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# Structure and magnetic properties of hot pressed powder $Co_{77}Si_{11.5}B_{11.5}$ alloy

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**Properties**

## ABSTRACT

**Purpose:** The aim of the work is to investigate the structure and magnetic properties of the cobalt based hot pressed $Co_{77}Si_{11.5}B_{11.5}$ powder obtained in high-energy ball milling process.
**Design/methodology/approach:** The nanocrystalline ferromagnetic powders were manufactured by high-energy ball milling (SPEX 8000 mill) of metallic glasses ribbons in as state. The hot pressing process was made on machine “Degussa”. Observations of the structure of die stampings were made on the OPTON DSM-940 and ZEISS SUPRA 35 scanning electron microscope. Tests of magnetic properties were carried out by the use of Lake Shore’s Vibrating Sample Magnetometer VSM model 7307.
**Findings:** The analysis of the results enabled determination of the hot pressing parameters on magnetic properties and structure of obtained stampings.
**Research limitations/implications:** For the metallic Co-based amorphous ribbons, further mechanical and structure examinations are planed.
**Practical implications:** Structure and magnetic properties analysis of die stampings of powdered amorphous metallic ribbons is helpful to prepare this material by laboratory methods. Feature an alternative to commercial alloys and composite materials are the amorphous and nanocrystalline metal amorphous ribbons obtained by melt spinning technique and make it possible to obtain the new composite materials with best magnetic properties, which dimensions and shape can be freely formed.
**Originality/value:** The paper presents influence of hot pressing parameters process of metallic powdered ribbons $Co_{77}Si_{11.5}B_{11.5}$ on structure and magnetic properties of obtained die stampings.
**Keywords:** Metallic alloys materials; Nanocrystalline materials; Magnetic properties; Powder metallurgy

## 1. Introduction

Bulk soft and hard magnetic materials can be obtain in different methods [1-4]. Method the most often be used is pressing or hot pressing of powders [5, 6]. All exchanged methods influence on structure and the same on magnetic properties of materials [7].

The amorphous and nanocrystalline alloys in case of soft magnetic materials with the best properties characterize (high saturation magnetization $B_S$, high permeability, and low core loss,) on matrix of iron, the cobalt and nickel [8, 9] with addition of metalloid how do the silicon and boron? However with regard on method their obtainment (melt spinning) accessible they are in

Figure of thin tapes only. Toroidal produces with them first of all cores. Fact this makes difficult them commercial use often.

The hot pressed magnetic bulk materials which may be obtained and used in the powder state, seems to be a very interesting issue from the point of view of the production technology, processing and application [10, 11].

The production of the hot pressed powders obtained in the high energy ball milling or in the mechanical alloying, enables the scientists to work on the ferromagnetic bulk materials which dimensions and shape may be freely formed [12-15].

The aim of this work is to investigate the structure and magnetic properties of the hot pressed powder $Co_{77}Si_{11.5}B_{11.5}$ alloy obtained from the metallic glass in the high energy ball milling process.

## 2. Material and methods

The investigations were carried out on a $Co_{77}Si_{11.5}B_{11.5}$ metallic glass in form of 0.03 mm thick and 10.2 mm wide ribbons. A 8000 SPEX CertiPrep Mixer/Mill high energy ball mill was applied to mill the ribbons both in „as quenched" state.

The hot pressing process was made on machine "Degussa" was subjected metallic powder obtained in high energy ball milling amorphous ribbon $Co_{77}Si_{11.5}B_{11.5}$ by 5, 15, 20 and 80 hours. Amorphous ribbons $Co_{77}Si_{11.5}B_{11.5}$ were milled at a ball-to-powder mass ratio (BPMR) of 6:1. Such away prepared powder was compacted in uniaxial press in vacuum ($2 \times 10^{-2}$ Tr), in temperature 800°C by 20 minutes, with pressure of stamp the P = 15 MPa.

In next step of experiment metallic powder obtained in high energy ball milling amorphous ribbon $Co_{77}Si_{11.5}B_{11.5}$ by 5 hours was compacted with the same parameters like before but pressure of stamp the P = 5, 10 and 15 MPa.

The X-ray tests were realized with the use of the XRD 7 SEIFERT-FPM diffractometer equipped with the lamp of the cobalt anode of 35 kV voltage and 30 mA filament current was used. Diffraction tests were carried out in the 2θ angle range from 40 to 120° (measurement step 0.1°). Pulse counting time was 5 s.

