Analysis of selected properties of powdered compacts

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Abstract. Magnetic materials are large and specific group of materials with interesting properties and useful applications. Some of them have been known for many years, but many important materials have only been discovered in recent decades. It can be expected that many newly discovered materials with specific properties will soon be used in applications in which magnetic materials have been used for a long time, but their properties will be better. The development of new magnetic materials will certainly bring the possibility of their use in such applications in which they have not been used before. This paper contains the review of the results of research focused on the study of soft magnetic ferromagnetic materials. Specifically, they are materials of chemical composition Fe19Ni81 (called Permalloy) and Fe16Ni79Mo5 (called Supermalloy). These materials were prepared in the form of powders by the technique of the mechanical milling. Subsequently, these powders were compacted with aim to prepare a compacted material of the desired shape and size with excellent magnetic properties. This research was focused on the study of the structure and magnetic properties of massive magnetic materials prepared by the compaction of the powders in order to prepare soft magnetic material with excellent properties competing with the material used so far.

1. Introduction

Magnetic materials are very important for technical practice and these materials have revolutionized in materials research, electrical engineering and electronics. They are used in the construction of magnetic circuits, in generators, electric motors, transformers, coils with a core, sensors, but also as storage media in computer technology. Some of the magnetic materials have been known for many years, other important magnetic materials have only been discovered in recent decades. It can be expected that the advancing development of newly discovered magnetic materials will bring their use even in areas where they have not been used before [1].

Very important consumer of magnetic materials is electrical engineering industry, where high demands are placed on the quality of these materials. High consumption of materials also determines the direction of their development. One of the most important requirements is to achieve the same magnetic effect by using a smaller amount of material (lower weight transformers, smaller permanent magnets and others). The attention of material researchers has attended to the research and the preparation of ferromagnetic alloys in the form of ribbons, thin films and powders, which are characterized by excellent magnetic properties. Polycrystalline and nanocrystalline materials in the form of metal ribbons are brittle, which limits their application capabilities and therefore new materials in the form of powder samples have begun to be prepared by mechanical milling or by mechanical alloying.
The prepared powder samples are then pressed into compacts of different shapes, which have a similar structure as ribbons of the same chemical composition [2].

Methods of the preparation of non-traditional materials by mechanical milling and alloying has found wide application in many industries. This technology caused a revolution in metallurgy by a team that made it possible to prepare such materials, which had not been possible until then using traditional methods.

The first targeted industrial use of metal powders was in 1826 and it is associated with the name of P. G. Soboljevsky. At that time, it was not possible to reach the melting point of platinum (1773.5 °C). The method used at the time with the addition of arsenic to platinum to lower the melting point of platinum was disadvantageous, as the highly toxic arsenic vapors both endangered the health of the workers and contaminated the environment. Soboljevsky found a method to produce platinum powder by calcination of ammonium platinum chloride. The platinum powder thus obtained was then pressed into bars, sintered, hot forged to obtain platinum which was suitable for further processing. The development of platinum production was supported by the fact that platinum coins (rubles) were minted in Russia [3].

Nowadays, it is a growing interest in powder materials, which are further used for the preparation of compacted and composite soft magnetic materials, as there is a growing interest in materials that meet the requirements for miniaturization of magnetic cores of electronic power equipment.

2. Soft magnetic materials

There are many different criteria for the distribution of magnetic materials. According to the arrangement of the basic magnetic moments of the atoms of which the material is composed, we distinguish between materials without an arrangement of magnetic moments (diamagnetics and paramagnetics) and materials with an arrangement of magnetic moments (ferromagnets and antiferromagnets). Ferromagnetic materials are usually metals or alloys based on 3-d transition elements (Fe, Co, Ni) and they can be divided (according to basic magnetic properties, for example coercivity) into soft and hard magnetic materials [4, 5].

In technical practice, we consider metallic and non-metallic substances with spontaneous magnetization of the ferromagnetic type of magnetic materials, which are usable from a practical point of view [5].

