INVERSE-HEUSLER Mn_2FeSi ALLOY PREPARED BY POWDER METALLURGY ROUTE

[1]Ondřej ŽIVOTSKÝ, [2]Kateřina SKOTNICOVÁ, [2]Tomáš ČEGAN, [2]Jan JUŘICA, [1]Lucie GEMBALOVÁ, [3,4]František ZAŽÍMAL, [3]Yvonna JIRÁSKOVÁ, [2]Ivo SZURMAN

[1]VSB – Technical University of Ostrava, Department of Physics, Ostrava, Czech Republic, EU, ondrej.zivotsky@vsb.cz

[2]VSB – Technical University of Ostrava, Regional Materials Science and Technology Centre, Ostrava, Czech Republic, EU, katerina.skotnicova@vsb.cz

[3]Czech Academy of Sciences, Institute of Physics of Materials, Brno, Czech Republic, EU, zazimal@ipm.cz

[4]Masaryk University, Department of Physical Electronics, Brno, Czech Republic, EU

https://doi.org/10.37904/metal.2022.4434

Abstract

The Mn_2FeSi inverse-Heusler alloy was prepared by solid-state reactions using ball milling for 168 h in n-hexane. Two milling procedures varying in the ball-to-powder ratio, namely 4:1 and 10:1, were used to follow their influence on alloy formation and its physical properties. In both cases no Heusler structure was obtained directly and therefore the subsequent annealing at 1223 K for 1.5 h in pure Ar was applied. The energy-dispersive X-ray analysis resulted in the chemical composition about 49.0-49.9 at% Mn, 25.3-25.6 at% Fe, and 24.8-25.4 at% Si, in a good agreement with nominal one. X-ray diffraction of both powders confirmed inverse-Heusler XA structure of lattice parameters 0.5675 nm (4:1) and 0.5677 nm (10:1), only slightly higher as theoretically obtained 0.560 nm. The presence of minor oxidation phases was also observed in the particle structure of powders. Magnetic properties were analysed at low and room temperatures. Both alloys exhibit paramagnetic behaviour at room temperature confirmed by transmission Mössbauer spectroscopy measurements. Different magnetic behaviour of alloys is observed below 65 K.

Keywords: Heusler alloy, powder, ball milling, microstructure, magnetism

1. INTRODUCTION

Heusler alloys represent special class of tunable materials with more than 4000 potential members and offer a wide range of applications [1]. Currently, many papers are devoted to theoretical calculations of existing and/or newly proposed compositions of Heusler alloys with possible applications mainly in microelectronics and spintronics [2,3]. Similarly, various laboratories over the world try to prepare such Heusler compositions experimentally and to study their structural and physical properties [3]. Among them, the Heusler Mn_2FeSi compound was also subjected to theoretical DFT-based calculations [4] and subsequently synthesized by several procedures either in a form of ingots or thin films [5,6]. However, the unified view concerning its physical properties in connection with microstructure and mainly magnetic ordering is still vague. Moreover, experimental results at low temperatures show different magnetic behaviour than predicted by theoretical calculations and are strongly dependent on the production technology.

Present work continues previous study of the Mn_2FeSi alloy prepared by mechanical alloying resulting in the inhomogeneous para- and ferro-/ferrimagnetic phase composition at room temperature [7]. Here, the same ball milling technology is used with two different ball-to-powder ratios (BPR), namely 4:1 and 10:1. Both solid-state synthesized Mn_2FeSi compounds are subsequently annealed (Ar atmosphere, 1223 K / 1.5 h) and subjected to detail structural and magnetic investigations.

2. EXPERIMENTAL

The Heusler Mn_2FeSi alloys were prepared using the mixture of powdered pure elements – manganese (≥ 99.3 wt%), iron (≥ 99.5 wt%), and silicon (≥ 99.9985 wt%). This mixture was divided into two parts and placed in two stainless-steel water-cooled milling bowls together with stainless-steel balls of 5 mm in diameter and n-hexane serving as a solvent. The ball-to-powder ratio was adjusted to 4:1 in the first bowl and to 10:1 in the second one. The milling in both cases was done by a high-energy ball mill E-max, Retsch (GmbH) at 500 rpm for 168 h of milling. After this time, small amounts of powders were checked and because no pure elements were detected the milling procedure was stopped. Nevertheless, the X-ray diffractograms did not show patterns corresponding to Heusler structure of Mn_2FeSi alloy. Therefore, the next step of the previously established heat treatment at 1223 K/1.5 h in the atmosphere of pure Ar was applied using a sintering furnace, Xerion Advanced Heating, Ofentechnik (GmbH) for both samples.

