Abstract

„Influence of alloying additives on the magnetic, catalytic properties and crystalline structure of high-induction iron-based soft magnetic materials"

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The subject of this dissertation is high-induction (>1.5 T) amorphous and nanocrystalline soft magnetic Fe-M-B alloys (where M = Cu, Co, Mo, Nb, Cr) in the form of ribbons obtained using the melt-spinning method. High-induction amorphous and nanocrystalline soft magnetic Fe-based materials are increasingly used in power electronics as materials for magnetic cores in power transformers, stators in electric motors, and magnetic components in energy storage systems. Their main advantages include high saturation induction, low coercive field strength, and minimal energy losses. These properties result from the appropriate selection of alloy chemical composition and heat treatment conditions, which control the material's microstructure. Even slight changes in alloy composition can significantly affect magnetic exchange between atoms, the ability to form an amorphous phase during ribbon casting and the process of nucleation and growth of α-Fe crystallites from the amorphous matrix. Additionally, the chemical composition and crystalline structure influence the electrochemical potential and oxidation susceptibility of the outer layer, as well as the catalytic activity of the material in advanced oxidation processes.

A review of the literature on the subject, combined with the author's own research, suggests that the chemical composition and crystal structure (resulting from both composition and heat treatment) play a crucial role in determining the physicochemical properties of amorphous and nanocrystalline iron-based soft magnetic alloys. In view of the above, **the main objective of this doctoral dissertation was to develop a manufacturing technology for high-**

induction (> 1.5 T) amorphous and nanocrystalline Fe-M-B soft magnetic materials in the form of metallic ribbons, and to determine the correlations between the influence of selected alloying additions (M = Cu, Co, Mo, Nb, Cr) and heat treatment on thermodynamic parameters, crystallisation processes, crystal structure, and selected magnetic, electrochemical, and catalytic properties.

To achieve this goal, the following specific objectives were defined:

- development of alloy compositions using thermodynamic calculations by modifying the binary Fe-B alloys ($Fe_{86}B_{14}$ and $Fe_{85}B_{15}$) with alloying elements such as Cu, Co, Mo, Nb, and Cr, substituting Fe atoms;
- development of a method for obtaining amorphous ribbons using rapid quenching of the molten alloy on a rotating wheel - melt-spinning method;
- determination of the correlation between chemical composition and the process and kinetics of crystallisation of amorphous ribbons;
- development of a heat-treatment technology (in vacuum and in air) for amorphous ribbons based on the crystallisation process of the material;
- determination of the correlation between the percentage of alloying additions and heat-treatment temperature, and the resulting crystal structure as well as magnetic properties (and, for selected alloys, also electrochemical and catalytic properties) of the materials.

Based on the literature review and the results of the author's own work, the following research hypothesis was formulated:

The physicochemical properties (thermal stability, saturation induction, coercivity, core power losses, complex magnetic permeability, corrosion resistance, and catalytic activity) of Fe-B-based alloys in the form of ribbons depend primarily on their chemical composition and crystal structure. The presence of alloying elements (Cu, Co, Nb, Mo, Cr) and the applied heat treatment process enable the tailoring of these properties for specific applications.

To verify this hypothesis, the following research questions were formulated:

- Can optimisation of chemical composition based on thermodynamic parameter calculations influence the final properties of the material, and if so, how?
- How does the substitution of a small amount of alloying elements (M = Cu, Co, Nb, Mo, Cr) for Fe affect the crystallisation process of Fe-M-B alloys?
- How do heat-treatment parameters affect the crystal structure and, consequently, the magnetic properties of metallic ribbons?
- Does the heat-treatment process in air influence the crystal structure and physicochemical properties of the materials, and if so, how?
- Is it possible, through chemical composition modification and controlled heat treatment, to obtain magnetic cores with a saturation induction above 1.5 T while maintaining low core losses?
- Can the developed Fe-based materials be used as catalysts in advanced oxidation processes?
- How does the addition of Cr affect the corrosion resistance of the material, and does its presence enable a more controlled process of organic pollutant degradation?