Soft magnetic materials are characterized by low coercivity, low pre-magnetization losses, they are easily pre-magnetizable, achieve high values of magnetization, permeability and saturation induction. They are usable as cores of various transformers, magnetic sensors, amplifiers, magnetic heads, etc. The magnetic "softness" of ferromagnetic alloys is achieved in some cases also due to low magnetostriction and disappearing magnetocrystalline anisotropy [4].

Hard magnetic materials are characterized by high coercivity and remanent magnetization. In practice, they are used as permanent magnets [4].

Soft magnetic materials include pure iron, iron alloys with silicon, iron alloys with nickel and others. Iron is one of the most used ferromagnetic metals. It is produced in the form of technical iron, which may contain various impurities (carbon, sulfur, phosphorus, silicon, manganese, nickel, copper, etc.).

Alloys based on Fe-Ni belong to soft magnetic materials and they have become an integral part of materials in the field of electrical engineering, despite the higher price of nickel and it cannot be replaced by another ferromagnetic element.

Based on the facts that the trend in the world is the preparation of "tailor-made" magnetic material. However, the disadvantage of soft magnetic materials is their shape limitation (thin ribbons, thin layers, micro wires, rods with a minimum cross-section and others). The aim of the current research is to find a material that will be a combination of excellent magnetic properties (material composition) and at the shape usable in various applications (material preparation method). One of the ways is to prepare compacted powder (preparing by mechanical milling or alloying).
3. Experimental methods
Crystalline and amorphous materials, prepared in the form of thin ribbon (up to 30 µm thick), are important from a practical point and interesting from the basic research. These ribbons are characterized by excellent properties of soft magnetic materials, but in practice the usage of these materials is complicated because of their small thickness, and in the case of crystalline tapes also because of high brittleness. One of the solutions how to bridge these two negative properties of materials in the form of ribbons is the preparation of a compacted material, prepared for example by compaction of the powder obtained by the mechanical milling of these crystalline ribbons.

For this research thin crystalline Fe-based ribbons (width approx. 20 mm, thickness approx. 30 µm) with the chemical composition Fe19Ni81 (called Permalloy) was prepared by the method of rapid cooling of the melt on a rotating cylinder (Figure 1). The crystalline Fe16Ni79Mo5 alloy (called Supermalloy) could not be prepared by the rapid melt cooling method, probably because the surface tension of this alloy in contact with the cylinder surface led to the rupture of the alloy. In this case, chips from an ingot of the same chemical composition were prepared using a lathe (Figure 1).

Mechanical milling is a technique in which particles of a substance are crushed into smaller parts without the need for transport of the substance at the atomic level. Mechanical milling does not affect the chemical composition of the powder, but it is characterized by a change in structure (including a change in the volume fraction of crystalline and thus amorphous phase), a change in grain size (increasing time of milling) and a change in magnetic, technological and physical properties of milled powder. The advantage of mechanical milling is that we can prepare a large amount of powder. The preparation process is easy to control, and this technique is also suitable for commercial application [6].

Mechanical alloying is also a high-energy process for the preparation of powder materials, where individual parts of the powder are broken, deformed and connected. Mechanical alloying leads to the transport the substance at the atomic level. This transport can lead to the preparation of the compound or homogeneous alloy [6].

Powder materials Fe19Ni81 and Fe16Ni79Mo5 were prepared by mechanical milling in high-energy planetary mill (Figure 2) by the mechanical milling of crystalline ribbon Fe19Ni81 (wt.%) and chips Fe16Ni79Mo5 (wt.%), respectively (Figure 3).

The compaction of powders, which have been prepared by mechanical milling of alloys, makes it possible to prepare materials which have excellent magnetic properties and a shape suitable for usage in technical practice. Residual stresses remain in the material during mechanical milling and compaction. After heat treatment, the residual stresses relax and the sample shows as good magnetic properties as the ribbons or powders [6].

Compacted samples in the form of rings or cylinders were prepared by compaction of milled powders Fe19Ni81 (wt.%) and Fe16Ni79Mo5 (wt.%) using compression equipment (Figure 2).

After giving a certain weight of powder into the compression machine in the desired form (ring or cylinder) and closing the compression machine, the evacuation was started by means of a rotary and turbomolecular pump. After reaching the vacuum, it was started with induction heating of the powder to the required pressing temperature (500 °C and 600 °C). For the compaction of powders, it was used a pressure at 800 MPa during the pressing time of 5 minutes.

