RESEARCH ON THE DEVELOPEMENT OF CERAMIC PERMANENT MAGNETS BY MICROWAVE SINTERING

SUMMARY

A number of advanced technical fields such as telecommunications, mechatronics and robotics, electronics, miniaturized products, etc. contain soft or hard magnetic materials and their products, magnets.

It can be said that today almost no one electronic or electrical product can be developed without the presence of magnets. One of the industries concerned, namely micro-electromechanical systems (MEMS) involving an extensive use of soft or hard magnetic materials for products such as micro motors, actuators, etc.

In the permanent magnets field there are two trends: the development of magnets with higher properties and provide a low price / performance ratio.

In chapter one named **Current state of research on the development of permanent ceramic magnets** are presented aspects such as:

- Permanent magnets;
- Magnetic materials and magnetization processes;
- Technologies for manufacturing permanent magnets;
- Characteristics of permanent ceramic magnets;
- Applications of ceramic permanent magnets;
- Comparative analysis of the properties of permanent magnets

The main goal of the doctoral thesis aimed on the one hand, the development of the Ba ferrite nanopowders type M ($BaFe_{12}O_{19}$) (FB-M) by high energy mechanical milling in vario planetary ball mill and on the other hand, setting parameters for developing ceramic magnets from barium FB-M nanopowders by microwave sintering.

To achieve the intended purpose the following objectives were followed:

1. Setting up the optimal parameters for the development of barium ferrite nanoscale powders by mechanical milling using a Pulverisette 4 vario-planetary ball mill;
2. Studies on wet milling liquid additive to flow the slurry used for wet anisotropic die pressing;
3. Studies on the additive effect of milling fluid on the milling time and morphological and magnetic parameters of ferrite nanopowders;

4. Studies on the effects of microwave heating on structural and magnetic parameters of barium ferrite nanostructured magnets;
5. Optimization of microwave sintering parameters to reduce the sintering temperature and time.

Chapter II entitled **Design and implementation of experimental equipments** presents aspects on the design of equipments used for anisotropic wet pressing respectively for microwave sintering.

Thus, for guiding the FB-M nanopowders in the pressing process were calculated and made a coil that folds the die with the following parameters:

- Intensity of the magnetic field: H = 5000 Oe = 400 kA/m;
- Intensity of the electrical current: I_n = 6 A;
- Supply voltage: Un = 220 V, adjustable by the transformer;
- Diameter of the copper conductor d = 1 mm;
- Number of turns per layer: 74 turns;
- Number of layers: 11.

The direction of the magnetic field lines is parallel to the axis of the coil and hence the die.

Measurement of pressing force was achieved with a measurement system consisting of: transducer strain gauges 100kN and a digital indicator device type DDAD 06/A MOM-Hungary. Measurement uncertainty of the system is 0.5%.

For microwave sintering (MWS) was used two systems, namely: a system that has mono mode room and other that has multi mode room.

The technical characteristics of mono mode microwave sintering system are:

- Maximum power 1250 W, adjustable in the field of 10 to 100%;
- Frequency of electromagnetic field 2450 MHz ± 10Hz;
- anodic voltage 3.5 kV;
- Magnetron power source air cooled 0.4 kV, 5 A;
- Pressurized water cooled magnetron;
- Temperature monitoring system and automatic power;
- Automatic tuning system of impedance load to minimize the reflected wave power;
- Software for acquisition and analysis of incident wave power, wave power absorbed and reflected power, calculation and display of real and imaginary part of impedance load;
- Software for data acquisition and storage temperature measured by infrared pyrometer and adjusting the power based on the parameters of the cyclogram to obtain.

The technical characteristics of multi mode microwave sintering system are:

- Maximum power 1250 W, adjustable in the field of 10 to 100%;
- Frequency of electromagnetic field 2450 MHz ± 10Hz;
- anodic voltage 4 kV;
- Source of microwave - air cooled magnetron;
- Temperature monitoring system and automatic power;
- Software for data acquisition and storage temperature measured by infrared pyrometer and adjusting the power based on the parameters of the cyclogram to obtain.

The mono-mode system is used when the sample volume is small, the order of a few cm^3 and the second one when there are large samples (tens of cm^3).