To address these research questions, thermodynamic parameter calculations were performed, a series of materials was obtained, and studies were conducted using appropriately selected measurement methods. The results of these studies, along with their detailed analysis and interpretation, were presented as a cycle of eight scientific publications published in peer-reviewed journals in the field of Materials Engineering, with a total Impact Factor (IF) of 28.5 for 2024, a Cite Score of 53.6 for 2024, and a total of 1,110 MNiSW points. The collected works present both fundamental and applied research findings, enabling the identification of potential applications in power electronics and catalytic processes. The current outcome of this work includes four patents based on results obtained during the implementation of this industrial PhD project. Complementing the experimental part is an extensive literature review aimed at illustrating the relationship between the presence of alloying elements, crystal structure, and the physicochemical properties (especially magnetic properties) of Fe-based soft magnetic materials.

The methodology and scope of the work were designed so that the obtained materials and research results could be correlated with each other and with other materials currently used in power electronics. For this purpose, seven groups of materials (31 chemical compositions) were developed. The Cu content was determined based on thermodynamic parameter calculations, such as configurational entropy (ΔS^{conf}), Gibbs free energy of mixing (ΔG^{mix}), and Gibbs free energy of amorphous phase formation (ΔG^{amorph}). Master alloys were prepared using a vacuum induction furnace with pure elements (Cu, Co, Cr, Mo) and alloy precursors (Fe-B, Fe-Nb). Differential thermal analysis (DTA) was used to determine the solidus-liquidus temperatures, which in turn defined the casting temperature for ribbons produced by rapid quenching of the molten alloy on a rotating wheel - melt-spinning method. The casting parameters (ejection pressure, casting temperature, crucible height above the wheel, crucible slit length, wheel linear speed) were selected to obtain ribbons with an amorphous structure and thickness in the range of 15–30 µm. The amorphous structure of the ribbons after casting was confirmed by wide-angle X-ray diffraction (XRD). Differential scanning calorimetry (DSC) was applied to determine the characteristic crystallisation temperatures (the onset temperature of crystallisation process T_x and the peak temperature T_p corresponding to the maximum crystallisation rate) of α-Fe and Fe-B phases, to assess the thermal stability of the amorphous phase (the maximum temperature at which the material remains fully amorphous) and the α-Fe phase (ΔT_x – the difference between the crystallisation onset temperature of Fe-B and α-Fe). Crystallisation kinetics parameters of the α-Fe phase were determined using various theoretical models (e.g., activation energy calculated by Kissinger's and Ozawa-Flynn-Wall methods, Avrami exponent). Additionally, dynamic mechanical analysis (DMA) was used for selected amorphous materials to determine dynamic-mechanical properties as a function of temperature (storage modulus E', loss modulus E'', and loss factor $tan\delta$).

For each of the seven groups of materials, a series of heat treatments was carried out on toroidal cores formed from the cast ribbons. Heat treatment was conducted in vacuum or in air, from room temperature up to the defined temperature, with a heating rate of 10°C/min and an isothermal annealing time of 20 minutes at temperatures derived from DSC measurements. For one selected material, the annealing time was extended. After heat treatment, hysteresis loops were measured (at f = 50 Hz and H corresponding to magnetic saturation of the sample), and the specific core loss Ps was determined at f = 50 Hz and B = 1 T ($P_{10/50}$). For selected materials, the dependence of Ps on frequency f and induction B was also determined. The crystal structure after heat treatment was analysed by X-ray diffraction, neutron diffraction, transmission electron microscopy (TEM), and scanning electron microscopy (SEM). Based on these studies, the relationships between Hc, Bs, Ps, crystal structure, and heat-treatment temperature were established.