The microstructure and chemical composition of the alloy powders were analysed by the scanning electron microscope (SEM) QUANTA 450 FEG (FEI Company) used in the backscattered electron (BSE) mode completed by an energy-dispersive X-ray (EDX) analyser APOLLO X. The crystal structure and phase composition were studied using the powder X-ray diffractometer AXS D8 Advance (Bruker) equipped with CuKα (0.1540598 nm) radiation. Room-temperature (RT) diffractograms were measured in 2θ range 20° - 95° with the step 0.014° and time per step 2 s. Rietveld structure refinement method using ICDD PDF-2 database was used for the phase analysis and determination of the lattice parameters.

A standard Mössbauer spectrometer operating in the constant acceleration mode and transmission geometry was used to collect the data along with a ^{57}Co (Rh) source at RT. Calibration of the velocity scale was done with α-Fe thin foil and the isomer shifts are given with respect to its Mössbauer spectrum. The program CONFIT [8] was used to analyse the experimental points by the double- and single-line components yielding values of isomer shift (δ), quadrupole splitting (Δ), and their relative representations (A).

Magnetic properties were measured at low and room temperatures by the vibrating sample magnetometer (VSM, Microsense, model EZ 9) and the physical property measurement system (PPMS, Quantum Design, model P935A). VSM was used for measurements of RT magnetization curves with maximal magnetic field of ±1600 kA/m. PPMS was applied to obtain the field-cooled (FC) and zero-field-cooled (ZFC) curves measured in the temperature range 2-300 K at a magnetic field of 80 kA/m.

3. RESULTS AND DISCUSSION

3.1. Phase and chemical analysis

The SEM images of the Mn_2FeSi samples are shown in **Figures 1a** and **1b** for BPR = 4:1 and 10:1, respectively. They consist of very small mostly rounded particles in size below 2 μm and by the larger particle agglomerates (> 100 μm). It is supported by the particle size distributions in **Figure 1c** which documents that a use of a higher amount of balls during milling results in a formation of the finer powder. The mean value 16.9 μm was obtained for the sample prepared by BPR 4:1 and 3.8 μm for the sample prepared by BPR 10:1. The chemical element compositions of both samples were determined using EDX on the cross-sections prepared by metallographic cutting of largest particles. The analysis resulted in a relatively high amount of oxygen in both samples as it is documented in **Table 1** and by corresponding element maps for BPR = 4:1 and BPR = 10:1. The element maps show a uniform homogeneous distribution of Mn, Si, Fe and O elements and the chemical compositions obtained by oxygen elimination at both samples agreed well with nominal one.

