Abstract of Thesis

Thesis topic: **"Microstructure to magnetic behaviour relationship of amorphous and nanocrystalline Fe-based alloys"**

In the last few years, amorphous and nanocrystalline alloys have been intensively studied. These materials are example of soft magnetic materials, which are important for technological applications and interesting from the basic point of view. Nanocrystalline soft magnetic materials are usually obtained by appropriate annealing of a melt-spun amorphous precursor. Generally, these materials may be a single or multiphase polycrystals with ultra fine grains embedded in a highly disordered residual amorphous matrix. The amount of the crystalline phase and of the amorphous matrix depends on alloys composition, annealing conditions, and influences the magnetic properties of these alloys. The nano size grains structure leads to the excellent soft magnetic properties, which arise from the great reduction in the mean magnetocrystalline anisotropy and the very low saturation magnetostriction, low coercivity, low core loss, high susceptibility and nearly zero its disaccommodation. Usually, only two phases were considered in the description of the magnetic properties of the nanocrystalline Fe-based alloys. However, the additional component consisting Fe atoms at the grain surfaces is also considered. The other results of magnetic and structural studies of Fe-based alloys were reported in several papers. However, the relation between microstructure and magnetic properties of amorphous and nanocrystalline Fe-based alloys with different amount of the crystalline phase has not been fully explained.

The purpose of this paper is to investigate the microstructure and magnetic properties for the as-quenched and annealed near the crystallization temperature Fe-based alloys.

The Fe-based as-quenched ribbons were obtained by using a single roller melt-spinning method in protective atmosphere. Investigations were curried out for the samples in the as-quenched state, after stress relief and after annealing at temperature close to the primary crystallization temperature for different time periods. Moreover, annealing above the secondary crystallization temperature was done. The microstructure of all the ribbons was examined at room temperature by X-ray diffractometry with Cu K_α radiation and Mössbauer spectroscopy (^{57}Co in a Rh source). The DC and AC magnetic properties were performed for the toroidal samples and 100 mm long ribbons using a completely automated set-up (designed and constructed by Rogowski and co-workers of the Research System Laboratory "Pentalab", Warsaw) for initial susceptibility, and DC *M-H* Loop Tracer (4850, Tesla Co., Ltd.) and MMS-4001 (Ryowa Electronics Co., Ltd.), respectively.

On the base obtained results, we can conclude that:

1. The nanocrystalline Fe-based alloys obtained by annealing of melt-spun amorphous precursor at temperature close to primary crystallization temperature consist of crystalline α-Fe(Si) (FINEMET-type alloys) or α-Fe (Fe-TM-B-(Cu) alloys, TM-transition metal) phase with average grain size of about 10-20 nm.
2. The low temperature ageing of the $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ alloy also allows obtaining the nanocrystalline materials exhibiting good soft magnetic properties, which depend on the annealing time.

3. The heat treatment of the $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ alloy below the primary crystallization temperature increases of the average hyperfine field at ^{57}Fe nuclei. It is connected with annealing out of some free volumes and increase of the packing density of the atoms. Moreover, in the crystalline α-FeSi phase only short-range order was observed.
4. Sample of the $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ alloy annealed below primary crystallization (733 K) exhibits tendency to clusterization. This effect is caused by addition of Cu atoms into Fe-Si-B alloy.
5. In the initial stage of the crystallization the amount of the iron content in the amorphous matrix is the same as in the as-quenched precursor. With progressing crystallization, the intergranual phase is depleted in iron, which is connected with more complete diffusion of TM-elements out of the regions where crystallization takes place.
6. The magnetic properties of the Fe-based alloys depend on their composition, preparation conditions of as-quenched ribbons, and heating and cooling rates. The optimal magnetic properties of the FINEMET-type alloys were obtained for the sample annealed at 813 K for 1 h (the optimal conditions) and then cooled to room temperature with average rate of 80 K/min (in air). The slow cooling (in furnace – 2 K/min) leads to the local induced anisotropy whereas the rapid cooling (in water – 300 K/min) allows to introduce the internal stresses to the sample. It is worth noticing that the phase composition and the iron content in the amorphous matrix do not depend on the cooling rate.
7. The internal stresses in the amorphous ribbons of the Fe-based alloys leads to the randomly distributed of the magnetization (the intensity of the second line in the Zeeman fulfil relation: $3{:}A_{2,5}{:}1 \approx 3{:}2{:}1$). During the

stress relief of the ribbons the higher values of $A_{2,5}$ indicate the tendency of the magnetization to rotate into the plane of the ribbons.

8. In the ribbons of the Fe-Zr-based alloys besides the amorphous and crystalline phases the additional structural component consisting of iron atoms at the grain surfaces is also considered (interfacial zone).
9. The Mössbauer spectra investigations show the difference between structures of the surface and the bulk. The complex magnetic behaviour is demonstrated by the magnetic field obtained for the bulk of Fe-Zr-B alloy due to the magnetic interactions between the crystalline grains.
10. The ultrafine grain structure of the nanocrystalline Fe-based alloys obtained by appropriate annealing of the amorphous ribbons leads to the excellent soft magnetic properties, which arise from the great reduction in the mean magnetocrystalline anisotropy due to the random anisotropy effect. The formation of the nanocrystalline structure is ascribed to the combined addition of Cu and Nb atoms.
11. In the amorphous Fe-rich materials, the broad magnetic relaxation spectrum is observed. The relaxation processes in the amorphous materials are connected with reorientation of the mobile atom pairs in the vicinity of free volumes.
12. The isochronal disaccommodation curves for the amorphous Fe-based alloys can be described as superposition of three elementary processes with Gaussian distribution of relaxation times. The results obtained for the activation energies and pre-exponential factor in Arrhenius law show that the disaccommodation phenomenon is attributed to the reorientation of the mobile atom pairs near free volumes in the amorphous matrix. Therefore, the amorphous matrix plays the dominant role as the main source of the magnetic after-effect in the nanocrystalline alloys.