To further characterise the effects of chemical composition modifications and heat treatment, additional studies were carried out on selected materials: the magnetisation of amorphous ribbons was measured as a function of temperature using a vibrating sample magnetometer (VSM) to determine the Curie temperature; the real μ' and imaginary μ'' components of magnetic permeability of toroidal cores were determined using an impedance analyser to describe the frequency dependence of soft magnetic properties; magnetostriction was measured as a function of magnetic field using strain gauges; Mössbauer spectroscopy was performed to determine the local magnetic field at the Fe nucleus; and open circuit potential (OCP) measurements as well as dynamic tests were conducted to assess electrochemical properties in a 3.5% NaCl solution. The catalytic potential of the materials in advanced oxidation processes (AOP) was evaluated in the photo-Fenton process of organic dyes degradation (methylene blue and rhodamine B), with decomposition monitored by ultraviolet-visible (UV-VIS) spectroscopy.

The research results were presented in the form of a cycle of eight scientific publications published in peer-reviewed journals in the field of Materials Engineering. The dissertation includes the following scientific publications:

- [1] **Warski T.**, Włodarczyk P., Polak M., Zackiewicz P., Radoń A., Wójcik A., Szlezynger M., Kolano-Burian A., Hawełek Ł.; Influence of Cu Content on Structure and Magnetic Properties in Fe86-xCuxB14 Alloys; Materials 2020; 13(6):1451; DOI:10.3390/ma13061451,

- [2] Hawełek Ł., **Warski T**., Włodarczyk P., Polak M., Zackiewicz P., Radoń A., Wójcik A., Kolano-Burian A.; Effect of Co Substitution on Crystallization and Magnetic Behavior of Fe85.45xCoxCu0.55B14 Metallic Glass; Materials 2020; 13(4):919; DOI: 10.3390/ma13040919,

- [3] Hawełek Ł., Zackiewicz P., Kądziołka-Gaweł M., Wójcik A., Maziarz W., Chulist R., Fábián M., **Warski T.**; Structure and magnetic properties of vacuum- and air-annealed rapidly quenched Mo- and Co-modified Fe85.3Cu0.7B14 alloy; Archives of Civil and Mechanical Engineering 2025, 25: 188. DOI: 10.1007/s43452-025-01238-y,

- [4] Hawełek Ł., **Warski T.**, Zackiewicz P., Hudecki J., Kolano-Burian A.; Magnetic properties evolution and crystallization behaviour of vacuum- and air-long-term-annealed rapidly quenched Fe80.3Co5Cu0.7B14 alloy; Scientific Report 2022; 12, 21387; DOI:10.1038/s41598-022-25925-5,

- [5] **Warski T.**, Gutiérrez J., Orue I., Zackiewicz P., Łoński W., Babilas R., Kolano-Burian A., Hawełek Ł.; Effect of minor Cr addition on the crystallisation process, magnetic, electrochemical and catalytical properties of high induction Fe86B14 alloy; Journal of Physics and Chemistry of Solids 2025; 202, 112687; DOI: 10.1016/j.jpcs.2025.112687,

- [6] Hawelek L., **Warski T.**, Radon A., Pilsniak A., Maziarz W., Szlezynger M., Kadziolka-Gawel M., Kolano-Burian A.; Structure and Magnetic Properties of Thermodynamically Predicted Rapidly Quenched Fe85-xCuxB15 Alloys; Materials 2021; 14(24):7807; DOI: 10.3390/ma14247807,

- [7] **Warski T.**, Pilśniak A., Wójcik A., Szlezynger M., Dadiel J.L., Kolano-Burian A., Hawełek Ł.; Annealing Optimization of High Induction (> 1.7 T) Fe85−(x+y)CoxCuyB15 Alloys With Enhanced Magnetic Properties; Metallurgical and Materials Transactions A 2024; 55, 1174–1182. DOI: 10.1007/s11661-024-07313-y,

- [8] Hawełek Ł., Zackiewicz P., Wójcik A., Hudecki J., **Warski T.**; Influence of Nb and Mo Substitution on the Structure and Magnetic Properties of a Rapidly Quenched Fe79.4Co5Cu0.6B15 Alloy; Materials 2023; 16(18):6288. DOI: 10.3390/ma16186288.

