

Magnetic Properties of Co₂MnSi-based Heusler Alloy Glass-coated Microwires

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Abstract

We have successfully fabricated nanocrystalline Co₂MnSi Heusler alloy glass-coated microwires with a metallic nucleus diameter of 10.2 μm and total diameter 22.2 μm by the Taylor–Ulitsky technique. Magnetic and structural investigations have been performed to clarify the basic magneto-structural properties of the Co₂MnSi glass-coated microwires. XRD showed a well-defined crystalline structure with a lattice parameter $a = 5.62 \text{ \AA}$. Metallic nucleus of both annealed and as-prepared sample show L2₁ cubic ordered structured mixed with the amorphous glass coating. The hysteresis loops showed unique thermal stability with temperature, the coercivity (H_c) exhibits roughly stable temperature behavior. The annealed sample shows anomalous magnetic behavior with temperature at applied external magnetic field $H = 5 \text{ kOe}$, where different four trends of magnetization curves with temperature are observed. The obtained results illustrate the sensitivity of Co₂MnSi-based glass coated microwires to the temperature and magnetic field which make it a promising material for sensing application.

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We have successfully fabricated nanocrystalline Co₂MnSi Heusler alloy glass-coated microwires with a metallic nucleus diameter of 10.2 μm and total diameter 22.2 μm by the Taylor–Ulitsky technique. Magnetic and structural investigations have been performed to clarify the basic magneto-structural properties of the Co₂MnSi glass-coated microwires. XRD showed a well-defined crystalline structure with a lattice parameter $a = 5.62 \text{ \AA}$. Metallic nucleus of both annealed and as-prepared sample show L2₁ cubic ordered structured mixed with the amorphous glass coating. The hysteresis loops showed unique thermal stability with temperature, the coercivity (H_c) exhibits roughly stable temperature behavior. The annealed sample shows

anomalous magnetic behavior with temperature at applied external magnetic field $H = 5$ kOe, where different four trends of magnetization curves with temperature are observed. The obtained results illustrate the sensitivity of Co_2MnSi -based glass coated microwires to the temperature and magnetic field which make it a promising material for sensing application.

Index Terms —Nanocrystalline magnetic materials, Coercive force, Magnetic hysteresis, Heusler alloy.

Introduction

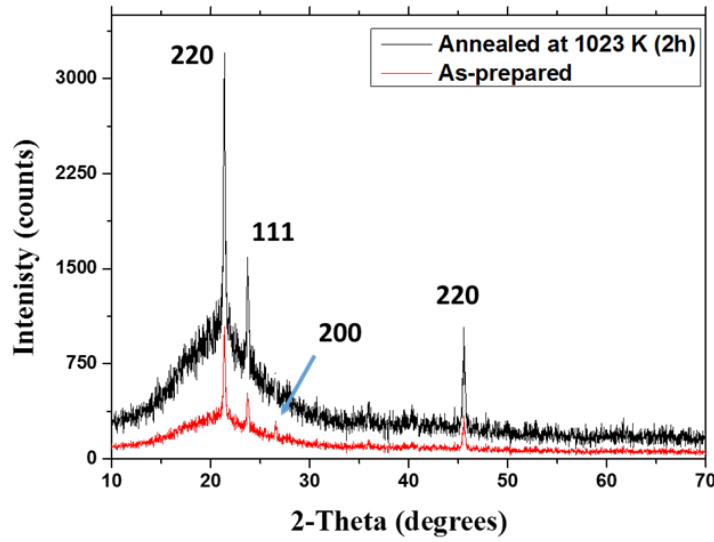
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icro/nanostructured magnetic materials in various physical forms have gained the interest of researchers due to their potential applications in spintronics, magneto optics, and thermoelectricity [1–6]. Glass-coated micro- and nanowires with amorphous and nanocrystalline structure are particularly fascinating materials in terms of both theoretical and technological applications. The modified Taylor-Ulitovsky method can be used to manufacture large amount of these microwires [7]. As a result, research on glass-coated microwires has gained a lot of attention lately, partly because of their technical applications, particularly as sensor components in various systems [8,9].

