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Development of Magnetic Properties during Annealing of $Hf_2Co_{11}B$ Amorphous Alloy

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Influence of heat treatment on magnetic properties of amorphous $Hf_2Co_{11}B$ alloy was investigated. Hard magnetic phase, characterized by high magnetic anisotropy, appears during crystallization. The highest coercive field equal to 1.86 kOe, was obtained for sample annealed in third crystallization stage. Longer heat treatment at $T_a = 650\,^{\circ}$C leads to decrease in coercive field, which can be the result of excess of the $HfCo_3B_2$ phase volume fraction and additionally eutectoid transformation of hard magnetic phase into soft magnetic $Co_{23}B_6$ and fcc-Co. Decrease of volume fraction of hard phase is confirmed by the remanence ratio m_r. Value of m_r, for $T_a = 650\,^{\circ}$C, is decreasing with annealing time from 0.4 to 0.27 for 30 min and 120 min, respectively. The magnetocrystalline anisotropy constant K_1 increases from 2.23 Merg/cm^3 for the amorphous ribbon to 15.84 Merg/cm^3 for the sample annealed at 650 °C for 30 min.

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1. Introduction

Trend for "green energy" applications, as for example wind power generators or motors for electric vehicles create growing demand for the permanent magnets. Nd–Fe–B alloys are nowadays the most widely used materials in the industry for this purpose [1], moreover addition of iron, dysprosium or terbium is used to improve their properties [2]. The rising prices of rare earth elements facilitates the development of new permanent magnet materials without rare earth elements, for example those with 5d elements, as Mn–Al or Fe–Co [3, 4]. These compounds did not match the energy product value of Nd–Fe–B system, but more than a half of Nd–Fe–B energy product can be still useful for many applications.

Hf-Co is another group of compounds which are characterized by favorable magnetic properties as high Curie temperature above 500 °C and good corrosion resistance. Rapid quenching technique allowed to obtain Hf–Co–B alloy in amorphous state. Isothermal annealing leads to crystallization of magnetic nanocrystalline phases, where hard magnetic properties are connected with the existence of $HfCo_7$ or Hf_2Co_{11} phase [5, 6]. The boron addition to the Hf-Co compounds can enhance magnetic properties of the hard phase [5] and simultaneously plays main role in the improvement of glass forming ability and thermal stability. The magnetic properties of amorphous $Hf_2Co_{11}B$ alloy and their evolution for isothermally annealed samples are presented.

2. Experiment

The master alloy of $Hf_2Co_{11}B$ was prepared in arc furnace by melting of high purity Hf (99.9%), Co (99.9%), B (99.9%). The ingot was remelted several times to ensure homogeneity. The whole process was performed in the argon atmosphere. The sample was rapidly quenched by melt-spinning on a copper wheel rotating with the surface velocity of 30 ms^{-1}. The thickness of the as-quenched ribbons was equal to 30 μm. Magnetic properties were acquired by use of the VSM option in Quantum Design Physical Property Measurement System.

3. Results and discussion

Coercive field H_c and remanent magnetization M_r of $Hf_2Co_{11}B$ alloy in as-quenched state and after annealing at three different temperatures 570 °C, 595 °C and 650 °C for 60 min are shown in Fig. 1a. Annealing temperatures were close to the maxima of the first, second, and third crystallization stages and were determined by differential scanning calorimetry. X-ray diffraction (XRD) confirmed the existence of fully amorphous state [7, 8]. Based on mentioned analysis, hard magnetic phase was identified as Hf_2Co_{11} with rhombohedral structure. Alloy density was preconceived from Ref. [9] and used to recalculate quantities from magnetic measurements. Sample in as-quenched state possess insignificant H_c equal to about 0.01 kOe and M_r = 15 emu/cm^3, which is typical feature of amorphous alloy. The coercive field and remanence increases from 0.73 to 1.51 kOe and from 133 to 257 emu/cm^3, respectively, with the increase of annealing temperature from 570 °C to 650 °C (Fig.1a). The highest values of H_c and M_r were obtained for the ribbon annealed at 650 °C. Therefore, annealing time dependence of H_c and M_r is shown for this annealing temperature (Fig. 1b). The largest values, H_c = 1.87 kOe and M_r = 284 emu/cm^3, were acquired after annealing for 30 min. Longer annealing again decreases coercive field and remanent magnetization to H_c = 1.21 kOe and M_r = 193 emu/cm^3, for τ_a = 120 min.

