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Właściwości magnetyczne anizotropowych stopów na bazie $Hf_2Co_{11}B$ oraz $(FeCo)_2B$, otrzymywanych z faz metastabilnych strukturalnie

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II. Abstract

One of the most common permanent magnet materials are intermetallic compounds containing rare earth elements such as Nd, Sm and Dy. Increasing demand for these elements, crucial for construction of electric motors or wind turbines, has stimulated interest in new rare earth free permanent magnet materials. These alloys should be characterized by physical properties suitable for further applications, as a high Curie temperature or significant values of coercive field and magnetic remanence, both in turn resulting in a high energy product.

In this thesis, physical phenomena in Hf-Co-B-based systems, especially in $Hf_2(Fe_xCo_{1-x})_{11}B$ (x = 0; 0.2; 0.4) and $(Fe_{0.7}Co_{0.3})_2B$, $(Fe_{0.675}Co_{0.275}X_{0.05})_2B$, X = W; Re, were studied. Analysis of the $Hf_2(Fe_xCo_{1-x})_{11}B$ (x = 0; 0.2; 0.4) alloys was aimed at description of crystallization process and in depth description of crystalline structure of hard magnetic phase, which crystallizes upon isothermal annealing. Up to date, its crystal structure has not been clearly defined. At first, chemical compositions and annealing conditions were optimized in terms of hard magnetic properties. Additionally, to create microstructural modifications, unconventional methods such as high magnetic field annealing and high pressure torsion, were used.

The motivation for the studies on $(Fe_{0.7}Co_{0.3})_2B$ and $(Fe_{0.675}Co_{0.275}X_{0.05})_2B$ systems were the theoretical results obtained by the group from the Uppsala University, suggesting an increase in magnetocrystalline anisotropy of Fe-Co-B systems, caused by 5*d* element addition.

The samples were synthesized using the rapid quenching technique (melt-spinning) under argon atmosphere. The samples with metastable structures, fully amorphous or partially crystalline had the form of narrow ribbons or flakes with the thicknesses from the range of 20 to 35 micrometers. For realization of the aim of the study, a number of complementary experimental methods were used, including: X-ray diffraction, differential scanning calorimetry, transmission electron microscopy and vibrating sample magnetometry. Combination of these techniques allowed determination of physical quantities and a complex description of physical phenomena in investigated alloys. Their analysis included determination of crystalline structure, thermal stability, description of crystallization processes and characterization of the magnetic properties. The Kissinger–Akahira–Sunose method enabled determination of the local Avrami exponent for the first crystallization event in the $Hf_2Co_{11}B$ alloy. Its values and dynamic changes indicated a decrease in the rate of nucleation and growth along with an increase in the crystallized volume fraction, connected with the change in the nucleation mechanism from volumetric, three dimensional, to the surface one. Magnetocrystalline anisotropy constant exceeded 10 MGOe for the crystalline $Hf_2Co_{11}B$ alloy, exhibiting high magnetic anisotropy of hard magnetic phase, which crystallized after isothermal annealing. The analysis of simulations results, which were obtained the Visualisation for Electric and Structural Analysis programme, indicated a possibility of $AuBe_5$-type structure to be a parent structure of the hard magnetic phase.

The Curie temperature of amorphous ribbon equal to 540°C was determined on the basis of thermomagnetic measurements, along with Curie temperature for the other Hf-Co-B samples. Moreover, the presence of two magnetic Hf_2Co_{11} phases, crystallizing in rhombohedral and orthorhombic structure, was evidenced from these data. The Curie temperature of hard magnetic phase was above 500°C, which exceeded the Curie temperature of Nd-Fe-B based compounds. The results obtained from magnetization derivative as a function of magnetic field induction dependences, set together with isotropic remanence ratio values, suggest the occurrence of exchange-spring mechanism between the magnetic phases formed upon isothermal annealing of partially crystalline metastable $Hf_2Co_{11}B$ alloy at 570°C for 60 or 120 minutes.

The studies helped to establish the conditions and mechanisms of microstructural modifications which resulted in optimization of the hard magnetic properties of $Hf_2Co_{11}B$ compound. The polycrystalline alloy synthesized from the amorphous precursor, with coercive field 0.7 kOe, was subjected to high pressure torsion process, resulting in the alloy vitrification. Subsequent isothermal annealing, at the same conditions as in the initial stage, 570°C for 60 minutes, resulted in doubled value of coercive field, which reached about 1.3 kOe, in comparison to that of the as-quenched sample after annealing. Isothermal annealing of $Hf_2(Fe_xCo_{1-x})_{11}B$ ($x = 0.2;\ 0.4$) ribbons led to crystallization of α-Fe and $FeCo_2B$ phases, enhancing saturation magnetization and reducing coercive field at the same time.

Annealing of the amorphous $(Fe_{0.7}Co_{0.3})_2B$ and $(Fe_{0.675}Co_{0.275}X_{0.05})_2B$, X = W; Re alloys resulted in crystallization of a tetragonal $(Fe,Co)_2B$ phase. Magnetocrystalline anisotropy of this phase was estimated in theoretical calculations to exceed 1 MJ/m^3. The measured value of coercive field equal to 348 Oe for $(Fe_{0.7}Co_{0.3})_2B$ did not confirm these results. Nevertheless, one has to bear in mind that further enhancement of energy product in this systems can be obtained by optimization of microstructure. To the best of my knowledge single phase $(Fe_{0.675}Co_{0.275}W_{0.05})_2B$ alloy was synthesized and characterized for the first time.