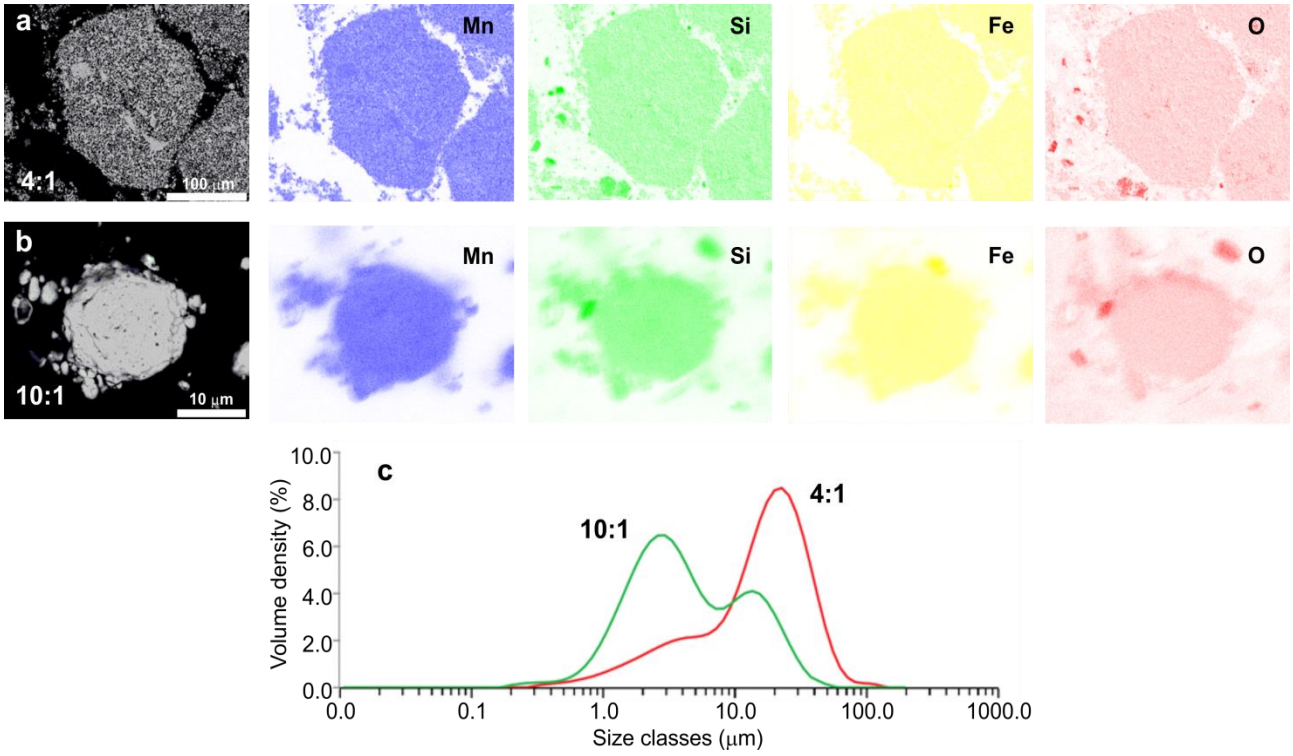

Figure 1 Scanning electron microscopy (SEM) images of the Mn_2FeSi alloy powders milled for 168 h at ball-to-powder ratio (a) 4:1 and (b) 10:1 with distribution maps of Mn, Si, Fe and O elements. (c) Particle size distributions with bimodal character

Table 1 Chemical composition including oxygen and after oxygen elimination of the annealed Mn_2FeSi powders at ball-to-powder ratios (BPR) 4:1 and 10:1. Values were obtained as the average of three measured spectra

BPR	Mean values (at%)						
	Mn	Fe	Si	O	Mn	Fe	Si
4:1	39.5	20.1	19.2	21.2	49.9	25.3	24.8
10:1	39.4	20.9	19.9	19.8	48.8	25.9	25.3

The X-ray diffraction patterns of Mn_2FeSi samples for BPR = 4:1 and 10:1 are shown in **Figure 2**. The Rietveld analysis of both diffractograms evidences the cubic Heusler phase with the lattice parameters 0.5675 nm (4:1) and 0.5677 nm (10:1) practically identical and well agreed with the theoretical value 0.560 nm [4]. In both cases the inverse-Heusler XA structure is confirmed by the higher relative intensity of the (111) diffraction peak compared to (200) peak well seen in the inset of **Figure 2**. The several small peaks at both diffractograms reflect a presence of the minor not specified impurity phase(s) formed during preparation procedure and/or manipulation with powdered samples. Based on the chemical analysis, resulted in relatively high content of oxygen in both samples, these peaks could be speculatively ascribed to (Mn, Fe, Si)-oxides formed mainly at defects rising during mechanical alloying and not fully annealed out in the subsequent treatment. The similar peaks were also detected by XRD measurement of the Mn_2FeSi ingot-type samples in Ref. [9]. The presence of oxides is partially also confirmed by Mössbauer results presented below.

