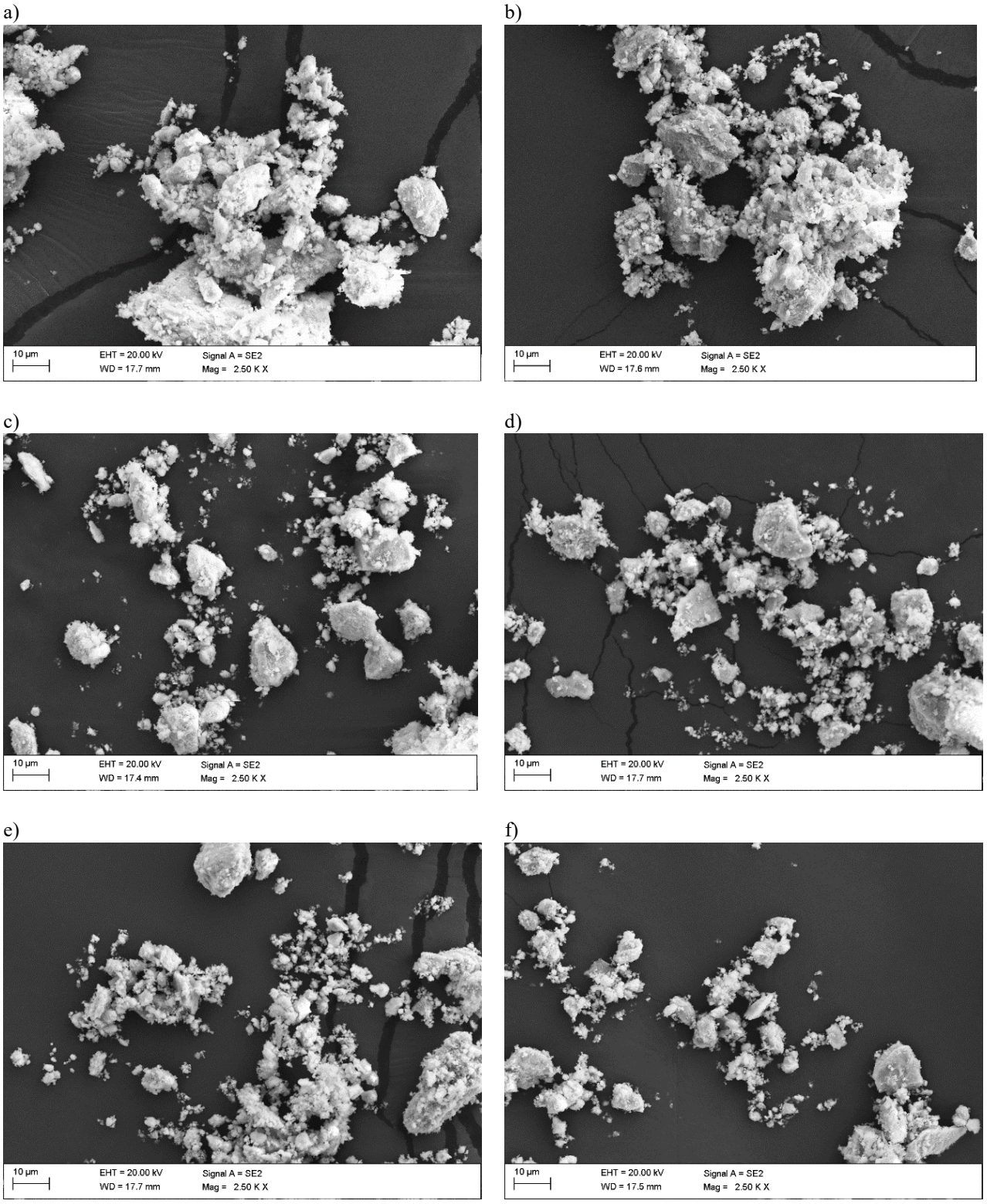

Fig. 2. Morphology of $CoCO_3$-Fe_2O_3 powder mixture after: a) 1; b) 2; c) 3; d) 4; e) 5 and f) 6 hours of milling

The powder pictures exhibit clear particles with well-defined boundaries having sharp edges. Mostly, the particles were homogeneously dispersed, but some agglomerated patches in some images. Longer milling time helped to suppress this agglomeration, and larger clusters were broken into smaller ones or individual particles. This can be recognised as the effects of a ball to ball, a ball to powder and ball to vial collisions on particles of mechanical milling leading to the particles refinement.