Figure 1. Material Fe19Ni81 (Permalloy) and Fe16Ni79Mo5 (Supermalloy) in the form of ribbon, chips and milled powder (obtained by the mechanical milling), which was used for the further compaction.
4. Experimental results
The aim of this experimental work was to prepare powder material by the mechanical milling of crystalline ribbon Fe19Ni81 (sample A – powder material prepared by the mechanical milling of ribbon) and by the mechanical milling of crystalline chips Fe16Ni79Mo5 (sample B – powder material prepared by the mechanical milling of chips), to determine their structure and magnetic properties and to select the best powder sample suitable for the compaction of milled powder and prepared compacted Fe19Ni81 (sample C – compacted material prepared by the compaction of the powder) and Fe16Ni79Mo5 (sample D – compacted material prepared by the compaction of the powder) with excellent properties of soft magnetic material (Figures 1, 2, 3).

4.1. Powder sample FeNi (sample A)
The magnetization processes in the magnetic materials depend to a large part on the shape of the sample. In many cases, it is only possible to prepare samples in powder form for research of magnetic properties, for example the examining of the structure (DSC, X-ray) or the measuring of magnetic properties (Curie temperature, magnetic moment). Powder materials are also very suitable for certain applications, for example information recording materials [7].

The most commonly milled ferromagnetic materials suitable for compaction are often pure iron or iron and nickel based alloys. Mechanical milling often degrades magnetic properties and then heat treatment of compacted samples is appropriate [8].

The crystalline ribbon of the chemical composition Fe19Ni81 was milled in a high-energy planetary ball mill in argon atmosphere from 0 to 30 hours. Before starting the process of mechanical milling, the ribbon was broken into small pieces to increase the milling efficiency. Scanning morphology (Figure 4) by the electron microscopy (SEM) has shown that particles with sharp edges of about 30 µm predominate at the beginning of milling, but as the milling time increases, the particle size decreases and these particles aggregate (they may be magnetostatic state) [9].

The crystal structure of the ribbon and the powder (prepared by the milling of the ribbon) was confirmed by measurement of a diffractometer (X-ray) and differential scanning calorimeter (DSC).

DSC diagrams (Figure 5) up to 1000 °C show two endothermic maxima. Achieving thermal equilibrium at the beginning of the measurement is associated with a maximum of about 150 °C (first
peak). The second peak may mean structural defects accumulated in the material during mechanical milling this value is probably related to the Curie permalloy temperature of Permalloy (550 °C) [10].

**Figure 4.** Scanning morphology obtained by the electron microscopy for a) ribbon Fe19Ni81, b) powder samples obtained by mechanical milling of ribbon Fe19Ni81 for 1 hour and c) for 30 hours.

**Figure 5.** Diagram reported by differential scanning calorimeter for ribbon Fe19Ni81 and powder sample obtained by mechanical milling of ribbon Fe19Ni81 for 30 hours.

**Figure 6.** Thermomagnetic curves for ribbon Fe19Ni81 and powder sample obtained by mechanical milling of ribbon Fe19Ni81 for 30 hours.

Using Rietveld analysis, it was determined the phase composition of the samples and FeNi3 phase with the phase fraction (at least 90%) was confirmed. This phase was also confirmed by the measuring of the thermomagnetic curves of the powder samples and subsequently determining the Curie temperature of the alloy [10]. In the milling process, the crystallinity of the FeNi3 phase decreases, which may be due to an increase in the deformation energy during milling. As the milling time increases, the lattice stress also increases, which is probably caused by mechanical deformations during mechanical milling and the increasing proportion of grain boundaries. From the results of X-ray diffraction, it can conclude that mechanical milling of the crystalline ribbon Fe19Ni81 does not cause the formation of further phases and we can consider this system is single-phase [9, 10, 11].

By the measuring of thermomagnetic curves (Figure 6), the Curie temperatures was determined and it was found that the magnetization decreases with increasing temperature to zero, at a temperature of
approximately 550 °C, which corresponds to the Curie temperature of the Fe19Ni81 alloy prepared by a conventional method [9, 10].