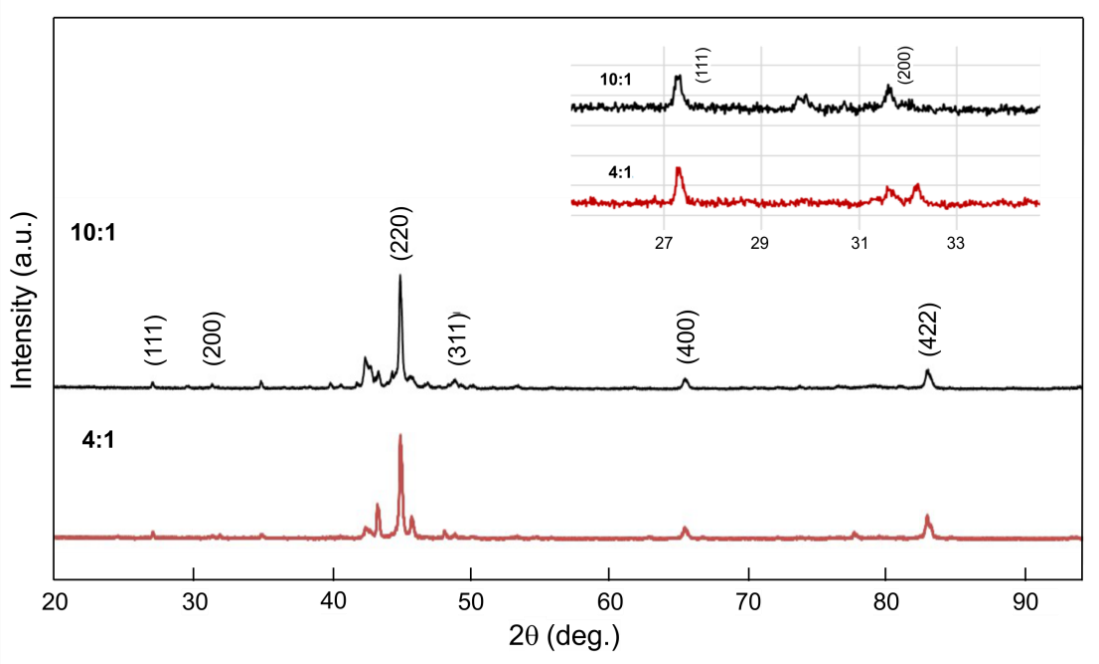

Figure 2 X-ray diffraction patterns of the Mn_2FeSi samples milled for 168 h at ball-to-powder ratios 4:1 and 10:1 and annealed at 1223 K/1.5 h. The inset shows (111) and (200) diffraction peaks.

3.2. Magnetic and Mössbauer properties

The Mössbauer spectra of the mechanically alloyed powdered Mn_2FeSi samples in **Figures 3a** and **3b** reflect a paramagnetic origin at room temperature. They were analysed using a single-line (S) corresponding to the Mn_2FeSi phase and several two-line (D) subcomponents that can be speculatively ascribed to a non-stoichiometric (Fe,Mn)-oxides and/or to chemical disorder at grain boundaries. All subcomponents were analysed using the same line width of 0.246 mm/s obtained from the calibration spectrum. The hyperfine parameters of all sub spectra are summarized in **Table 2**. A ratio of S/ΣD is better on behalf of the sample obtained for BPR = 4:1 with slightly higher content of Mn. Paramagnetic nature of both alloy powders is fully confirmed by RT magnetization curves (**Figure 3c**) that are not saturated and show linear dependence of mass magnetization on an applied external magnetic field. Samples slightly differ in derived mass susceptibilities being $3.6 \cdot 10^{-7}$ m^3/kg (BPR = 4:1) and $4.5 \cdot 10^{-7}$ m^3/kg (BPR = 10:1), respectively.

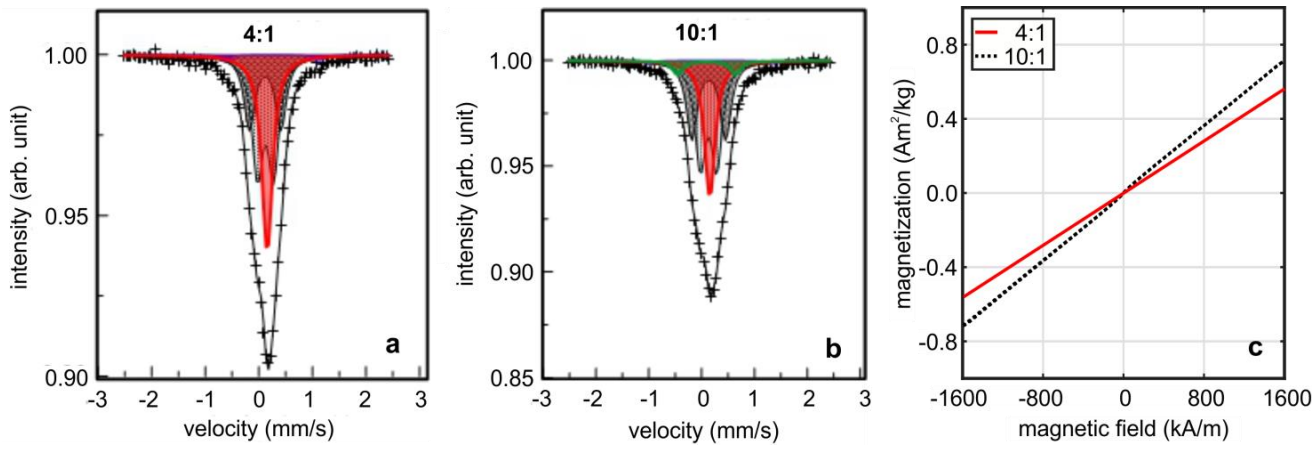

Figure 3 (a,b) Room temperature Mössbauer spectra of the annealed Mn_2FeSi powders at ball-to-powder ratios 4:1 and 10:1. (c) Corresponding room temperature magnetization curves