Sizes of Co-β crystallites were determined with Scherrer's method [16]:

$$B = \frac{k \cdot \lambda}{d \cdot \cos\theta_B} \tag{1}$$

where:
d – diameter of the crystalline particle,
B – width of the diffraction peak measured at half of its height,
k – coefficient assumed as equal to 1 [16]
λ – X-ray radiation wavelength,
$2\theta_B$ – radiation beam diffraction angle corresponding to the Bragg maximum.

## 3. Results and discussion

The obtained powders have the highest portion of the 40-100 μm fraction at the beginning stage of milling of the $Co_{77}Si_{11.5}B_{11.5}$ amorphous alloy. The most probable sizes in the powder grains population (mode) are 53.3 μm for the material obtained after 15 hours of milling (Fig. 1a).

Milling the material for 20 hours causes further size reduction of particles (Fig. 1b). The highest portion of ≈ 19% was found out for particles from the range of 500-600 μm, the arithmetic average of the powders diameter is 524.1 μm.

Milling the material for 80 hours causes further size reduction of particles (Fig. 1c). The highest portion of ≈ 25% was found out for particles from the range of 12-14 μm, the arithmetic average of the powders diameter is 11.95 μm.

a)

b)

c)

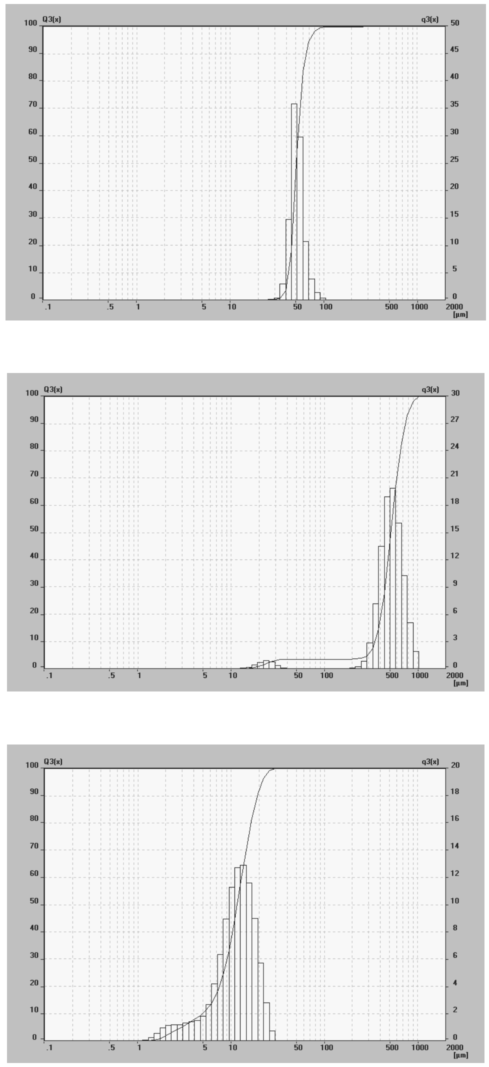


Fig. 1. The cumulative percentage portions curve and the grain size distribution curve for the powder obtained after a) 15, b) 20 and c) 80 hours long milling of the $Co_{77}Si_{11.5}B_{11.5}$ amorphous ribbon of the metallic glass

Observations on the scanning electron microscope (SEM) revealed that the sharp edges dominates among powder grains obtained after 5 and 15 hours long milling (Fig. 2). Spherical grains dominate in the powder obtained after 25 hours of milling with a small number of flake-shaped grains. Powder grains obtained after 60 hours of milling are characteristic for their spherical shape with no sharp edges (Fig. 3).

The mean value of powder grains after 20 hours milling is more than after 15 hours milling (Fig. 1a), because in time of high energy ball milling process the size reduction proceed all time and then joining (by local partial melting in microsqueres) the grains of powder (Fig. 2).