After the above-mentioned evaluation of the structure and magnetic properties of Fe19Ni81 powder samples, we can confirm that high-energy milling of the crystalline ribbon is a suitable method for preparing powder materials for the compaction.

4.2. Powder sample FeNiMo (sample B)
Chips of chemical composition Fe16Ni79Mo5 (wt.%) were milled in a high-energy planetary ball mill by cryomilling from 0 to 500 hours. In Figure 7 we can see the images of the surface of Fe16Ni79Mo5 chips. Particles obtained by the milling of chips for 100 hours have sharp edges in contrast to particles prepared by the milling of chips for 300 hours. The particle size decreases with increasing milling time. The particle size is in the range of approximately 5 µm to 20 µm for chips milled for 100 hours and from 1 µm to 10 µm for chips milled for 300 hours (Figure 7) [10, 12].

![Figure 7. Scanning morphology obtained by the electron microscopy for a) chips Fe16Ni79Mo5, b) powder samples obtained by mechanical milling of ribbon Fe16Ni79Mo5 for 100 hour and c) for 300 hours.](image)

Analysis of the diffractograms (X-ray) showed that all investigated samples (chips, chips milled for another time) consist of a single FeNi3 phase, as well as the Fe19Ni81 alloy. It has been reported that with increasing milling time, the diffraction curves widen and their intensity decreases, which is probably due to the fact that the largest amount of Mo is dissolved in FeNi3 [9, 13].

High-energy milling of crystalline Fe16Ni79Mo5 chips for up to 500 hours leads to the formation of a coarse-grained powder due to the high hardness of the material. The results of the examination of the structure and magnetic properties lead to the conclusion that this prepared powder is a suitable precursor for the preparation of a compacted material.

4.3. Compacted sample FeNi (sample C)
Alloys type of Permalloy and Supermalloy are widely used in various electronic devices and in industry due to their high permeability. High permeability causes the disappearance of crystal anisotropy and magnetostriction. At a certain concentration of Ni relative to Fe (approx. 80% by weight), Permalloy and Supermalloy shows a zero value of magnetostriiction. If powders of this alloy with zero magnetostriction are compacted, it can be assumed that the induced stresses will not cause additional anisotropy and the alloy will have good magnetic properties of soft magnetic ferromagnet [4, 5, 14]. Therefore, the powder obtained by the milling of the crystalline ribbon Fe19Ni81 and the crystalline chips Fe16Ni79Mo5 was further compacted, since this system is single-phase, and no other phases are formed or disappeared during the process of mechanical milling.

The powder prepared by mechanical milling of the crystalline ribbon Fe19Ni81 in a planetary ball mill was further compacted. Two series of compacted samples were prepared by the compaction, applying a uniaxial pressure of 800 MPa for 5 minutes at a compacting temperature of 500 °C and 600 °C. Compacted samples were prepared by the compaction of the powder obtained by milling ribbon Fe19Ni81 for different milling times.
X-ray diffraction of crystalline ribbon Fe$_{19}$Ni$_{81}$ milled for 30 hours and sample compacted from this milled powder confirmed the crystalline structure in all samples. The compression of the powder does not affect the structure and as with the Fe$_{19}$Ni$_{81}$ ribbon and the powder prepared by milling it, the FeNi$_3$ phase was found in the compacted samples [9, 10, 15, 16].

Before starting the compaction, the crystalline ribbon was broken into small pieces, which were very brittle and after the compaction the particle size was reduced to 5 µm. Surface of a compacted sample prepared from powder milled for 5 hours pointed to particles with relatively sharp edges and a size of approximately 3 µm. By studying the SEM images (Figure 8), it is possible to see the presence of pores in these compacted samples, which largely determine the resulting properties of the compacted sample. However, the surface of the sample compacted from the powder milled for 30 hours is already smooth and without clear pores [9, 16].

![Figure 8](image_url)

**Figure 8.** Scanning morphology obtained by the electron microscopy for compacted sample prepared by the compaction of d) small pieces of ribbon Fe$_{19}$Ni$_{81}$, e) powder samples obtained by mechanical milling of ribbon Fe$_{19}$Ni$_{81}$ for 1 hour and f) for 30 hours.