Heusler alloys, which have compositions of X_2YZ (full-Heusler) or XYZ (half-Heusler), where X and Y are transition metals and Z is the main group element, are among the promising ferromagnetic alloys [10]. These materials have a number of potential applications. Co-based Heusler compounds are among the most promising materials for multifunctional applications because of their high Curie point ($T_c > 1200$ K), tunable band structure, and low magnetic damping coefficients [11]. Due to its high band gap for minority spins (0.5 to 0.8 eV), high Curie temperature (985 K), high tunnel magnetoresistance, large magnetoresistance ratios, and perpendicular magnetic anisotropy, Co_2MnSi is a strong candidate for an advanced spintronic device [12,13]. Thus, Co_2MnSi Heusler alloy is one of the most studied Co-based Heusler compounds.

The most common method for fabricating the magnetic Heusler alloy is arc melting, followed by thermal treatment to improve its physical structure [3]. it Using this preparation technique was possible to create bulk Heusler alloys with variable chemical compositions using this technique. Furthermore, several processes are used to produce Heusler alloys in a variety of forms, including thin films, nanoparticles, ribbons, and nanostructured materials, according to reports elsewhere [14]. Miniaturization, as previously stated, allows for the modification and enhancement of several physical properties of bulk Heusler alloys [14,15]. Nevertheless, there are a number of issues and difficulties that must be addressed before any potential "multifunction and smart" Heusler alloy can be prepared. First, large-scale production of alloys made from Heusler compounds with identical chemical and physical properties. Furthermore, specialized processes were costly and limited by extremely precise physical requirements (ultra-high vacuum, pressure, power, high temperature and specific substrate).

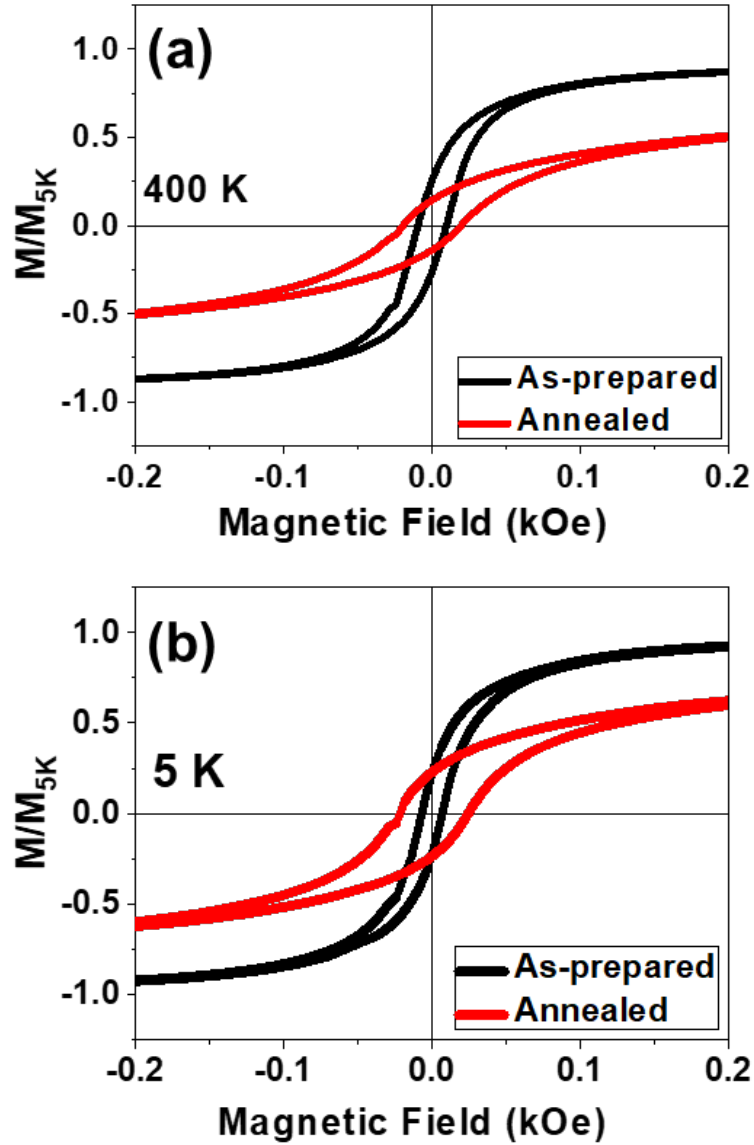
Recently, Heusler alloys-based glass-coated microwires prepared by Taylor-, Ulitovsky method show a promising ability to tailor the magnetic and physical properties of the metallic core materials as reported elsewhere [15,21].



