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Magnetic properties of modified amorfous and nanocrystalline alloys based on Fe and Co

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Influence of thermal and thermomagnetic treatments conditions on the magnetic properties and time-temperature stability of amorphous and nanocrystalline alloys based on Fe and Co with additions of Mo, Hf, Zr was studied. It was established that the nanocrystallization in an alternating magnetic field of modified amorphous alloys based on Fe and Co improved significantly their static and dynamic properties and maintained the high thermal stability of the properties.

Исследовано влияние условий термических и термомагнитных обработок на магнитные свойства и температурно-временную стабильность аморфных и нанокристаллических сплавов на основе Fe и Co с добавками Mo, Hf, Zr. Установлено, что нанокристаллизация в переменном магнитном поле модифицированных аморфных сплавов на основе Fe и Co существенно улучшает их статические и динамические свойства, сохраняя высокую температурную стабильность свойств.

1. Introduction

The great progress in developing and obtaining of soft magnetic amorphous-nanocrystalline alloys with high magnetic characteristics was achieved recently [1–5]. At the present time an active search is carried for nanocrystalline soft magnetic alloys with optimal magnetic properties, operating at elevated temperatures. In some of studies for improvement of thermal stability of the magnetic material characteristics the following measures are proposed: 1) alloying with refractory metals, 2) increasing the temperature of nanocrystallization annealing of modified alloys [6, 7]. At the same time it is expressed the significant interest to investigation of correlation between thermal stability of the nanocrystalline structure of magnetic alloys based on Fe and temperature stability of magnetic properties [8, 9]. Group of authors has been developed $(Fe_{0.6}Co_{0.4})_{86}Hf_7B_6Cu_1$ nanocrystalline alloy which had high thermal stability of magnetic properties. The operation temperature of the alloy was 400°C $\leq T \leq$ 550°C. However, the coercive force H_c of $(Fe_{0.6}Co_{0.4})_{86}Hf_7B_6Cu_1$ nanocrystalline alloy is high and equals to 40 A/m [9–11]. The high and differentiate requirements depending on the operation conditions and tasks are imposed to equipment intended for operation at elevated temperatures. Under certain operating conditions it is demanded a higher thermal stability of magnetic properties and low coercive force, for example, the magnetometers for ultra-deep wells. The aim of this work was improving the magnetic parameters of soft magnetic amorphous and nanocrystalline alloys based on Fe and Co while keeping high thermal stability properties. For this purpose the effects of condition of thermal and thermomagnetic treatments (TMT), such as: temperature and annealing time, cooling rate after annealing, magnetic field strength at TMT, on the magnetic properties and thermal stability were investigated.

2. Experimental

Amorphous alloy ribbons: $Fe_5Co_{70}Si_{15}B_{10}$, $Co_{81.5}Mo_{9.5}Zr_9$, $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$, $Fe_{73.5}Cu_1Nb_{1.5}Mo_{1.5}Si_{13.5}B_9Fe_{69}Cu_1Nb_{1.5}Mo_{1.5}Si_{13.5}B_9Co_{4.5}$, $(Fe_{0.6}Co_{0.4})_{86}Hf_7B_6Cu_1$, $(Fe_{0.7}Co_{0.3})_{86}Hf_4Mo_2Zr_1B_4Cu_1$ were obtained by the melt quenching on a rotating disk in an argon atmosphere. The ribbons had thickness of 20–25 μm and width of 5–10 mm. The samples had the form of strips and toroids with an outer diameter of 22 mm and an inner diameter of 16 mm. To remove quenching stresses samples were subjected to pre-annealing in vacuum in the temperature range of 350–400°C for 30 min, and then the samples were cooled to room temperature at 200°C/h. The samples were annealed in vacuum in the temperature range of 500–600°C to obtain the nanocrystalline structure depending on the chemical composition of the alloy. Annealing time was varied from 30 min to 1 h. The cooling rate after annealing was different: 200°C/h, 1000°C/h, 5000°C/min. Some samples were nanocrystallized in DC or AC (f = 50 Hz, f = 80 kHz) magnetic fields of various intensity (0–12000 A/m). Initial permeability μ_0, static and dynamic hysteresis loops were measured on the toroidal samples. The initial permeability was determined at 80 Hz in a field of 0.05 A/m. The static hysteresis loops values were measured using microfluxmeter F-190. The dynamic hysteresis loops were defined by the automatic magnetometric installation developed in the Institute of Metal Physics, UD RAS. The values of Curie temperature T_c and crystallization temperature T_x were determined by standard methods. T_c was determined from the temperature dependence of the saturation magnetization, T_x was obtained from the temperature dependence of the electrical resistivity, heating rate of samples was 5°C/min.