In the discussed cycle of works published as part of the doctoral dissertation, a total of 31 amorphous materials in the form of ribbons were prepared. To optimise their magnetic properties through controlled crystallisation, these materials were subjected to heat treatment. The main physicochemical properties of these materials—namely, the onset temperature of α-Fe phase crystallisation (T_{x1}) and the temperature difference between the onset of α-Fe and Fe-B phase crystallisation (ΔT_x) (determined using DSC at a heating rate of 10°C/min), the activation energy of α-Fe crystallisation calculated by the Kissinger method ($Ea_{\alpha\text{-}Fe}$), the optimal annealing temperature at which the minimum core loss was recorded (T_{opt}), as well as the magnetic parameters saturation induction (Bs), coercive field (Hc), and core loss (measured at a frequency of 50 Hz and induction of 1 T – $P_{10/50}$) for samples annealed at T_{opt}, are summarised in Table 1.

Table 1. Summary of materials and their selected physicochemical properties presented in the publication cycle.

Chemical composition	T_{x1} [°C]	ΔT_x[°C]	$Ea_{\alpha\text{-}Fe}$ [kJ/mol]	T_{opt} [°C]	Magnetic properties			Publication
					Bs [T]	Hc [A/m]	$P_{10/50}$ [W/kg]	
$Fe_{86}B_{14}$	369.8	106.5	201.8	290	1.51	12.4	0.19	[1]
$Fe_{85.6}Cu_{0.4}B_{14}$	380	103.2	211.6	280	1.47	13.1	0.25	
$Fe_{85.45}Cu_{0.55}B_{14}$	369.8	79.8	202.56	280	1.5	13.1	0.21	
$Fe_{85.3}Cu_{0.7}B_{14}$	377.6	97.9	219.15	290	1.53	9.71	0.13	
$Fe_{85}Cu_{1}B_{14}$	378.9	97.1	228.74	300	1.6	9.91	0.14	
$Fe_{82.95}Co_{2.5}Cu_{0.55}B_{14}$	382.9	97.2	187	310	1.6	16.2	0.34	[2]
$Fe_{80.45}Co_{5}Cu_{0.55}B_{14}$	363.7	115.2	177	310	1.73	55.8	1.1	
$Fe_{77.95}Co_{7.5}Cu_{0.55}B_{14}$	368.7	113.4	197	310	1.77	26.3	0.43	
$Fe_{75.45}Co_{10}Cu_{0.55}B_{14}$	374.6	109.5	195	310	1.78	23.8	0.37	
$Fe_{80.3}Co_{5}Cu_{0.7}B_{14}$	371.2	101.2	188.7	310/air	1.75	18.9	0.28	[3]
$Fe_{80.3}Mo_{5}Cu_{0.7}B_{14}$	419.1	135.6	245.7	330/air	0.76	5.79	-	
$Fe_{75.3}Co_{5}$ $Mo_{5}Cu_{0.7}B_{14}$	419	124.3	247.8	330/air	1.13	6.84	0.11	
$Fe_{80.3}Co_{5}Cu_{0.7}B_{14}$	-	-	-	260/5h	1.77	20	0.34	[4]
$Fe_{80.3}Co_{5}Cu_{0.7}B_{14}$	-	-	-	210/20h	1.71	23.5	0.43	
$Fe_{85}Cr_{1}B_{14}$	387.8	65.5	190.5	320	1.41	12.5	0.21	[5]
$Fe_{83}Cr_{3}B_{14}$	403.3	60.3	213.9	320	1.26	8.14	0.14	
$Fe_{81}Cr_{5}B_{14}$	421.6	45,9	225.9	320	1.03	6.51	0.13	
$Fe_{85}B_{15}$	410	41.3	199	300	1.59	9.53	0.15	[6]
$Fe_{84.4}Cu_{0.6}B_{15}$	409	34.2	223	330	1.61	10.5	0.17	
$Fe_{83.8}Cu_{1.2}B_{15}$	395.9	54.8	215	320	1.62	9.2	0.14	
$Fe_{83.5}Cu_{1.5}B_{15}$	-	-	-	Material too brittle				
$Fe_{81.9}Co_{2.5}Cu_{0.6}B_{15}$	405.4	41.5	216.1	330	1.69	16	0.21	[7]
$Fe_{79.4}Co_{5}Cu_{0.6}B_{15}$	388.6	89.9	189.7	330	1.74	15.1	0.24	
$Fe_{76.9}Co_{7.5}Cu_{0.6}B_{15}$	376.3	102.4	168.6	300	1.75	26.4	0.39	
$Fe_{81.3}Co_{2.5}Cu_{1.2}B_{15}$	349.5	122.3	157	310	1.67	14.7	0.24	
$Fe_{78.8}Co_{5}Cu_{1.2}B_{15}$	357.9	117.4	184.2	300	1.73	18.5	0.3	
$Fe_{76.3}Co_{7.5}Cu_{1.2}B_{15}$	370.9	106.3	208.4	310	1.78	23.9	0.31	
$Fe_{78.4}Co_{5}Cu_{0.6}Nb_{1}B_{15}$	398.4	114.6	203.4	340	1.62	16.7	0.25	[8]
$Fe_{77.4}Co_{5}Cu_{0.6}Nb_{2}B_{15}$	417.4	129	230.9	340	1.53	11.5	0.18	
$Fe_{76.4}Co_{5}Cu_{0.6}Nb_{3}B_{15}$	426.9	154.7	231.5	360	1.43	9.9	0.15	
$Fe_{78.4}Co_{5}Cu_{0.6}Mo_{1}B_{15}$	409.5	90.8	219.8	340	1.6	13.4	0.18	
$Fe_{77.4}Co_{5}Cu_{0.6}Mo_{2}B_{15}$	416.6	104.4	229.4	360	1.51	10.5	0.15	
$Fe_{76.4}Co_{5}Cu_{0.6}Mo_{3}B_{15}$	425.3	100.2	236.3	360	1.53	9.3	0.14	