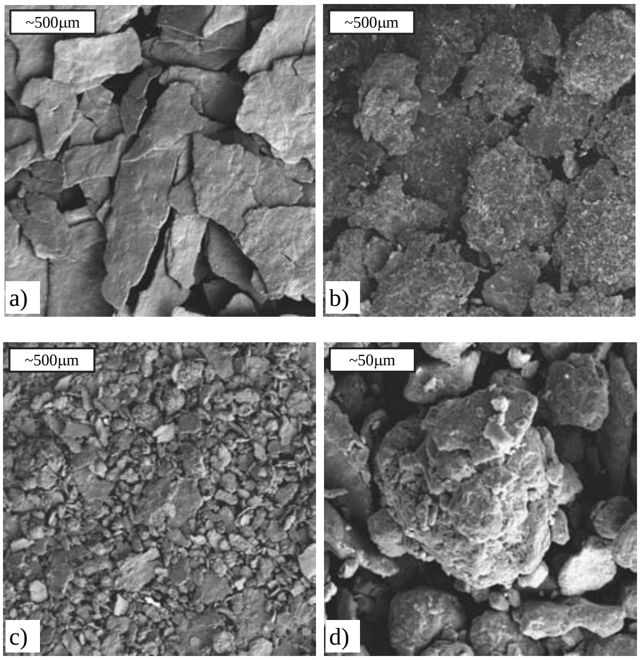



Fig. 2. Powder grains image after a) 5 h, b) 15 h, c) 25 h and d) 60 h, of the high energy ball milling, scanning microscope

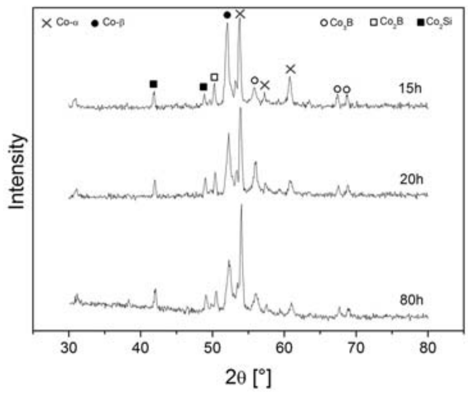



Fig. 3. X-ray diffraction pattern of the $Co_{77}Si_{11.5}B_{11.5}$ alloy in as powder materials obtained after 15, 20 and 80 hours of milling time and hot pressed in temperature 800°C in argon atmosphere per 20 minutes

The mass density of material of amorphous $Co_{77}Si_{11.5}B_{11.5}$ ribbon which was the precursor of die stampings carries out 7.7 g/cm$^3$. The mean mass density of powder after hot pressing in vacuum was calculated, which carries out $\rho_{5h}$=7.34 g/cm$^3$ for powder obtained after 5 hours of high energy ball milling.

The mass density of powder after hot pressing in vacuum was calculated, which carries out $\rho_{15h}$=7.57 g/cm$^3$ for powder obtained after 15 hours of high energy ball milling, $\rho_{20h}$=7.6 g/cm$^3$ for powder after 20 hours of milling and $\rho_{80h}$=5.88 g/cm$^3$ for powder obtained after 80 hours of milling.

The mass density of powder obtained after 5 hours of high energy ball milling after hot pressing with different pressure force was calculated too and for pressure 5 MPa $\rho_{5MPa}$=7.20 g/cm$^3$ for pressure 10 MPa, $\rho_{10MPa}$=7.59 g/cm$^3$ and $\rho_{15MPa}$=7.22 g/cm$^3$ for pressure 15 MPa of hot pressing.

On the basis of the analysis of the electron diffraction pattern (Fig. 4) it may be supposed that apart from the stress relaxation, the hot pressing process results in the structural changes which consists of new phase nucleation in higher temperatures.

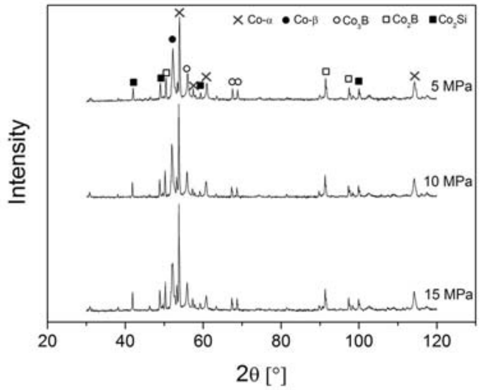



Fig. 4. X-ray diffraction pattern of the $Co_{77}Si_{11.5}B_{11.5}$ alloy in as powder materials obtained after 5 hours of milling time and hot pressed in temperature 800°C in argon atmosphere per 20 minutes

On the basis of the X-ray analysis of the electron diffraction pattern calculated of grain size Co-α phases in accordance with formula (1). The pressed powder obtained after 15 hours of milling characterized of Co-β phase crystallites size 37 nm (crystallographic plane 100), 21 nm (101) and 34 nm (002). After 20 hours of milling the crystallites size is 29 nm (100), 42 nm (101) and 26 nm (002) whereas after 80 hours of milling 37 nm (100), 59 nm (101) and 29 nm (002) as well as the $Co_3B$ (021) and (022) phases were identified (Table 1).