Taylor-Ulitovsky fabrication method allows to produce ultra-thin and uniform glass-covered microwires, composed of a metallic nucleus (diameter 0.1-100 μm) coated by a glass cover (thickness 2-10 μm) [8,9]. Due to the low cost of large-scale manufacturing (i.e., a few kilometers from a small ingot (5 g)), it is a very promising approach for the creation of multifunctional & smart materials for a wide range of applications. Furthermore, the versatility of creating Heusler-based glass-coated microwires with different structures, such as amorphous, nanocrystalline, and granular, provides a unique opportunity to investigate the impact of different microstructure types of the same material on its physical properties [8,9,14]. Furthermore, flexible, insulating, and continuous glass coating provides electrical short-circuit protection, allowing the use of Heusler-based glass-coated microwires in harsh chemical environments, as well as biocompatibility for the often biologically incompatible structure of Heusler alloys [22,23]. However, to our best knowledge, such promising Heusler alloys, namely Co_2MnSi -based glass-coated microwires, have not been investigated. As a result, this study, along with our recent studies [14,18] is regarded as a pioneering investigation aimed at revealing the primary magneto structural properties of Co_2MnSi -based glass-coated microwires.

In current paper we illustrate the effect of annealing and external magnetic field on the magneto-structural properties of Co_2MnSi based glass-coated microwire.

Experimental technique;



To prevent the Mn deficit due to Mn evaporation of the Co_2MnSi alloy during the melting process, we used a commercial arc furnace with a Mn excess from highly pure elements, Co (99.99%), Si (99.9%), and Mn (99.99%) under vacuum and in an argon atmosphere. The Co_2MnSi alloy's nominal chemical composition was determined using energy dispersive X-ray (EDX)/ scanning electron microscopy (SEM) [14,18]. Then, we fabricate glass-coated Co_2MnSi microwires. In brief, a high frequency inductor heated an ingot above its melting temperature, and then a glass capillary was formed, which was filled with molten Co_2MnSi alloy, drawn out, and wound onto a rotating pick-up bobbin [14,18]. The details of the thermal annealing condition of Co_2MnSi glass coated microwires reported in [18]. To investigate the structure, we used X-rays Diffraction for the annealed and as-prepared sample.

Room temperature and thermal magnetic behavior of Co₂MnSi glass-coated microwire samples has been performed by using the physical property magnetic system, PPMS (Quantum Design Inc., San Diego, CA, USA), for the field cooling and field heating magnetization curves for a temperature range from 5 K–350 K with an applied external magnetic field up to 5 kOe.

experimental results and discussion

From the XRD analysis of the as-prepared and annealed Co₂MnSi glass-coated microwires, we deduced that the structure consists of an amorphous glass-coating combined with the ordered L2₁ cubic phase as shown in Fig. 1. The XRD of annealed sample shows an increased XRD peaks intensity, as- compared to the as-prepared sample. Both of sample show a mixed ordered structure overlapping with the amorphous signal at $2\theta = 22.5^\circ$. In addition, the peak at $2\theta = 27^\circ$ with (200) is disappeared in the annealed sample. The average grain size evaluated using Debye-Scherrer formula increases from 46 to 64 nm for as-prepared and annealed sample, respectively.

Figures 2 summarize the magnetic hysteresis behavior of as-prepared and annealed Co₂MnSi glass-coated microwires over a wide temperature range of 400 K to 5 K. For a better comparison of the magnetic behavior of the samples, all M-H loops are represented as M/M_{5K} , where M_{5K} is the maximum magnetic moment obtained at 5K. The normalized M/M_{5K} values are calculated by comparing the maximum magnetic moment at various T to the M_{5K} -value. As illustrated in Figure 2, all samples, annealed and as-prepared, exhibit ferromagnetic behavior because the Curie point is much higher than the room temperature. Furthermore, the annealed sample has lower normalized saturation magnetization than the as-prepared sample.