Table 1. Values T_c and T_x of some amorphous and nanocrystalline alloys

Alloy	T_c, °C	T_x, °C
$Fe_5Co_{70}Si_{15}B_{10}$	380	480
$Co_{81.5}Mo_{9.5}Zr_9$	460	540
$Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$	570	540
$Fe_{73.5}Cu_1Nb_{1.5}Mo_{1.5}Si_{13.5}B_9$	570	540
$Fe_{69}Cu_1Nb_{1.5}Mo_{1.5}Si_{13.5}B_9Co_{4.5}$	470	520
$(Fe_{0.6}Co_{0.4})_{86}Hf_7B_6Cu_1$	570	600

3. Results and discussion

The values of Curie temperature and crystallization temperature for amorphous and nanocrystalline alloys are shown in Table 1.

The magnetic properties of amorphous $Fe_5Co_{70}Si_{15}B_{10}$, $Co_{81.5}Mo_{9.5}Zr_9$ alloys with different Curie temperatures and crystallization temperatures, after annealing without field, TMT in AC field (f = 80 kHz) and quenching in water from T_c are presented in the Table 2. The cooling rate after the treatments indicated in the Table too.

The Table 2 shows that for amorphous alloys with $\lambda_s \sim 0$ as the TMT in a high-frequency field as quenching in water, leading to destabilization of the domain structure, significantly reduce magnetic losses, coercive force and increase permeability. However, after the quenching of $Fe_5Co_{70}Si_{15}B_{10}$ amorphous alloy the temperature-time instability of the magnetic properties was observed. The relative change of the initial permeability of the specimens after quenching and subsequent isothermal aging at 120°C for 60 h is $\Delta\mu_0/\mu_0 \sim 7\ \%$. The metalloid free $Co_{81.5}Mo_{9.5}Zr_9$ alloy has a higher temperature-time stability of magnetic properties. For this alloy the relative change of the initial permeability after

Table 2. The magnetic properties of the amorphous alloys after various treatments

Alloy	Treatment	μ_0	H_c, A/m	$P_{0.2/20000}$, W/kg
$Fe_5Co_{70}Si_{15}B_{10}$	Annealing	4500	1.3	30
	Quenching in water	45000	0.4	5
	TMT, $H_\sim$ (80 kHz)	46000	0.4	5
$Co_{81.5}Mo_{9.5}Zr_9$	Annealing	1200	1.5	35
	Quenching in water	50000	0.3	5
	TMT, $H_\sim$ (80 kHz)	50000	0.3	5

Table 3. The magnetic properties of the nanocrystalline alloys after various treatments

Alloy	Treatment	μ_0	H_c, A/m	$P_{0.2/20000}$, W/kg
$Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$	Annealing, 520°C, 30 min	40000	0.56	8.0
	TMT, $H_\sim$ (80 kHz)	53000	0.48	5.5
	Quenching in water	10000	1.6	–
$Fe_{73.5}Cu_1Nb_{1.5}Mo_{1.5}Si_{13.5}B_9$	Annealing, 520°C, 30 min	42000	0.48	8.0
	TMT, $H_\sim$ (80 kHz)	60000	0.32	4.5
	Quenching in water	12 000	1.1	–
$Fe_{69}Cu_1Nb_{1.5}Mo_{1.5}Si_{13.5}B_9Co_{4.5}$	Annealing, 520°C, 30 min	45 000	0.4	7.5
	TMT, $H_\sim$ (80 kHz)	60 000	0.24	4.0
	Quenching in water	14 000	0.8	–

aging at 120°C for 60 h after quenching is about 3 %. This is probably due to the high values of T_c and T_x of this alloy.