Table 1.
Grain size Co-α phases of hot pressed powder

| Powder milling time [h] | Plane Coordinates | | | |
|---|---|---|---|---|
| | (100) | (101) | (002) | Average size |
| 15 | 37 nm | 21 nm | 34 nm | 30.6 nm |
| 20 | 29 nm | 26 nm | 26 nm | 32.3 nm |
| 80 | 37 nm | 59 nm | 29 nm | 41.6nm |

The medium size of Co-α phase crystallites of hot pressed powder obtained after 15 hours of milling is 30.6 nm. After 20 hours of milling the medium size of crystallites is 32.3 nm whereas after 80 hours of milling the medium size of crystallites is 41.6 nm.

Received after different time near the same parameters of sintering the sample of milling characterized the grain size which increase with growth of time milling together with. Therefore temperature near which sintering followed it does not eliminate stresses (it does not cause even partial be recovering).

The size of Co-β phase crystallites of hot pressed powder obtained after 5 hours of milling sintered under press 5 MPa is 57 nm (100) and 31 nm (101), under 10 MPa is 42 nm (100) and 32 (101) and under press 15 MPa crystallites size is 47 nm (100) and 31 nm (101).

The magnetic research of the $Co_{77}Si_{11.5}B_{11.5}$ powders obtained in the process of milling of the ribbons in the "as quenched" state proved that the process of the high energy ball milling causes significant increase in the coercive force. The powder obtained after 5-hour milling of the amorphous ribbon is characterized by the highest value of the coercive force field ($H_C$=517.1). The hot pressed powder obtained after 5-hour milling and subsequently hot pressed in temperature 800°C per 20 minutes is characterized by the highest value of the coercive force ($H_C$=9512 A/m). The longer the time of milling is, the higher the value of the parameter after 15-hour milling $H_C$=11405 A/m. For a power obtained after 20 hours of high energy ball milling subsequent hot pressed in the same parameters the coercive force decrease to $H_C$=8022 A/m but for powder obtained after 80 hours of milling amount to $H_C$=20412 A/m already. The significant deformation of particles of powder the growth of coercion be caused the most probably during high energy ball milling by 80 hours.

The longer the milling process and hot pressing, the smaller the value of the saturation of magnetization, which for the hot pressed powder obtained after 5-hour milling amounts to $B_S$=0.67 and after 15-hour amounts $B_S$=0.69 T. But for the powder obtained in 20-hour milling, the value $B_S$ equals 0.49 T and after 80-hour milling amounts only 0.44 T (Fig. 5).

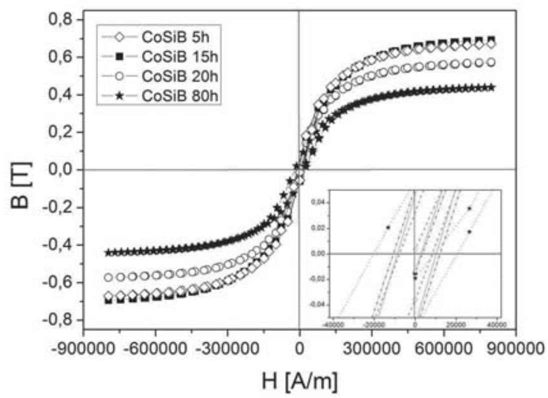



Fig. 5. Histeresis loop of the powder of $Co_{77}Si_{11,5}B_{11,5}$ alloy hot pressed in 800°C/20 minutes

The magnetic research of the hot pressed powder $Co_{77}Si_{11.5}B_{11.5}$ obtained in the process of pressing of the powders proved that the process causes significant increase in the coercive force. The die stamping material obtained 5 hours of milling is characterized by the highest value of the coercive force ($H_C$=9512 A/m) than metallic powder as a precursor $H_C$=517 A/m. When the time of high energy ball milling of metallic powder increase, the value of the coercive force increase too. For powder obtained after 80 hours of milling $H_C$=20412 A/m (Table 2).

