Instytut Fizyki Molekularnej Polskiej Akademii Nauk

Termodynamiczne aspekty tworzenia faz magnetycznie twardych o strukturze tetragonalnej w wybranych stopach na bazie żelaza oraz charakteryzacja ich właściwości fizycznych

ROZPRAWA DOKTORSKA

mgr Mieszko Kołodziej

Promotor: dr hab. inż. Zbigniew Śniadecki
Promotor pomocniczy: dr hab. inż. Agnieszka Grabias

Poznań 2023

II. Abstract

The main scope of the thesis is focused on the determination of structural stability and possibility of formation of various Fe-based phases crystallizing in tetragonal structure (characterized with hard magnetic properties) and further description of their stability range and physical properties. This research is motivated by the necessity to develop rare-earth lean or rare-earth free hard magnetic materials. It is strictly connected with the ever-shrinking global resources. All of the investigated phases are characterized with the limited possibility of their synthesis in bulk form. Therefore, the research relies not only on the experimental methods, but also employs the semiempirical calculations. Their main purpose was to define and compare the enthalpies of formation of phases competing during solidification process, *i.e.* solid solution, amorphous phase and selected intermetallic compounds. These results allowed to optimize the chemical composition and to select adequate synthesis methods to improve the stability and possibility of formation of designed alloys.

The experimental studies were carried out for three groups of alloys: (i) Fe-Ni doped with other elements such as Co and Cu; (ii) $Zr_{0.4-x}Nd_xCe_{0.6}Fe_{10}Si_2$ ($0 \leq x \leq 0.3$) and (iii) $(Fe_{0.7-x}Co_{0.3-x}M_{2x})_2B$ (M = W, Re; x = 0, 0.025). These results were complementary to those determined on the basis of semiempirical calculations and brought information regarding physical properties of newly synthesized alloys.

The calculations performed for the Fe-Ni system led to the conclusion, that Cu doping can induce structural disorder in these alloys. Introduction of topological disorder was one of the main experimental goals, as the formation of diffusion paths for Ni and Fe was believed to be necessary to facilitate the formation of $L1_0$-FeNi. The alloys synthesized by utilization of the metallic fraction of the Morasko meteorite crystallized in the face-centered cubic phase. Additionally, a microstructure of the obtained alloys was strongly modified by the high pressure torsion processing, which led to significant refinement of crystallites.

Calculations of the formation enthalpy of desired phases (especially that of the $ThMn_{12}$-type) in (Zr, Nd, Ce)-Fe-Si system, confirmed that zirconium and silicon played a crucial role in decreasing of this quantity. Synthesized $Zr_{0.4-x}Nd_xCe_{0.6}Fe_{10}Si_2$ ($0 \leq x \leq 0.3$) alloys are indeed mostly composed of the $ThMn_{12}$-type phase. It was confirmed that the presence of Zr and Si balanced the negative influence of Nd. Si atoms, except of the stabilizing role, diffused into the α-Fe structure (9-10 at.% Si).

$(Fe_{0.7-x}Co_{0.3-x}M_{2x})_2B$ (M = W, Re; x = 0, 0.025) alloys, synthesized by annealing of amorphous precursors, crystallized in tetragonal Fe_2B structure (*I4/mcm* space group). Thermal stability of the as–quenched amorphous phases was estimated, indicating Re-containing alloy as the most stable one. This is in accordance with the highest packing density of this alloy, compared to the parent compound or W-containing counterpart. These results were also confirmed by rf-Mössbauer spectra. The less stable amorphous alloys crystallized during the measurement. According to the results of *ab-initio* calculations, substitution of 5*d* atoms (mainly Re) was supposed to maximize magnetocrystalline anisotropy. In contrary, the experimental results suggested that the investigated compounds were magnetically soft. Nevertheless, the presence of strong magnetocrystalline anisotropy cannot be excluded, as the reported low coercive field (~300 Oe) could still be diminished by not fully optimized microstructure.

Calculations performed in this thesis allowed to optimize compositions of the selected alloys in order to improve the stability of the desired phases and to increase the possibility of introduction of structural disorder. Experimental results are in accordance with the conclusion drawn from the theoretical approach. Initial characterization, especially extended studies of alloys' structural properties, is promising when aiming further improvement of the magnetic properties of these novel alloys, and their possible development as hard magnetic materials.