Figure 3 shows the particle size distribution of $CoCO_3$-Fe_2O_3 powders milled at different times. The particle size distribution of the $CoCo_3$-Fe_2O_3 powder is characterised by two apexes, which can be explained by the fact that the investigated powders are a mixture of particles with a largely differentiated size. The bimodal behaviour of particles size distribution at lower milling time is converted into uniform distribution with increasing milling time. The further analyses of milled powders confirmed the details obtained by SEM (Fig. 2).

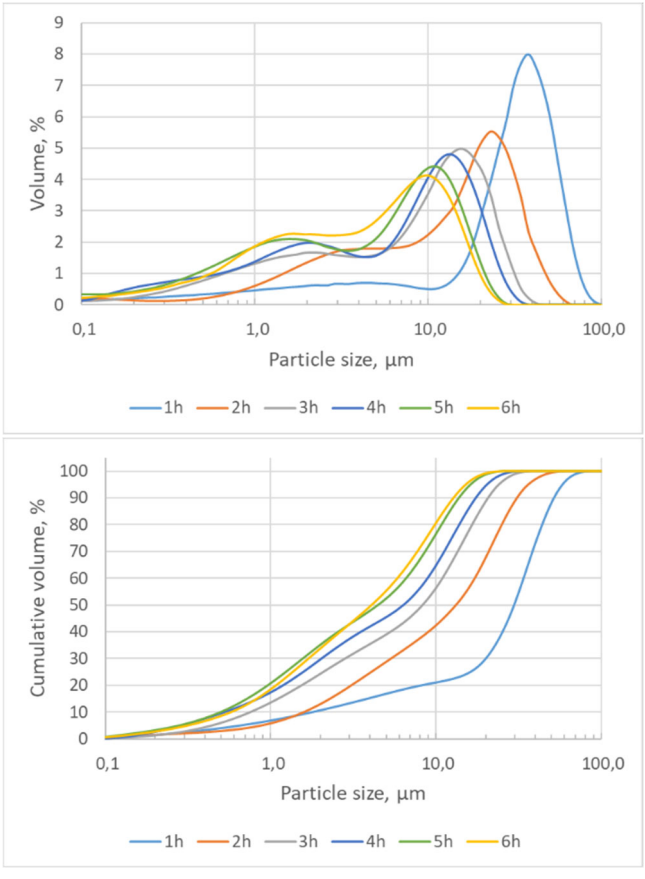

Fig. 3. Particle size distribution of $CoCO_3$-Fe_2O_3 powder mixture after different time of mechanical alloying

There are particles of a few micrometres and particles whose size is even in the nanometric range. For example, the median particle size D50 (Table 1) determined for the 1h milled powder is 29.17µm and decreases by increasing the milling time up to 4.17µm after 6h of milling.

Table 1.
Particle size parameters of $CoCO_3$-Fe_2O_3 powders

Milling time	1 h	2 h	3 h	4 h	5 h	6 h
D10	1.75	1.57	0.75	0.53	0.50	0.58
D50	29.17	13.01	8.39	6.35	4.34	4.17
D90	51.50	31.02	20.80	17.25	13.93	12.74

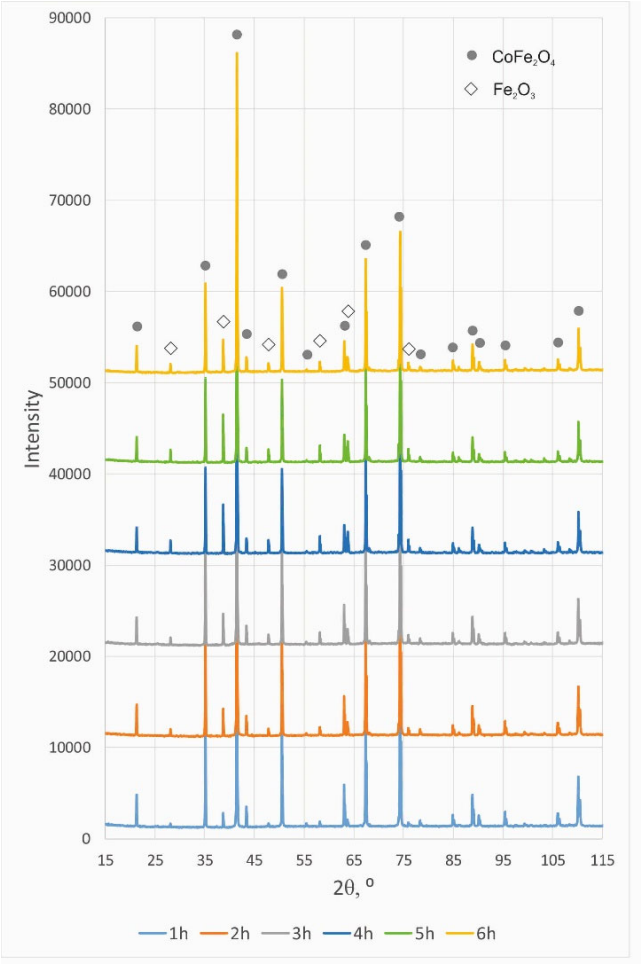

Fig. 4. XRD diffraction patterns of the calcinated samples

Figure 4 displays the X-ray patterns of milled samples under various milling times and subsequently calcinated at