Table 2.
Magnetic properties of powder $Co_{77}Si_{11.5}B_{11.5}$ alloy from cores obtained in hot pressing process

| Materials | $B_s$ [T] | $H_c$ [A/m] | $B_r$ [T] | $H_{max}$ [T] |
|---|---|---|---|---|
| 5h HEBM | 0.67 | 9512 | 0.05 | 796178 |
| 15h HEBM | 0.69 | 11405 | 0.05 | |
| 20h HEBM | 0.49 | 8022 | 0.03 | 1592356 |
| 80h HEBM | 0.44 | 20412 | 0.05 | |

HEBM – High Energy Ball Milling process

The growth of coercion be connected from enlargement the time of milling the powder, during which the particle powder were unceasingly deformed. The deforming the grains of powder induced the stress as well as defect the crystalline structure, which make up the natural places of anchoring the domain walls, which makes difficult their movement during remagnetization (the change of vector of magnetical field).

The magnetic research of the hot pressed powder $Co_{77}Si_{11.5}B_{11.5}$ obtained after 5 hours of high energy ball milling proved that the pressure of stamp causes significant decrease in the saturation magnetization ($B_S$) 1.25 T, 0.73 T and 0.63 T suitably for 5, 10 and 15 MPa pressure of stamp (Fig. 6). It insignificant differences and value for coercion were noticed was for pressure 5 and 15 MPa are almost the same (Table 3). However to get saturation magnetization of samples obtained under pressure 15 MPa indispensable use of magnetic field about intensity 100% larger than for samples obtained under pressure 5 and 10 MPa. The structure of hot pressed samples with different pressure of stamp presented on Figure 7. For comparison on Fig. 8 show structure hot pressed powder obtained after 80 hours of high energy ball milling but sample with the same pressure.

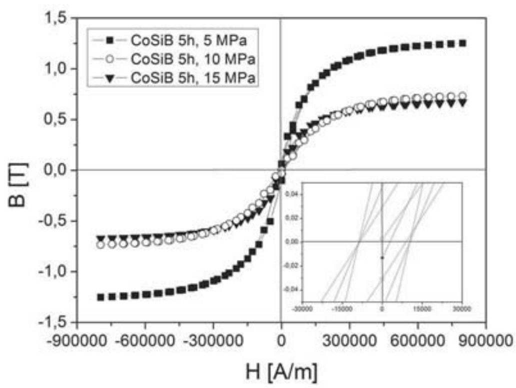
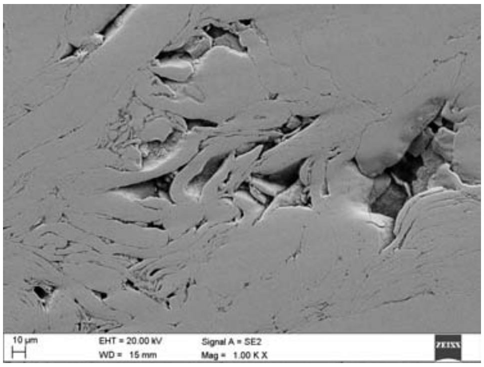



Fig. 6. Histeresis loop of the powder of $Co_{77}Si_{11.5}B_{11.5}$ alloy hot pressed in 800°C/20 minutes with different pressure force

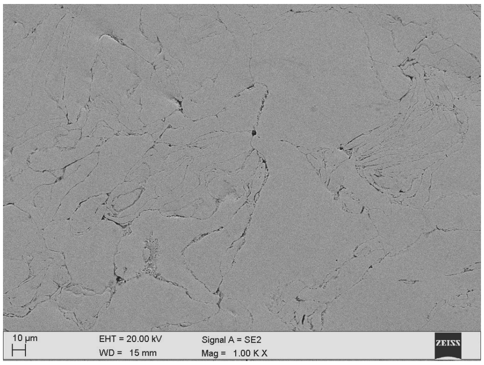
Table 3.
Magnetic properties of powder cores $Co_{77}Si_{11.5}B_{11.5}$ alloy obtained in hot pressing process from powder after 5 hours of milling with different pressure force

| Materials | $B_s$ [T] | $H_c$ [A/m] | $B_r$ [T] | $H_{max}$ [T] |
|---|---|---|---|---|
| 5 MPa | 1.25 | 9552 | 0.09 | 796178 |
| 10 MPa | 0.73 | 8683 | 0.03 | |
| 15 MPa | 0.67 | 9512 | 0.05 | 1592356 |
| All powders obtained after 5 hours of milling time | | | | |

a)




b)




c)