It should be noted that the TMT in high frequency magnetic field reduces the thermal hysteresis of the initial magnetic permeability of these alloys. This effect can be explained by follows. After heat treatment in high frequency magnetic field the local magnetic anisotropy of the sample is close to zero. The initial magnetic permeability has a maximum value. During thermal cycling from room temperature to 120°C the change of the initial permeability is minimal, since in this temperature range the formation of local magnetic anisotropy is difficult because of the low activity of diffusion processes at these temperatures and the pinning of the domain walls is just started ($\Delta\mu_0/\mu_0 \le 3$ %).

The magnetic properties of nanocrystalline alloys after annealing, the TMO in the high-frequency magnetic field and water quenching from T_c are compared in the Table 3. The Table shows that the samples after quenching have higher values of coercivity and lower permeability. It should be noted a substantial difference in the effect of water quenching on the magnetic properties of amorphous and nanocrystalline alloys. Apparently this is due to the fact that as a result of quenching from Curie point the internal stresses arise in the investigated nanocrystalline samples. It occurs due to the presence in the structure of alloys of nanoscale precipitates of the phase α–Fe–Si with magnetostriction $\lambda_s \sim -5\cdot10^{-6}$. The realized structural studies [12] showed that in the picture of microdiffraction fine reflections from nanophases α–Fe–Si and Fe_3Si were revealed.

Under thermomagnetic treatment of the samples in the field with a frequency of 80 kHz the destabilization of the domain structure of nanocrystalline alloys leads to a round hysteresis loops with low coercivity and low magnetic losses and high permeability values. In this case the microdiffraction picture is characterized by an absence of internal stresses in the alloy [12].

Investigation of temperature-time stability of magnetic properties of nanocrystalline alloys after TMT in the high-frequency magnetic field, such as μ_0 and H_c, showed that the magnetic properties after the holding at 120°C for 60 h do not change practically.

The phase composition of the investigated nanocrystalline alloys influences not only on their magnetic properties, but also on their thermal stability. Nanocrystalline $Fe_{73.5}Cu_1Nb_{1.5}Mo_{1.5}Si_{13.5}B_9$ alloy has unique magnetic properties ($H_c \le 0.3$ A/m) and the increased time-temperature stability. The temperature interval of stability of the magnetic characteristics of this alloy is 20–300°C. Magnetic properties, such as, initial permeability and coercivity do not change significantly for the nanocrystalline $Fe_{73.5}Cu_1Nb_{1.5}Mo_{1.5}Si_{13.5}B_9$ alloy after the isothermal holding at 300°C for 60 h in different atmosphere (both in vacuum and in air): $\Delta\mu_0/\mu_0 \le 3$ %, $\Delta H_c/H_c \le 3$ %. It was found that the increased temperature-time stability of magnetic properties is conditioned by the precipitates on borders of the nanophase α–Fe–Si with nanophase Fe(Nb,Mo)B, which has the high thermal stability and hampers further growth of nanophases α–Fe–Si (Fig. 1) [13].

Nanocrystalline $(Fe_{0.6}Co_{0.4})_{86}Hf_7B_6Cu_1$ alloy (annealing at 600°C for 1 h) has the highest temperature-time stability of mag-