The coercivity of the milled ribbon Fe$_{19}$Ni$_{81}$ as a function of the milling time compared with the compacted samples, which were prepared from the milled powder and compacted at a temperature of 500 °C and 600 °C, is shown in Figure 9. The coercivity increases with increasing milling time and it is similar for milled ribbon and compacted samples. Higher coercivity values were also recorded for samples milled for longer periods due to the stress induced by the anisotropy that occurs during compaction. The coercivity values of the compacted samples are lower than that of the milled ribbon. This decrease in coercivity may be due to magnetic "contact" between the powder particles, which has been amplified during compaction, and overmagnetization takes place to a greater extent by shifting the domain walls. The coercivity reaches lower values for all massive samples compacted at 600 °C than those pressed at 500 °C [9, 16].

![Figure 9](image_url)

**Figure 9.** The coercivity as a function of the milling time for milled ribbon Fe$_{19}$Ni$_{81}$ and compacted samples prepared from the milled powder and compacted at a temperature of 500 °C and 600 °C.

### 4.4. Compacted sample FeNiMo (sample D)
Fe-Ni alloys are characterized by a wide range of excellent magnetic properties. Low coercivity and high permeability guarantee the use of these materials in practice, despite the higher price of nickel. The addition of molybdenum to these alloys creates an alloy called supermalloy with also excellent magnetic properties, and at the same time molybdenum leads to a reduction in magnetic losses.

The crystalline chips of the chemical composition Fe16Ni79Mo5 were milled by cryomilling in a planetary ball mill, and then the obtained powder was compacted. By applying a uniaxial pressure of 800 MPa for 5 minutes at a pressing temperature of 600 °C, two series of compacted samples were prepared from powder milled for 1 hour and 100 hours.

The crystal structure and phase composition consisting of the majority phase of FeNi3 with a phase content of at least 90% were confirmed by X-ray diffraction [10, 12].

![Figure 10](image.png)

**Figure 10.** The coercivity as a function of the frequency for compacted sample Fe16Ni79Mo5 prepared from the chips milled for 1 hour and 100 hours.

In Figure 10 we can see the dependence of coercivity on frequency (0.5 Hz - 50 Hz) for a sample compacted from powder milled for 1 hour (FeNiMo1) and for 100 hours. (FeNiMo100). Higher values of coercivity are achieved by a sample consisting of larger particles, prepared from powder milled for a longer milling time. During mechanical milling and subsequent compaction, defects were introduced into the sample, which can be eliminated by annealing the sample and thus achieve lower coercivity values [12].

5. Conclusion
Permalloy (Fe19Ni81) and Supermalloy (Fe16Ni79Mo5) magnetic materials are characterized by good properties of soft magnetic material, but the shape in which they are prepared (thin crystalline ribbons, mixtures of pure elements) is not always suitable for application purposes. One of the ways to prepare a material that retains excellent properties and at the same time its use will be less complicated is for example to compact the powder, which can also be prepared by mechanical milling of the alloy.

Mechanical milling and compaction processes of the powder thus prepared can cause structural defects in the material and these can degrade the magnetic properties of the soft magnetic material by inducing stress-induced anisotropy through magnetostriction. Therefore, for the compaction of powders, it is suitable to choose alloys with zero or almost zero value of magnetostriction, which will reduce the influence of structural defects causing internal mechanical stress and at the same time improve the magnetic properties of material. The most suitable precursor for the preparation of a three-dimensional ferromagnetic material is a single-phase powder, because the domain walls move easily in the process of premagnetization. In the case of a powder magnetic material which consists of two phases, trapping centers can be created for the movement of the domain walls, which results in an increase in coercivity.

Powder compaction is an alternative way of preparing solid materials of various shapes and sizes. In order to achieve the required physical and magnetic properties, it is necessary to study magnetization processes, select the appropriate chemical composition of the material, determine the correct procedure for preparing powder materials suitable for compaction, select the appropriate type of alloy as a milling
precursor, know the morphology of particles and compaction properties. After compaction of the powder, the proportion of magnetization processes changes in favor of domain wall shifts compared to the process of rotation of the magnetic polarization vector that predominates in powder materials.

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