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The law of approach to saturation formula was used to determine magnetic anisotropy from the high field magnetization measurement [10]:

$$M = M_s \left(1 - \frac{\zeta}{H^2}\right) + \chi H, \tag{1}$$

where M_s is spontaneous magnetization, H — applied magnetic field, χ — magnetic susceptibility in high magnetic field and ζ is the constant expressed by the equation

$$\zeta = \frac{4K_1^2}{15M_s^2}. \tag{2}$$

The numerical coefficient of $4/15$ in formula (2) was used according to approach for polycrystalline ribbons with uniaxial anisotropy [11] and our previous analysis for partially crystalline $Hf_2Co_{11}B$ samples [8].

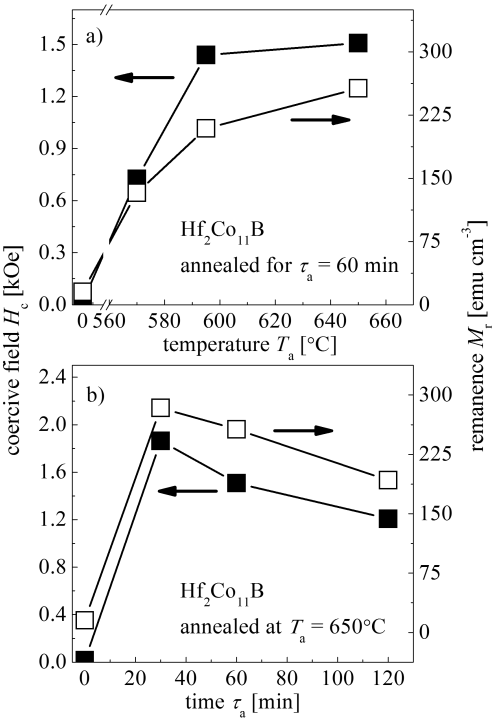

Fig. 1. Coercive field (filled squares) and remanence (open squares) of $Hf_2Co_{11}B$ alloy in as-quenched state and after annealing (a) at 570 °C, 595 °C, and 650 °C for an hour, and (b) at 650 °C for 30, 60, 120 min.

High field magnetization parts of the hysteresis loops ($H > 40$ kOe) measured at room temperature are depicted in Fig. 2. The magnetization curves are presented for the sample in as-quenched state, and for those annealed at different temperatures for 60 minutes (Fig. 2a) and for various annealing time at 650 °C (Fig. 2b). The K_1, M_s and ζ were obtained by fitting the measured data (black lines) according to Eq. (1). Magnetizations are not saturated even at 80 kOe which suggests high magnetic anisotropy.

The value of magnetization determined at 80 kOe decreases from 700 to 664 emu/cm^3 after annealing at 570 °C, then increases again with higher annealing temperatures. Similar behavior was reported for the partially crystalline sample after 15 min of annealing at 570 °C [8]. This phenomenon can be explained by growing content of boron atoms in the residual amorphous matrix, due to isothermal heat treatment. Boron atoms cause dilution of soft magnetic amorphous phase and reduce saturation magnetization. This process lasts longer for the glassy sample in comparison to the partially crystalline counterpart. Higher annealing temperatures result in superior magnetization and the maximum was achieved after annealing at 650 °C. It can be connected with the crystallization of additional soft magnetic phase. Annealing at 650 °C longer than 30 min does not change the saturation magnetization. All values determined from magnetic measurement are listed in Table I.