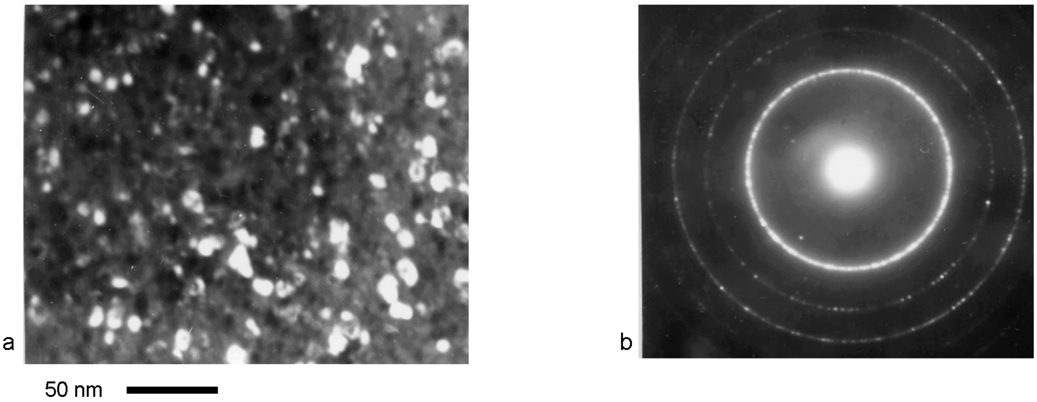

Fig. 1. Electron micrograph of structure (a) and electron diffraction pattern (b) of $Fe_{73.5}Cu_1Nb_{1.5}Mo_{1.5}Si_{13.5}B_9$ nanocrystalline alloy after annealing at T = 400°C — 30 min and subsequent annealing at T = 540°C — 30 min. In the micrograph of the structure it can be seen the electronic contrast in the form of rings and on diffraction pattern — reflexes within the position of the first diffuse halo belonging to phase Fe(Nb,Mo)B [13].

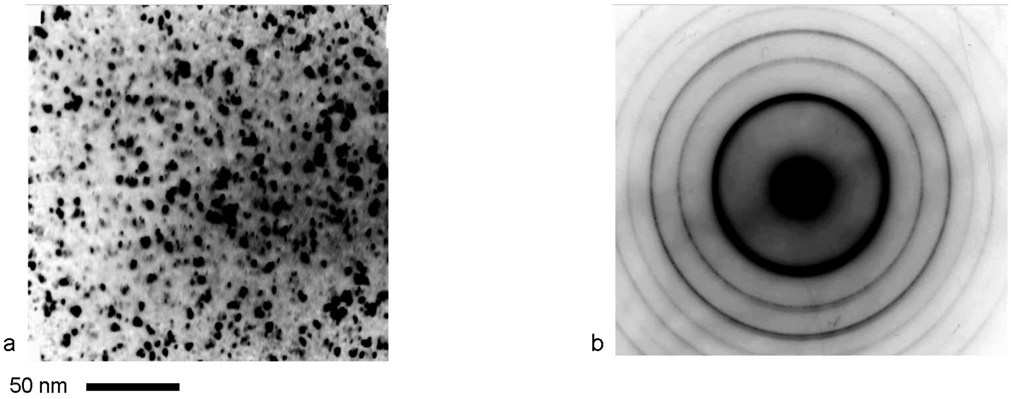

Fig. 2. Electron microscopic image of structure (a) and selected-area electron diffraction pattern (b) of $(Fe_{0.6}Co_{0.4})_{86}Cu_1Hf_7B_6$ nanocrystalline alloy after annealing at 600°C for 1 h in an alternative magnetic field [14].

netic properties, due to the precipitation of Fe_2B, Co_2B nanophases, which are thermally stable, and the presence of Hf in the phase (Fe,Co)B (Fig. 2) [14]. The stability temperature interval of the magnetic characteristics of this alloy is 20–500°C. Change of coercive force H_c did not exceed 3 % after annealing at 500°C for 30 h. However, the coercive force value of $(Fe_{0.6}Co_{0.4})_{86}Hf_7B_6Cu_1$ nanocrystalline alloy is 40 A/m, that is higher then H_c of $Fe_{73.5}Cu_1Nb_{1.5}Mo_{1.5}Si_{13.5}B_9$ nanocrystalline alloy.

The effect of thermomagnetic treatments in alternating and direct fields on the static coercive force of the nanocrystalline $(Fe_{0.6}Co_{0.4})_{86}Hf_7B_6Cu_1$ alloy are studied (Table 3). The data show that with increasing magnetic field strength the effect of thermomagnetic treatment increases.