The obtaining of the materials was preceded by calculations of thermodynamic parameters as a function of Cu content for the chemical compositions $Fe_{86-x}Cu_xB_{14}$ [1] and $Fe_{85-x}Cu_xB_{15}$ [6]. These calculations revealed a nonlinear dependence of ΔG^{amorph} on Cu content, showing a parabolic trend with a minimum for the alloys $Fe_{85.45}Cu_{0.55}B_{14}$ and $Fe_{84.4}Cu_{0.6}B_{15}$. For these Cu concentrations, critical values (local minima or maxima) of characteristic crystallisation temperatures and magnetic properties were observed.

The relationship between chemical composition modification through substitution of Fe atoms with alloying elements (M = Cu, Co, Nb, Mo, Cr), crystallisation processes, and physicochemical properties of Fe-B alloys was investigated for two base compositions: $Fe_{86-x}M_xB_{14}$ and $Fe_{85-x}M_xB_{15}$. The influence of alloying additions was determined for the following groups: Cu in $Fe_{86-x}Cu_xB_{14}$ (x = 0, 0.4, 0.55, 0.7, 1) [1] and $Fe_{85-x}Cu_xB_{15}$ (x = 0, 0.6, 1.2, 1.5) [6], Co in $Fe_{85.45}Co_xCu_{0.55}B_{14}$ (x = 2.5, 5, 7.5, 10) [2], $Fe_{84.4}Co_xCu_{0.6}B_{15}$ and $Fe_{83.8}Co_xCu_{1.2}B_{15}$ (x = 2.5, 5, 7.5) [7], Co and Mo in $Fe_{85.3-(x+y)}Co_xMo_yCu_{0.7}B_{14}$ (x = 0, 5; y = 0, 5) [3], Cr in $Fe_{86-x}Cr_xB_{14}$ (x = 1, 3, 5) [5], Mo in $Fe_{78.4}Co_5Cu_{0.6}Mo_xB_{15}$ and Nb in $Fe_{78.4}Co_5Cu_{0.6}Nb_xB_{15}$ (x = 1, 2, 3) [8] (Table 1).