Table 2 Hyperfine parameters, isomer shift, δ, quadrupole splitting, Δ, and relative intensity, A, of prepared Mn_2FeSi alloy powders

BPR	component	δ (mm/s)	Δ (mm/s)	A (%)
4:1	S	0.155(1)		33.8(9)
	D1	0.123(2)	0.304(9)	38.9(10)
	D2	0.118(3)	0.587(9)	25.0(11)
	D3	0.249(26)	1.713(51)	2.2(3)
10:1	S	0.155(1)		26.0(6)
	D1	0.132(1)	0.313(6)	38.2(6)
	D2	0.134(2)	0.642(6)	29.3(6)
	D3	0.094(10)	1.095(21)	5.3(4)
	D4	0.185(38)	2.355(76)	1.2(3)

The low-temperature magnetic measurements are presented in **Figure 4**. The FC-ZFC curves and magnetization curves of both samples confirm the paramagnetic behavior from RT to about 160 K. The separation of the FC-ZFC curves is observed at a temperature of 150 K, which corresponds to the inflection point of both curves. By cooling both samples below this temperature, a structural transformation takes place, manifested by the formation of a new ferro-/ferrimagnetic phase. This is also evident from the measured magnetization curves (not presented), which in addition to the paramagnetic contribution show a typical magnetization reversal at small magnetic fields. Another significant point is the peak around 65 K, at which both curves differ in the values of mass magnetization. A markedly higher is a value at the sample with BPR = 10:1 being about 10 Am^2kg^{-1} compared to 3 Am^2kg^{-1} at the sample with BPR = 4:1. Below this temperature, mainly the ZFC curves yield fully different behaviour. A reason is unknown and the new low-temperature presently running magnetic and Mössbauer measurements below 65 K should contribute to the explanation.

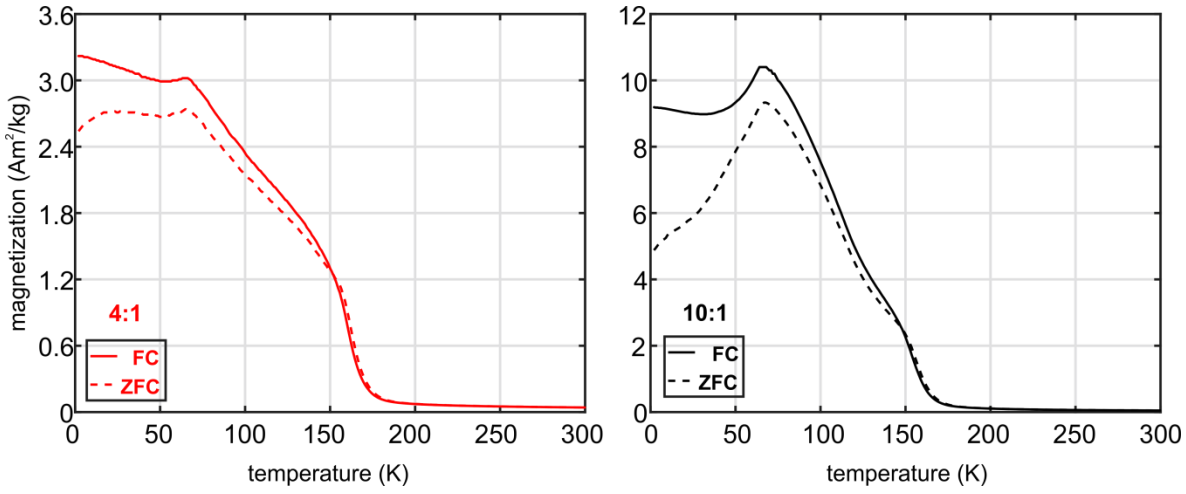

Figure 4 Field-cooled (FC, full lines) and zero-field-cooled (ZFC, dashed lines) curves of Mn_2FeSi alloy powders measured at magnetic field of 80 kA/m