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From the hysteresis loops measured at various temperatures, T , 5–400 K, of as-prepared and annealed (1023 K, 2 h) Co₂MnSi glass-coated microwires, we evaluated the temperature dependence of coercivity of annealed sample, $H_{c_{ann}}$, and the coercivity for as-prepared sample $H_{c_{asp}}$. Then we calculate the increasing factor $P = H_{c_{ann}}/H_{c_{asp}}$. As seen in Table 1, the annealed sample shows more than 3 times higher coercivity compared to the as-prepared sample at all range of measuring temperature, being the average of the increasing factor 3.02. Interesting behavior of P with temperature is observed: P shows a jump below $T = 200$ K, as the increasing factor increase from 2.3 to 3.2 time for temperature 200 K and 150 K, respectively. This sudden increase at P value is related to changing in microstructure of annealing sample which can be associated to the phase transition. Small variation of H_c with T is observed for the as-prepared and annealed samples. Higher H_c - values of the annealed sample can be related to various reasons, such as different microstructure of annealed sample, related to the recrystallization process of annealed samples or coexistence of ferromagnetic and antiferromagnetic interactions, which can affect the magnetic response with temperature and magnetic field as well. The small variation in the coercivity with temperature may manifest the unique thermal stability of coercivity with temperature. This type of H_c stability with temperature can be suitable for various applications.

TABLE I

Coercivity dependence on temperature for annealed and as-prepared Co₂MnSi glass-coated microwires.

T (K)	$H_{c_{asp}}$ (Oe)	$H_{c_{ann}}$ (Oe)	$P = H_{c_{ann}} / H_{c_{asp}}$
5	7	24	3.4
10	6	22	3.7
20	5	23	4.6
50	7	23	3.3

T (K)	H_{casp} (Oe)	H_{cann} (Oe)	$P = H_{cann} / H_{casp}$
100	6	21	3.5
150	6	19	3.2
200	8	18	2.3
250	8	19	2.4
300	9	20	2.2
350	8	20	2.5
400	9	19	2.1

To investigate the possible magnetic phase transition in as-prepared and annealed samples, we measure temperature dependence of magnetization at low magnetic field $H = 100$ Oe [14,18]. As illustrated in our previous studies, both of Co_2MnSi glass coated microwires sample show irreversible behavior combined with blocking temperature 200 K. In addition, we illustrated the different magnetic behavior for annealed and as-prepared sample below and above blocking temperature. Here we investigate the magnetization behavior with temperature with applied high magnetic field i.e., $H = 5$ k-Oe. As shown in Figure 3, both of samples show totally different magnetic behavior. For as-prepared sample notable mismatching between the field cooling (FC) and field heating (FH) magnetization curves, such mismatching did not observe for FC and FH measured at low magnetic field [18]. In case of annealed sample, substantial change in magnetization versus temperature is observed. Four different tendencies of magnetization with temperature are detected. First part a decreasing of normalized magnetization from 350 to 300 K then sharp increasing with temperature for temperature range 300 K to 200 K. Third region described by rapid decreasing of magnetization from 200 K to 100 K. Finally, gradual increase of FC and FH magnetization curves from 100 K to 5 K. These changing in FH and FC magnetization curves matched with the behavior of the increasing factor P with temperature. Such of this magnetic tendency with temperature for annealed sample is totally different of which reported at our previous article [18]. The magnetic behavior of annealed sample indicates the sensitivity of annealed Co_2MnSi glass-coated microwires to the temperature and magnetic field which make it a promising candidate for magnetic sensing.

Conclusions

In current work we illustrate the effect of the applied magnetic field and annealing for tailoring of the magnetic behavior of Co_2MnSi -based glass-coated microwires. The annealing substantially affects both the structure and magnetic behavior of Co_2MnSi alloy. However, the XRD profile of annealed sample show a notable change in its intensity, both of sample show $L2_1$ cubic ordered structured overlapping with the amorphous signal. In addition, an increase in the average grain size from 46.2 nm to 64.2 nm for the as-prepared and annealed sample, respectively. The annealed sample show different magnetic respond with the temperature and magnetic field compare to the as-prepared one. Firstly, the annealed sample shows 3 time higher coercivity than as-prepared sample. In addition, FC and FH magnetization curves show a unique magnetic tendency with temperature at applied external magnetic field 5 kOe, where four recognized temperature range have different magnetic behavior. The remarkable thermal stability of the coercivity values of annealed and as-prepared Co_2MnSi glass-coated microwires can be integrated in generators, sensors, transformers, and switching circuits based on glass-coated microwires for application possibilities.