For 30 amorphous alloys, 20-minute heat treatment processes at different temperatures were carried out. The influence of annealing on the crystalline structure was determined and correlated with magnetic properties. Although transformation temperatures strictly depended on chemical composition, the crystallisation process itself was similar across all materials studied. At low isothermal annealing temperatures (below T_{x1}), stress relaxation was observed, leading to a reduction of *Hc* and *Ps* values and an increase in *Bs*. With increasing annealing temperature, atomic structure reorganisation and short-range order correlations occurred, accompanied by the formation of α-Fe nanocrystallites within the amorphous matrix. In this temperature range, the microstructure ensured the lowest core loss values ($P_{10/50}$). Further temperature increase led to crystal growth, causing deterioration of soft magnetic properties. Depending on the thermal stability of the alloy (ΔT_x), this process could also be accompanied by the crystallisation of magnetically hard Fe–B phases. In alloys containing Mo and Nb, where ΔT_x was sufficiently high, two minima in $P_{10/50}$ were observed.

The effect of long-term low-temperature annealing of $Fe_{80.3}Co_5Cu_{0.7}B_{14}$ [4] was also investigated with respect to relaxation, crystallisation structure, and magnetic properties. The results indicated that such treatment was energetically insufficient to achieve the low core loss levels obtainable after 20-minute annealing at higher temperatures.

Additionally, a series of heat treatments in air was carried out, as described in publications [3–8]. The results showed that this process had no significant impact on *Hc*, *Bs*, or $P_{10/50}$ values.

Catalytic properties in advanced oxidation processes were investigated for selected amorphous ribbons. The results confirmed that all studied materials exhibited catalytic activity in the photo-Fenton process. Extended electrochemical and catalytic property analyses were performed for the $Fe_{86-x}Cr_xB_{14}$ series (x = 1, 3, 5) [5]. These studies demonstrated that the materials could be successfully applied as catalysts in photo-Fenton processes, achieving methylene blue decolourisation efficiencies after 60 minutes of 75–62% for as-cast alloys and 79–60% for heat-treated alloys. This indicates the potential for dual (magnetic and catalytic) applications of the developed materials.

In summary, the collected works present both fundamental and industrial research results, enabling the identification of potential applications in power electronics and catalytic processes. The applied outcomes of this work are four patents obtained based on the results generated during this industrial doctorate project:

- Pat. 246117: *"Method of producing a layered soft magnetic composite material with an insulating matrix"*;
- Pat. 245562: *"Soft magnetic composite for compensating choke applications"*;
- Pat. 245484: *"Method of producing a high-induction soft magnetic metallic composite with enhanced oxidation resistance"*;
- Pat. 242686: *"Method of producing a composite for 3D printing with a filling of soft magnetic powder and a thermoplastic polymer blend matrix"*.

Summary of the doctoral candidate's contribution: The candidate's work involved co-developing the research plan, co-obtaining ribbon materials and conducting their heat treatments, investigating crystallisation processes, determining crystallisation kinetics parameters, examining magnetic properties (magnetostriction, Curie temperature), investigating catalytic properties, analysing and discussing studies results (thermal analysis, XRD, TEM, magnetic, electrochemical, and catalytic properties), writing the original and revised versions of manuscripts, as well as participating in implementation works and preparation of patent applications.