Nanocrystallization in an alternating magnetic field (H_{TMT} = 12000 A/m) of the amorphous $(Fe_{0.6}Co_{0.4})_{86}Hf_7B_6Cu_1$ alloy allows significantly improve its magnetic properties, while maintaining high temperature stability properties (Table 4). H_c decreases in 4.8 times and the magnetic losses $P_{1.5/400}$ in 4 times, by reason of the change of behavior of the domain structure and greater completeness of relaxation processes, seemingly.

It was shown that an increase in the rate of cooling after annealing which leads to nanocrystallization, resulted in lowering the temperature stability of magnetic characteristics of the alloys. For the nanocrystalline $(Fe_{0.6}Co_{0.4})_{86}Hf_7B_6Cu_1$ alloy the increasing of cooling rate in 5 times (1000°C/h) changes the initial permeability $\Delta\mu_0/\mu_0$ = 18 % and the coercive force value $\Delta H_c/H_c$ = 15 % at isothermal holding

Table 4. The effect of magnetic field intensity on coercive force of $(Fe_{0.6}Co_{0.4})_{86}Hf_7B_6Cu_1$ alloy under nanocrystallization

H_{TMT}, A/m	H_c, A/m TMT (f = 0)	$\Delta H_c/H_c$, %	H_c, A/m TMT (f = 50 Hz)	$\Delta H_c/H_c$, %
0	13.5	–	13.5	–
1200	9.5	29	8.8	35
2800	7.2	47	6.4	52
5600	5.6	58	4.8	65
11200	4.8	65	4.0	70

300°C for 12 h. When the cooling rate of the nanocrystalline alloy is 200°C/h the value of $\Delta\mu_0/\mu_0$ not exceed 5 %, the value of $\Delta H_c/H_c$ does not exceed 3 % at isothermal holding 300°C for 12 h. Apparently, as a result of the rapid cooling in the investigated nanocrystalline samples the internal stresses appear due to the presence in the alloy structure of nanoscale precipitates of the phase α–Fe. Similar results were obtained for the nanocrystalline $(Fe_{0.7}Co_{0.3})_{86}Hf_4Mo_2Zr_1B_4Cu_1$ alloy.

4. Conclusion

It was shown that $Fe_{73.5}Cu_1Nb_{1.5}Mo_{1.5}Si_{13.5}B_9$ nanocrystalline alloy can be characterized by unique magnetic properties ($H_c \le 0.3$ A/m) and increased time-temperature stability. The temperature interval of the stability of magnetic characteristics of the alloy is 20–300°C.

It was found that the nanocrystallization in a magnetic field of amorphous $(Fe_{0.6}Co_{0.4})_{86}Hf_7B_6Cu_1$, $(Fe_{0.7}Co_{0.3})_{86}Hf_4Mo_2Zr_1B_4Cu_1$ alloys significantly improves the static and dynamic magnetic properties. The effect of thermomagnetic treatment of nanocrystalline alloys depends on the magnetic field intensity at the TMT: with increasing magnetic field intensity the effect of thermomagnetic treatment increases. The temperature range of the stability of the magnetic characteristics of alloys is 20–500°C.

It was also revealed that an increase in the rate of cooling after annealing, which leads to nanocrystallization, resulted in lowing the temperature stability of magnetic characteristics of the alloys.

Alloys with high magnetic softness and improved temperature-time stability, may be promising in devices operating under extreme conditions, such as at high temperatures (magnetometers for ultra-deep wells and for the inner generators of the More electrical aircraft).

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Магнітні властивості модифікованих аморфних і нанокристалічних сплавів на основі Fe і Co

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Досліджено вплив умов термічних і термомагнітних обробок на магнітні властивості і температурно-часову стабільність аморфних і нанокристалічних сплавів на основі Fe і Co з домішками Mo, Hf, Zr. Встановлено, що нанокристалізація у змінному магнітному полі модифікованих аморфних сплавів на основі Fe і Co істотно покращує їх статичні і динамічні властивості, зберігаючи високу температурну стабільність властивостей.