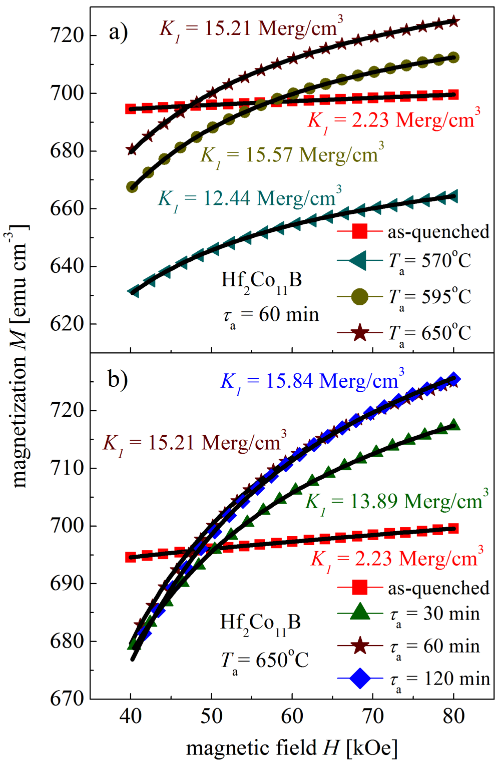

Fig. 2. Magnetic field dependences of magnetization measured in high fields at 300 K for $Hf_2Co_{11}B$ alloy in as-quenched state and after annealing (a) at different temperatures 570 °C, 595 °C and 650 °C for an hour, (b) at 650 °C for 30, 60, 120 min. Law of approach to saturation was used to calculate magnetic anisotropy constants. Black lines are fits to experimental data according to Eq. (1).

The remanence ratio m_r was determined in order to indicate the optimum annealing conditions. In a multiphase system value of m_r higher than 0.5 confirms the presence of exchange coupling between phases [12]. The highest $m_r = 0.4$ was achieved after heat treatment at 650 °C for 30 min. Longer heat treatment at the same temperature causes decrease in remanence ratio to 0.27. In the case of partially crystalline sample, the optimum value was obtained for the sample treated at 570 °C for an hour [8]. Combining these results with reduction of coercive field, one can conclude that soft phases ($Co_{23}B_6$, fcc-Co) crystallized at the expense of hard one. Sun *et al.* [13] have shown that the $Co_{23}B_6$ phase crystallizes during solidification of $Co_{79.5}Hf_{10.5}B_{10}$ compound, but mechanism can be similar to this presented by Lu *et al.* [14], where $Co_{23}Hf_6$ and α-Co phases have been formed via eutectoid reaction from Hf_2Co_{11}.

TABLE I

Magnetic properties of $Hf_2Co_{11}B$ obtained at room temperature for as-quenched sample and alloys annealed at different temperatures and for different time.

T_a [°C]	τ_a [min]	M (8 T) [emu/cm^3]	M_s [emu/cm^3]	M_r [emu/cm^3]	H_c [kOe]	K_1 [Merg/cm^3]
as-quenched						
–	–	700	700	15	0.01	2.23
annealed						
570	60	664	664	133	0.73	12.44
595	60	712	719	209	1.44	15.57
650	30	717	717	284	1.87	13.89
	60	725	727	257	1.51	15.21
	120	725	727	193	1.21	15.84

The magnetocrystalline anisotropy constant K_1 is equal to 2.23 Merg/cm^3 for the amorphous sample (Fig. 2a). There is constant growth of K_1 with the annealing temperature up to 15.57 Merg/cm^3, for $T_a = 650$ °C. As it was shown in Fig. 2b the highest value, equal to 15.84 Merg/cm^3, was obtained for the ribbon annealed at 650 °C for 120 min. Annealing of the amorphous sample leads to crystallization of different types of magnetic phases, where the hard magnetic one provides the main contribution to the calculated anisotropy constant. The K_1 indicates optimum volume fraction ratio of different magnetic phases crystallized in the alloy. The extension of annealing time for $T_a = 650$ °C, results in higher anisotropy constant, but prolonged heat treatment causes decrease of H_c, M_r and consequently of $|BH|_{\max}$ values. Decline of coercive field can be triggered by increasing volume fraction of $HfCo_3B_2$. Cobalt in the RCo_3B_2 phases seems to be paramagnetic at room temperature [15].

Determined values of K_1 are slightly higher than those for the Zr–Co system [16]. It places the Hf–Co–B system in the group of candidates for the application as the rare-earth free permanent magnet.

4. Conclusions

The largest coercive field was obtained for the amorphous alloy annealed at the temperature of third crystallization peak (650 °C) for 30 min. Additionally, the strongest exchange interactions, determined by remanence ratio, were obtained for the same annealing conditions, where m_r is equal to 0.40. Exchange coupling was not observed regardless of the annealing conditions. It suggests that volume fraction of hard magnetic metastable Hf_2Co_{11} phase is too low in comparison with the rest of crystallized phases. Annealing at 650 °C for time longer than 30 min leads to decrease of coercive field as a result of eutectoid recrystallization of Hf_2Co_{11} phase into $Co_{23}B_6$, and crystallization of large volume fraction of $HfCo_3B_2$ phase. The investigated $Hf_2Co_{11}B$ compound is characterized by high magnetocrystalline anisotropy constant $K_1 > 12$ Merg/cm^3, which exceeds the K1 value for Zr-Co systems.

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