To improve the heating process it was made a rotation device of the part subject to microwaves, similar to the system of domestic microwave ovens. Since the heating power is dependent on injected power and other factors such as volume or surface of the sample, heating problem can be considered solved by changing the generator power by raising or lowering the supply voltage of magnetron.

In the chapter III entitled **Researches regarding the elaboration of FB-M nanopowders by mechanical milling**, is presented the elaboration process of FB-M nanopowders by high energy ball mill.

For experiments was used barium hexaferrite of industrial origin, purchased from SC ROPEF S.A. Urziceni.

Currently materials used in the manufacture of barium hexaferrite by calcination process are barium carbonate and iron oxide (hematite).

For the mechanical milling was used a Pulverisette 4 vario ball mill with the following parameters:

- Milling bowls 2x250 ml made of stainless steel;
- Milling balls ϕ=10mm made of stainless steel;
- Milling times: 10, 20, 30, 40 hours.

For milling process, the following load of the milling bowls was used:

a) Dry milling
   - 100 g FB-M powder;
   - 50 balls;

b) Wet milling (distilled water)
   - 100 g FB-M powder;
   - 50 balls;

- ➢ 60 ml distilled water;

c) Wet milling with additive

- ➢ 100 g FB-M powder;
- ➢ 50 balls;
- ➢ 40 ml distilled water;
- ➢ 3% additive (DAXAD) reported to the quantity of solid mixture.

Powders obtained after milling process was characterized by electron microscopy SEM and by determining particle size distribution. Magnetic characteristics of powders obtained after milling process were studied too.

Based on the experimental research result the following partial conclusions:

- The shape of powder granules is flat because the system crystallization of Ba ferrites is hexagonal;
- Grain size is reduced, as is normal, with increasing of the milling time. Thus, after 10 hours of milling, the particles were larger than 1μm and as the milling time increase, the particles become nanometric. However, after 20 hours of dry milling the particles tend to become nanometric.
- After 10 hours of dry milling, the particles size is in the range of [0,07 – 1,0] μm and [1,0 – 100,0] μm having the equivalent mean diameter D[4,N] = 16,02 μm.
- After 20 hours of dry milling there are two groups of particles with particle size distribution in the range of [0,1 – 1,0] μm and [1,0 – 20,0] μm having the equivalent mean diameter D[4,N] = 4,74 μm.
- After 30 hours of dry milling, the particles size is in the range of [0,1 – 1,0] μm and [1,0 – 20,0] μm having the equivalent mean diameter D[4,N] = 3,28 μm.
- In case of wet milling it is shown that, after 20 hours of milling the particles size is in the range of [0,05 – 1,0] μm and [1,0 – 10,0] μm having the equivalent mean diameter D[4,N] = 3,66 μm.
- After 30 hours of wet milling there are particles with particle size distribution in the range of [0,1 – 1,0] μm and [1,0 – 10,0] μm having the equivalent mean diameter D[4,N] = 1,93 μm.
- After 10 hours of additive milling the particles size distribution is in the range of [0,1 – 1,0] μm and [1,0 – 100,0] μm having the equivalent mean diameter D[4,N] = 16,03 μm.
- Frequency curve corresponding to the particle size distribution for powders milled for 20 hours with liquid additives include two groups of particles that are in the ranges [0.1 to 1.0] μm and [1.0 to 50.0] μm having the equivalent mean diameter D[4,N] = 6,47 μm.