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Author Contributions:

Conceptualization, M.S. and A.Z.; methodology, V.Z. M.I.; validation, M.S., V.Z. and A.Z.; formal analysis, M.S and A.W.; investigation, M.S., A.W, and A.Z.; resources, V.Z. and A.Z.; data curation M.S, M.I. and A.W; writing—original draft preparation, M.S., A.W. and A.Z.; writing—review and editing, M.S. and A.Z.; visualization, M.S., A.W., and V.Z supervision, A.Z.; project administration, V.Z. and A.Z.; funding acquisition, V.Z., and A.Z. All authors have read and agreed to the published version of the manuscript.

References

1. M. Hoop, et al. “Mobile Magnetic Nanocatalysts for Bioorthogonal Targeted Cancer Therapy”. *Adv. Funct. Mater.* , vol. 28, p.1705920. 2018.
2. M. Salaheldeen, V. Vega, A. Fernández, and V.M. Prida, “Anomalous In-Plane Coercivity Behaviour in Hexagonal Arrangements of Ferromagnetic Antidot Thin Films”. *J. Magn. Magn. Mater.* , vol. 491, p. 165572. 2019.<https://doi.org/10.1016/j.jmmm.2019.165572>
3. M. Salaheldeen, A. Nafady, A.M. Abu-Dief, R. Díaz Crespo, M.P. Fernández-García, J.P. Andrés, R. López Antón, J.A. Blanco, and P. Álvarez-Alonso, “Enhancement of Exchange Bias and Perpendicular Magnetic Anisotropy in CoO/Co Multilayer Thin Films by Tuning the Alumina Template Nanohole Size”. *Nanomaterials* , vol.12, p. 2544. 2022. <https://doi.org/10.3390/nano12152544>
4. M. Salaheldeen, L. Martínez-Goyeneche, P. Álvarez-Alonso, and A. Fernández, “Enhancement the Perpendicular Magnetic Anisotropy of Nanopatterned Hard/Soft Bilayer Magnetic Antidot Arrays for Spintronic Application”. *Nanotechnology* , vol. 31, p. 485708. 2020.**DOI** 10.1088/1361-6528/abb109
5. S.H. Skjærvø, C.H. Marrows, R.L. Stamps, L.J. Heyderman, “Advances in artificial spin ice”. *Nat. Rev. Phys.* . vol. 2, pp. 13–28. 2019. <https://doi.org/10.1038/s42254-019-0118-3>
6. E. Maniv, et al. “Exchange bias due to coupling between coexisting antiferromagnetic and spin-glass orders”. *Nat. Phys.* , vol. 17, pp. 525–530. 2021. <https://doi.org/10.1038/s41567-020-01123-w>
7. H. Chiriac, H. and T-A. Ovari, Amorphous glass-covered magnetic wires: Preparation, properties, applications, *Prog. Mater. Sci.*, vol. 40, pp. 333-407, 1996.
8. A. Zhukov et.al, “Advanced functional magnetic microwires for technological applications”, *J. Phys. D: Appl. Phys.* , vol. 55, pp.253003, 2022, doi:10.1088/1361-6463/ac4fd7.
9. M. Salaheldeen, A. Garcia, P. Corte-Leon, M. Ipatov,; V.Zhukova, and A. Zhukov, “Unveiling the Effect of Annealing on Magnetic Properties of Nanocrystalline Half-Metallic Heusler Co₂FeSi Alloy Glass-Coated Microwires”. *J. Mater. Res. Technol.* , vol. 20, pp. 4161-4172, 2022. doi:10.1016/J.JMRT.2022.08.162.
10. K. Elphick, W. Frost, M. Samiepour, T. Kubota, K. Takanashi, H. Sukegawa, S. Mitani, A. Hirohata, “Heusler Alloys for Spintronic Devices: Review on Recent Development and Future Perspectives”. *Sci. Technol. Adv. Mate.* , vol.22, pp. 235–271, 2021. doi:10.1080/14686996.2020.1812364.
11. P. Li, et al. “Giant Room Temperature Anomalous Hall Effect and Tunable Topology in a Ferromagnetic Topological Semimetal Co₂MnAl”. *Nat. Commun.* , vol. 11, pp. 1–8, 2020. doi:10.1038/s41467-020-17174-9.