4. CONCLUSION

The paper is devoted to the microstructural and magnetic properties of the Mn_2FeSi alloys prepared using the mechanical alloying. Formation of the cubic inverse-Heusler phase was achieved by ball milling of the raw

materials (Mn, Fe, Si) for 168 h at different ball-to-powder ratios (BPR = 4:1 and 10:1) and additional annealing of the samples at 1223 K for 1.5 h in the protective atmosphere of Ar. The main experimental results obtained on both samples can be summarized as follows:

1) Both powders were formed by the very small particles about (1-2) μm and by particle agglomerates reaching the size up to 100 μm at BPR = 4:1 as documented by SEM. Mean particle size is 16.9 μm for BPR = 4:1 and 3.8 μm for BPR = 10:1.
2) The chemical compositions have shown relatively large amount of oxygen in both samples but the compositions after oxygen elimination agreed well with the nominal $Mn_{50}Fe_{25}Si_{25}$.
3) Both samples were paramagnetic at room temperature as the linear dependences of mass magnetization on applied external magnetic field and Mössbauer spectra measurements confirmed.
4) The zero-field-cooled (ZFC) and field-cooled (FC) measurements below 300 K resulted in no substantial differences up to the temperature of 65 K at which a sharp maximum was observed. Below this temperature, different behaviour of mainly ZFC curves has provoked new magnetic and Mössbauer measurements that should contribute to its explanation.

ACKNOWLEDGEMENTS

This work was supported by the Czech Science Foundation under the project No. 21-05339S and by the Ministry of Education, Youth and Sports of the Czech Republic via the project SP 2022/25.

REFERENCES

[1] FELSER, C., HIROHATA, A. *Heusler Alloys: Properties, Growth, Applications.* Cham: Springer, 2016.

[2] Al-ZYADI, J.M.K., ASKER, H.I. Preserving the half-metallicity at the full Heusler alloy Sc_2CrSi surfaces as well as Sc_2CrSi/HgTe (111) interface. *Journal of Magnetism and Magnetic Materials*. 2021, vol. 539, pp. 168371.

[3] ELPHICK, K., FROST, W., SAMIEPOUR, M., KUBOTA, T., TAKANASHI, K., SUEGAWA, H., MITANI, S., HIROHATA, A. Heusler alloys for spintronic devices: review on recent development and future perspectives. *Science and Technology of Advanced Materials*. 2021, vol. 22, pp. 235-271.

[4] MA, J.H., HE, J. G., MAZUMDAR, D., MUNIRA, K., KESHAVARZ, S., LOVORN, T., WOLVERTON, C., GHOSH, A.W., BUTLER, W.H. Computational investigation of inverse Heusler compounds for spintronics applications. *Physical Review B*. 2018, vol. 98, pp. 094410.

[5] ARYAL, A., BAKAR, S., SAMASSEKOU, H., PANDEY, S., DUBENKO, I., STADLER, S., ALI, N., MAZUMDAR, D. Mn_2FeSi: An antiferromagnetic inverse-Heusler alloy. *Journal of Alloys and Compounds*. 2020, vol. 823, pp. 153770.

[6] GRANOVSKII, A. B., SOBOLEVA, E.A., FADEEV, E. A., DUBENKO, I. S., ARYAL, A., SAMASSEKOU, H., PANDEY, S., STADLER, S., MAZUMDAR, D., ALI, N., LÄHDERANTA, E. Martensitic phase transition in magnetic thin films based on inverse Mn_2FeSi Heusler alloys. *Journal of Experimental and Theoretical Physics*. 2020, vol. 130, pp. 117-122.

[7] ŽIVOTSKÝ, O., SKOTNICOVÁ, K., ČEGAN, T., JUŘICA, J., GEMBALOVÁ, L., ZAŽÍMAL, F., SZURMAN, I. Structural and magnetic properties of inverse-Heusler Mn_2FeSi alloy powder prepared by ball milling. *Materials.* 2022, vol. 15, pp. 697.

[8] ZAK, T., JIRASKOVA, Y. CONFIT: Mössbauer spectra fitting program. *Surface and Interface Analysis*. 2006, vol. 38, pp. 710-714.

[9] BAKKAR, S. *New inverse-Heusler materials with potential spintronics applications*. Carbondale, 2017. Thesis. Southern Illinois University.