13. The magnetic after-effect in the nanocrystalline alloys is caused by the relaxation processes occurring in the amorphous matrix. The low disaccommodation intensity and decrease of the stabilization field for the nanocrystalline samples is connected with the annealing out of most of free volumes in the amorphous matrix during heat treatment.
14. The microstructure of the Fe-based alloys influences their magnetic properties. The substitution of 1 at% Fe atoms by Cu atoms in the $Fe_{87}Zr_7B_6$ alloy leads to the increase of the initial magnetic susceptibility of the nanocrystalline alloys. Moreover, the addition of Cu atoms to Fe-based alloys decrease the primary crystallization temperature.
15. The ribbons of the $Fe_{86}Zr_6B_8$ alloy annealed at 873 K for different time periods shows magnetic hardening. This behaviour must be interpreted within the framework of the random anisotropy model.
16. The partially replacing of Zr atoms in the Fe-Zr-B-Cu alloys by Nb, Mn and/or Ti atoms and further annealing of the as-quenched precursor leads to the improvement of soft magnetic properties of the investigated ribbons. The partially crystallized alloys (about 50-60 % of the crystalline phase) exhibit excellent soft magnetic properties (high permeability, high saturation magnetic flux density and low coercivity) as well as low core losses and good frequency characteristics.

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学位（博士）論文審査及び最終試験の終了報告書

学位（博士）の申請に対し、学位論文の審査及び最終試験を終了したので、下記のとおり報告します。

記

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論 文 題 目	Microstructure to magnetic behaviour relationship of amorphous and nanocrystalline Fe-based alloys						

審査要旨（２０００字以内）

別 紙 参 照

（次頁へ続く）

審査要旨

高度に電化された現代社会で消費されるエネルギーの約 80 %が電気エネルギー である。ところで、現在の発電熱効率は 40%程度であり、一方我が国において、電気機器鉄心中で消費される鉄損量は 1 年間で 300 億 kWh にも達する。それ故、現代社会の必要電力供給には莫大な熱エネルギーを必要とし、その結果は地球へ重い負担をかけている。その環境問題解決の一手段は電気機器の高効率化を促すことにより熱エネルギーの使用量を減ずることが焦眉の課題である。

本研究ではエネルギー効率向上のために、電気機器の主要構成部品に使用される高効率鉄心材料開発の基礎実験を行い、そのデータをまとめた。近年の鉄心材料開発研究は高配向薄板材料、又は非晶質材料の研究が主流であったが、何れも所期の目的を十分に達成することはできなかった。本論文は非晶質材料に適当な熱処理を施して、ナノ結晶磁性材料を作製し、従来の結晶質材料と非晶質材料両方の好い特性を合わせ持つ材料の開発を試みた結果をまとめたもので、8 章で構成されている。

第 1 章はナノ結晶磁性材料研究の歴史と有望性について記述している。

第 2 章では鉄系非晶質材料の歴史と背景、を述べるとともに、ナノ結晶材料に関する金属物理的及び熱力学的な考察を加えている。そしてナノ結晶材料作製に適した第 3 元素または第 4 元素の働きについて述べている。

第 3 章では諸測定装置について述べている。ナノ結晶の確認はメスバウワー装置、X 線回折装置および高解像度 TEM で行った。

第 4 章では飽和磁気、抗磁力、透磁率、鉄損や磁気余効の理論について述べている。

第 5 章では研究の目的と展望および焼鈍条件、第 3 及び第 4 元素の役割、メスバウワーデータの解析手法や磁気余効分析について述べている。また諸磁気特性や電気抵抗率測定装置について説明している。

第 6 章は実験結果を詳しく記述している。Fe-Si-B 系非晶質材料に Cu, Nb, Zr 或いは Co 等を種々の量で添加して、10 種類以上の材料を作製した。作製した材料の厚さは 20 μm 厚さである。その材料は760K-1hの焼鈍で材料全体に一様なナノ結晶が生長していることが確認された。その中で $Fe_{86}Zr_6B_8$ の材料が最とも優れた特性を示した。その材料の磁気余効は非晶質材料の 7 分の 1 位に減少し、磁気特性が安定していることを示した。電気抵抗は最大なり、鉄損 $W_{10/50}$ = 0.8 W/kg と商用鋼板 20%程度、非晶質材料の 33%程度に低下した。また $W_{10/1k}$ は 3W/kg と高周波特性も優れている事が分かった。抗磁力は 0.5A/m, 仮想最大磁束密度は 33T と優れた性質を示した。

第 7 章では研究の結論と本材料の応用の展望をまとめている。

以上本論文は、高性能磁気材料として良質の高安定鉄基ナノ結晶材料の作製に成功し、電力機器や高周波機器への応用に展望を開いた。その事は磁気工学・技術の発展に寄与すること大であり、所期の目的を十分に達成している。

一方、著者は最終試験において磁気物理学、結晶学や磁気材料学の質問に的確に答えることができた。

よって、本論文は博士（工学）の学位論文として合格と認める。また、最終試験も合格と認める。