12. S.J. Ahmed, C. Boyer, M. Niewczas, Magnetic and Structural Properties of Co_2MnSi Based Heusler Compound, *J. Alloys Compd.* 781 , pp. 216–225, 2019.<https://doi.org/10.1016/j.jallcom.2018.12.018>
13. M. Jourdan, et al.” Direct Observation of Half-Metallicity in the Heusler Compound Co_2MnSi ”. *Nat. Commun.*, vol. 5, p. 3974. 2014. <https://doi.org/10.1038/ncomms4974>
14. M. Salaheldeen, A. Talaat, M. Ipatov, V. Zhukova, and A. Zhukov, “Preparation and Magneto-Structural Investigation of Nanocrystalline CoMn-Based Heusler Alloy Glass-Coated Microwires”. *Processes* , vol. 10, p. 2248, 2022.<https://doi.org/10.3390/pr10112248>
15. C. Guillemard, et al.”Ultralow Magnetic Damping in Co_2Mn -Based Heusler Compounds: Promising Materials for Spintronics”. *Phys. Rev. Appl.* , vol. 11, p. 064009. 2019. <https://doi.org/10.1103/PhysRevApplied.11.064009>
16. M. Salaheldeen, A. Garcia-Gomez, P. Corte-Leon, M. Ipatov, V. Zhukova, J. Gonzalez, and A. Zhukov, “Anomalous Magnetic Behavior in Half-Metallic Heusler Co_2FeSi Alloy Glass-Coated Microwires with High Curie Temperature”. *J Alloys Compd.* , vol. 923, p. 166379, 2022. doi:10.1016/J.JALLCOM.2022.166379.
17. M. Salaheldeen, A. Garcia-Gomez, P. Corte-León, A. Gonzalez, M. Ipatov, V. Zhukova, J. Gonzalez, R. López Antón, and A. Zhukov,”Manipulation of Magnetic and Structure Properties of Ni_2FeSi Glass-Coated Microwires by Annealing”. *J Alloys Compd.* , vol. 942, p. 169026, 2023.<https://doi.org/10.1016/j.jallcom.2023.169026>.
18. M. Salaheldeen, M. Ipatov, P. Corte-Leon, V. Zhukova, and ; A. Zhukov, “Effect of Annealing on the Magnetic Properties of Co_2MnSi -Based Heusler Alloy Glass-Coated Microwires”. *Metals* , vol. 13, p. 412. 2023.<https://doi.org/10.3390/met13020412>.
19. M. Salaheldeen, A. Wederni, M. Ipatov, J. Gonzalez, V. Zhukova, and A. Zhukov, “Elucidation of the Strong Effect of the Annealing and the Magnetic Field on the Magnetic Properties of Ni_2 -Based Heusler Microwires”. *Crystals* , vol. 12, p. 1755. 2022. <https://doi.org/10.3390/cryst12121755>.
20. M. Salaheldeen, M. Ipatov, V. Zhukova, A. García-Gomez, J. Gonzalez, and A. Zhukov, “Preparation and magnetic properties of Co_2 -based Heusler alloy glass-coated microwires with high Curie temperature”. *AIP Adv.* , vol. 13, p. 025325. 2023.<https://doi.org/10.1063/9.0000482>
21. M. Salaheldeen, A. Wederni, M. Ipatov, V. Zhukova, and A. Zhukov, “Preparation and Magneto-Structural Investigation of High Ordered (L_{21} Structure) Co_2MnGe Microwires”. *Preprints* , 2023020494. 2023. <https://doi.org/10.20944/preprints202302.0494.v1>.
22. O. Mitxelena-Iribarren, et.al. Glass-Coated Ferromagnetic Microwire-Induced Magnetic Hyperthermia for in Vitro Cancer Cell Treatment. *Mater. Sci. Eng.C* vol. 106 , p.110261, 2020, doi:10.1016/J.MSEC.2019.110261.
23. D. Kozajova, et.al., Biomedical applications of glass-coated microwires, *J. Magn. Magn. Mater.* , vol. 470 pp. 2-5, 2019. doi:10.1016/J.JMMM.2017.11.004.