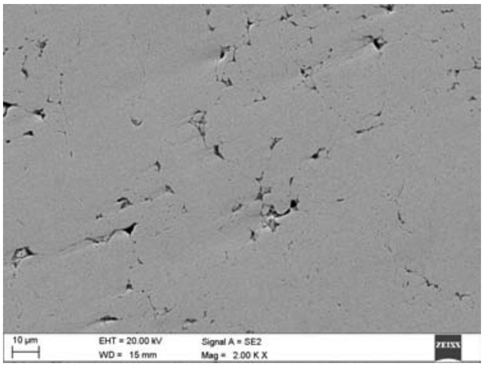



Fig. 7. Structure of hot pressed $Co_{77}Si_{11,5}B_{11,5}$ powder obtained after 5 hours of high energy ball milling pressed with a) 5, b) 10, c) 15 MPa force; scanning microscope

The magnetic research of the hot pressed powder $Co_{77}Si_{11.5}B_{11.5}$ proved that the sintering process causes significant increase in the coercive force ($H_c$). The die stamping material obtained after hot pressing in 800°C per 20 minutes in vacuum from the metallic powder is characterized by the highest value of the coercive force ($H_C$=1363.1 A/m) than powder before pressing. The higher the temperature of pressing is, the higher the value of the parameter after 950°C pressing $H_C$=3517 A/m too.

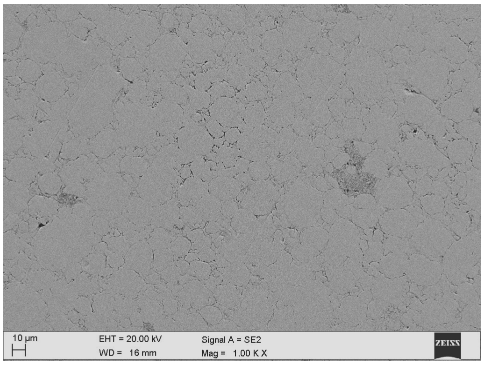



Fig. 8. Structure of hot pressed $Co_{77}Si_{11.5}B_{11.5}$ powder obtained after 80 hours of high energy ball milling pressed with 15 MPa force, scanning microscope

A specially significant is the growing value of coercive force $H_C$ with growing temperature of hot pressing. The coercive force value increases up to 950°C. The saturation magnetization $B_S$ changed too, the value decreases form 0.74 T for powder obtained after 20 hours of high energy ball milling to 0.48 T for die stamping obtained in 800°C per 20 minutes and for 0.52 T for die stamping obtained in 950°C.

## 4. Conclusions

On the basis on results of investigations of structure and magnetic properties of the hot pressed material, it was found out that compared to the amorphous ribbon one can we obtained that:

1. It was found out in observations on the scanning electron microscope that along with the milling time increase the powder particles size decreases, and that their shape changes also during the process. The powder grains were flake-sized at the first stage of the process, and actually they were parts of the strips. However, as the milling time grows the grains become spherical with a clear tendency to get smaller. Decreasing of the powder particles size is very intensive during the first hours of milling; whereas, at the later stage of the process changes of the average particle size are of the order of several percent per milling hour. The acquired results are comparable to results obtained by other authors [19-21].
2. The magnetic tests of the $Co_{77}Si_{11,5}B_{11,5}$ powders obtained in the high-energy ball of milling process proved that the process causes significant decrease in the magnetic properties. A specially significant is the growing value of coercion field

with milling time. The saturation magnetization does not change, or its changes do not have a clear effect on the magnetic properties. As the milling time passes the coercion field decreases; anyway, it grows again with the extended milling time.
3. The average grains size of hot pressed powders in the same temperature grows together with extension the time their milling.
4. Basing on analysis of diffraction patterns and using Scherrer relationship (1) the Co-β grains size was calculated. For hot pressed powder in range 5-15 MPa the average size of crystallites amount to between 37-42 nm what near applied method of calculation (1) of their size in borders of mistake
5. Consolidation of amorphous $Co_{77}Si_{11.5}B_{11.5}$ powder in range of pressure 5-15 MPa in the same temperature leads to amorphous soft magnetic bulk materials which possess magnetic properties changing to the worse that as-quenched ribbon as a precursor.
6. The hot pressing of metallic powder (obtained in high energy ball milling of amorphous ribbons) in range pressures 5-15 MPa, introduces a lot of slots (Figs. 5 and 6.) into the structure of material, with negative influence on the soft magnetic properties of the resulting bulk sample. It was confirmed in [17].
7. With the milling time increase (in preparing time of metallic powder) the magnetic flux density of obtained bulk material decreases (Table 2.).

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