1000°C in an air atmosphere. The calcinated powders present sharp peaks indicating the high crystallinity of the sample. For samples milled for several hours, it can be observed that mechanical milling produces a broadening of the Bragg peaks as a consequence of crystalline size reduction and the accumulation of lattice strain. The XRD peaks of the samples can be indexed with those of the $CoFe_2O_4$ [24] at 21.3°, 35.2°, 41.5°, 43.4°, 50.6°, 63.1°, 67.4°, 74.3° and 88.9°, which correspond to the crystal planes of (111), (022), (113), (222), (004), (224), (115), (044) and (335) respectively.

These peaks were indicative of single-phase spinel crystal structure. It is evident from the figure that in every ball-milling and calcinated powder mixture, the Fe_2O_3 phase as an unchanged base powder is visible. This may be due to the incomplete conversion of the basic substrates. However, the more likely cause is the effect of powder contamination during milling with iron from the milling vial and balls. Significantly, the iron oxide peak intensity increases gradually with increasing milling time. The approximate quantitative share of iron oxide in cobalt ferrite after calcination was estimated based on the RIR parameter (Reference Intensity Ratio). The amount of the Fe_2O_3 phase is increasing with the milling time from 7.5 to 11.2%. The EDX microanalyses (Fig. 5) confirmed the results obtained by XRD, which indicate contamination of the milled powders with elemental iron. In comparison, the starting sample EDX analysis indicated an iron/cobalt ratio of 2:1, this ratio increases upon increasing the milling time. For the 3 h milled sample, the Fe:Co weight ratio rises at 2.35:1, and after 6h of milling, the weight ratio of 2.63:1 is reached. A small amount of elemental chromium was also detected by X-ray microanalyses. The chromium impurities are provided by the vial material, which consists of stainless steel with around 20% of Cr. The contamination with chromium varying with the analyzed micro-areas and increases by increasing the milling time. The amount of chromium detected in the sample is about 0.5% at. for the sample milled by 1h and reaches 2.3% at. for the 6h milled samples. The samples are chemically homogeneous, and iron and cobalt are uniformly distributed in the milled powder. The chemical homogeneity is maintained upon increasing the milling time.

To determine the crystal structure of the obtained cobalt ferrites, TEM images have been analysed (Fig. 6). The selective area electron diffraction pattern (SAED) can be indexed to the contribution of polycrystalline $CoFe_2O_4$ phase.

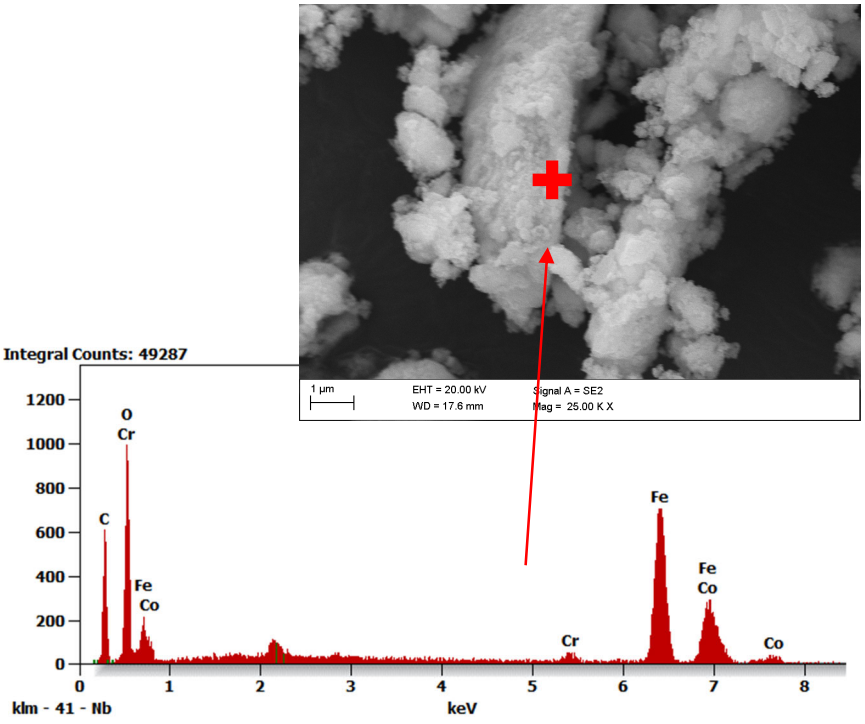

Fig. 5. Selected EDX micro-analyse obtained for a micro-area from 6 h milled powder