- The equivalent mean diameter D[4,N] = 3,46 μm for the powders obtained after 30 hours of additive milling.
- To obtain FB-M nanopowders is better to practice the first 20 hours in dry milling and after that continue to practice wet milling.
- The crystalline degree of the powders obtained after wet milling using water as a medium is always lower on average (6-10%) than the crystalline degree of powders obtained after wet milling using f 3% solution DAXAD as milling medium.
- Since the magnetic properties (coercive field and retention) are dependent on the particle size of powder, knowing dimensional composition of the powder function the milling time it can be separate fractions from the first or the second particle size interval to use them as required.
- In the case of ordinary permanent ceramic magnets or nanostructured the ideal situation is achieved when the powder granules used for their manufacture have the particles size close to the magnetic mono domain (about 0,8 μm). In fact it will be used a particle size distribution in the range of [0,6-0,9] μm with maximum frequency at 0.8 μm.
- The mixed-milling process, namely: 20 hours dry milling and 20 hours wet milling lead to a lower degree of crystalline, decreasing more during dry milling and less during wet milling.
- Magnetic parameters of milled powders decrease with milling time and depend on the type of fluid used.
- Samples obtained after milling using liquid additives medium has superior magnetic characteristics than the samples obtained after milling using water as medium.
- Retention is high for samples milled for 10 and 20 hours and decreases with increasing of milling time.
- The results are normal because of the interdependency of residual and coercive field function the crystallites size, namely, retention increases with particles increasing and coercive field increases with the volume reduction of particles.

In Chapter IV, entitled **Research on the elaboration of the ceramic magnets by microwave heating** are presented the experimental results on microwave sintering of ceramic nanostructured permanent magnets.

The microwave sintering parameters were:

- sintering temperature (950 ^{o}C), dwell time (10, 20 and 30 minutes);
- sintering temperature (1050 ^{o}C), dwell time (10, 20 and 30 minutes);
- sintering temperature (1200 ^{o}C), dwell time (10, 20 and 30 minutes);

Based on the experimental research result the following partial conclusions:

- From the experimental TG and DTG curves, in the temperature range 600-1000 °C mono ferrite formation is accompanied by an intense weight loss because of CO_2 elimination.
- After 10 minutes dwell time at sintering temperature (950 ^oC) the sintering process is at beginning level and this results because the lack of sintering decks.
- After 10 minutes dwell time at sintering temperature (1050 ^oC and 1200 ^oC) an increasing of sintering decks appear.
- After 20 minutes dwell time at 950 ^oC the sintering decks tend to multiply and at 1050 ^oC respectively 1200 ^oC the samples are completely sintered and present nanometric structure.
- After a dwell time equal to 30 minutes at sintering temperature (950 ^oC) the samples are sintered with nanometric structure but at sintering temperature (1050 ^oC and 1200 ^oC) the grains tend to increase.
- In the nanometric powders case, the degree of anisotropy K remains around 70% for Cs = 80%.
- Evolution of magnetic parameters values confirms that Br increases with increasing of crystalline grains instead the correlation with the development of the coercive field value must be considered.
- Temperature and sintering time influence as expected the magnetic properties and because of that we can choose the following options:
    - ➢ Heating at 1200 ^oC with 20 minutes dwell time ensure obtaining of nanostructured magnets with energy (BH) max ≤ 27 kJ;
    - ➢ Heating at 1050 ^oC with 20 minutes dwell time ensure obtaining of nanostructured magnets with energy (BH) max ≤ 25 kJ;
    - ➢ Heating at 950 ^oC with 30 minutes dwell time ensure obtaining of nanostructured magnets with energy (BH) max ≤ 25 kJ;

Chapter V, **Conclusions and original contributions** summarizes the overall conclusions and the original contributions of the author.

Analyzing the results obtained from literature and experimental research, the author contributes with the following elements of originality:

1. Using a liquid additive (DAXAD) as milling medium for the elaboration of FB-M nanopowders, which produced the following effects:

- ➢ reduced forces of attraction between particles;
- ➢ has increased the slurry flow;
- ➢ helped to reduce the milling time.

2. Design and construct of a solenoid for anisotropic die pressing in magnetic field with intensity 5000 Oe.
3. Sintering of the ceramic permanent nanostructured magnets by an unconventional process heating namely microwave sintering.
4. Design and construct a device to advance and rotate the sample in the mono mode microwave sintering furnace for increasing the uniformity of heating in the sample volume.
5. Adjustment of the multi mode oven to the MOM derivatograph for the thermo gravimetric analyzes of the Ba ferrites.
6. Achieving continuous adjustment of the incident wave power for the multi mode oven.
7. Sintering of the permanent ceramic nanostructured magnets by microwave heating at temperatures significantly lower than those necessary in a conventional sintering, much shorter time, achieving efficiency and high energy efficiency compared with conventional heating.