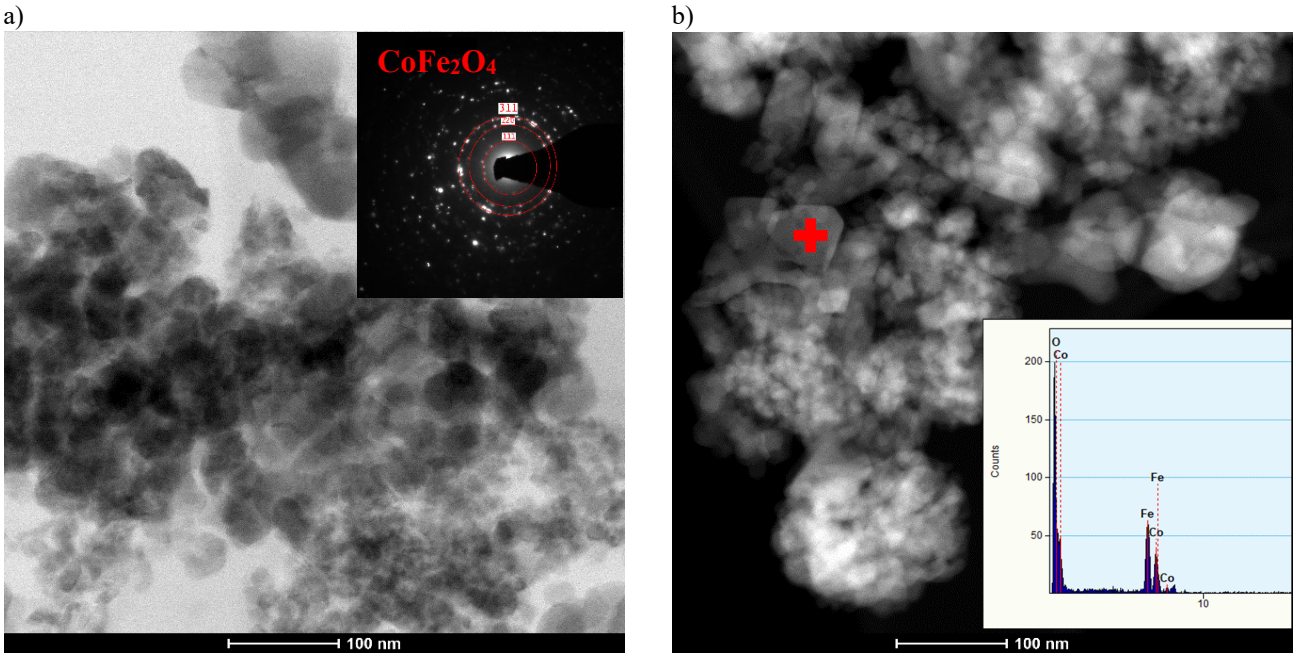

Fig. 6. TEM analysis of $CoFe_2O_4$ a) HAADF with SAED electron diffraction pattern and b) EDS results

The EDS analyses (Fig. 6b) confirm a high oxygen content (approximately 69-72% at.) and less than 19% at. of Fe and 9% at. Co content. TEM measurements show that the morphology of particles is equiaxed with a mean particle size of 20-30 nm. Additionally, it is worth noticing that small particles increased after thermal treatment.

4. Conclusions

Cobalt ferrite ($CoFe_2O_4$) has been synthesised from a stoichiometric mixture of oxides CoCo3 and α-Fe_2O_3 in a high energy planetary mill. Annealing at 1000°C (after milling) was used to improve the solid-state reaction. The milled powders were investigated by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, X-ray microanalysis and laser particle size analyser.

XRD patterns of the calcinated samples indicate that all samples have diffraction peaks related to the expected spinel structure of $CoFe_2O_4$. It is also revealed traces of Fe_2O_3 crystalline phase, caused by powder contamination during milling with iron. On the other hand, the milling time (considered here) does not affect on the transformation rate.

The obtained results confirm that mechanical alloying is a interesting technique for preparing of cobalt ferrite suitable for further processing. In this regard, changing the milling time may be a simple method to optimize the morphology of the ferrite particles.

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