New soft magnetic amorphous cobalt based alloys with high hysteresis loop linearity

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The abstract. The new amorphous Co$_{56.59}$ (Fe,Ni,Mn)$_{21.24}$ (Si$_{0.28}$B$_{0.8}$)$_{20}$-based metal alloys (AMA) with high saturation induction ($B_S \geq 1$T) were developed. Toroidal tape wound magnetic cores made from these AMA after heat-magnetic treatment (HMT) in a reversal field are characterized by high hysteresis loop linearity, minimum effective magnetic permeability and its high field stability in combination with low coercivity $H_c$ (1-3 A/m, 1 kHz). For the most prospecting alloy compositions the value of effective magnetic permeability decreases compared to known alloys up to 550 – 670 units and remains constant in the wide magnetic field range 1100 – 1300 A/m. Maximum remagnetization loop linearity is achieved after optimum HMT in high Ni containing AMAs, which are characterized by the record low squareness ratio values $K_s=0.002-0.02$ and $H_c=1.0$ A/m. Magnetic cores made from the new amorphous alloys can be used both in filter chokes of switch-mode power supply units and in matching mini-transformers of telecommunication systems; at that, high efficiency and accuracy of signal transmission including high frequency pulses are ensured under conditions of long-term influence of dc magnetic bias.

1. Introduction

It is known that programs of development of soft magnetic materials including AMA are directed to obtaining hysteresis loops of various types with necessary properties by selection of alloy chemical composition, heat and heat-magnetic treatment (HMT), thermomechanical processes and geometry of cores. So, linear loops, which are characterized by high stability of $\mu_e$ in a full range of acting driving (current) fields and achieve technical saturation in a quite strong fields (sometimes higher than 1000 A/m), are obtained commercially by an annealing of tape wound cores in transverse magnetic field that allows to induce magnetic anisotropy (MA) along direction of action of external field. Besides low values of $\mu_e=1000$–1300 this technology ensures extremely small $H_c$ – coercive force, low core loss unattainable for cores with nonmagnetic gap and cores after thermomechanical treatment. The experiments give evidence that MA of amorphous ferromagnetics is mainly contributed by magnetoelastic anisotropy and by anisotropy of orientationally ordered magnetic pairs (so called directed ordering). For prediction of macroscopic magnetic properties in metallic glass, especially those of technical importance (coercive force, saturation magnetization (induction), initial permeability, magnetic anisotropy etc.), one should know a local structure at large distances. Macroscopic (>1\(\mu\)m) and microstructural (from 100 up to 1000 Å) fluctuations in AMA influence especially a domain structure and mobility of domain walls, dynamics of approaching to saturation, temperature dependence of magnetization, magnetostriction stresses. Just volume and local magnetic
measurements, in their turn, can give extensive information on atomic structure fluctuations in glasses at medium distances. It is known that the smaller magnetostrictive effect of the alloy, the easier MA will be induced by annealing in magnetic field (IMA). Just therefore rapidly quenched Co based alloys, which have nearly zero magnetostriction [1], are suitable materials for magnetic cores working at high frequencies. Compositions with zero magnetostriction, magnetic properties and crystallization temperatures $T_x$ in (Fe,Co)$_{1-a-b}$Ni$_b$)$_{100-x}$(Si$_2$B$_{16-y}$) system as function of Ni (0<b<0,6) and metalloid content (20<y<30) are suggested. The main disadvantage of these AMA is the fact that $T_C$ exceeds $T_x$ for alloys with high $B_3=0,9-1,1T$, that doesn’t allow to expect an effective influence of thermomagnetic treatment on hysteresis loop shape. It was empirically shown that HMT should be carried out in immediate proximity to $T_C$ (somewhat below this temperature) for achieving a maximum positive result. The literature examination did not reveal works that study an effect of chemical composition of alloys on efficiency of their HMT in a transverse field. Recently these investigations were carried out in G.V.Kurdiumov Institute for Metal Physics of National Academy of Sciences of Ukraine.

The main goal of this work was to study an effect of HMT in a transverse field on magnetic properties of Co based AMA with various character of their complex doping and to determine their crystallization temperatures and Curie temperatures for achieving maximum HMT efficiency.

2. Results and discussion

Our manufacture of high-quality amorphous ribbons having thickness 20÷30 μm, width ~10 mm made of ten Co based alloys of various chemical composition by rapid quenching of the melt (RQM) revealed that their casting properties strongly depend on nickel and manganese content: the alloys with larger nickel content and smaller manganese content (No. 9 and 10) are characterized by better manufacturability and glass forming ability than the alloys No. 1 - Co$_{75,5}$Fe$_{14}$Si$_6$B$_{16,7}$, 2 - Co$_{73,6}$Fe$_{3,2}$Mn$_{3,2}$Si$_5$B$_{15}$, 3 - Co$_{74,2}$Fe$_{2,5}$Ni$_{0,2}$Mn$_{0,1}$Si$_4$B$_{16}$ and 4-8 (see Table 1) as well.

| Alloy No. | Chemical composition | $T_{x1}$ (by $\rho/\rho_s$) | $T_{x1}$ (by DTA) | $T_{x2}$ (by DTA) | $T_{x1}$ (by $\mu/\mu_{20}$) | $T_{C}$ (by $\mu/\mu_{20}$) |
|----------|----------------------|-----------------------------|------------------|------------------|----------------------|--------------------------|
| 4        | Co$_{75,5}$Fe$_{4,5}$Mn$_{0,2}$Si$_6$B$_{14}$ | 445 | 437 | 540 | 445 | 458 |
| 5        | Co$_{73,2}$Fe$_{3,3}$Mn$_{0,5}$Si$_{5,5}$B$_{16,7}$ | 445 | 437 | 540 | 445 | 458 |
| 6        | Co$_{72,5}$(Fe,Ni,Mn)$_{1,8}$Mn$_{0,7}$Si$_6$B$_{16,7}$ | 429 | 427 | 562 | 423 | 445 |
| 7        | Co$_{73}$(Fe,Ni,Mo,Mn)$_{4,7}$Si$_{6,2}$B$_{16,7}$ | 446 | 417 | 559 | 425 | 447 |
| 8        | Co$_{55,0}$(Fe,Ni,Mn)$_{4,2}$Si$_{6,2}$B$_{16,7}$ | 406 | 397 | 528 | 365 | 417 |
| 9        | Co$_{55,0}$(Fe,Ni,Mn)$_{4,2}$Si$_{6,2}$B$_{16,7}$ | 406 | 397 | 526 | 398 | 417 |

Attempts to obtain visible HMT effect for all studied alloy compositions showed that it is possible only at ribbon thickness less than 25 that can be connected with insufficient cooling rate, which stimulates development of atomic structure ordering in ribbons of relatively large thickness, and with formation of stable in-plane anisotropy in them, which partially or completely remains even after their HMT. Therefore ribbons of thickness 20-25 μm only were selected for further investigations.

Curie temperatures of the studied alloys in initial state presented in Table 1 were obtained by an analysis of the experimental dependences of $\mu/\mu_{20}$ on temperature under continuous slow heating with constant rate of the toroidal tape wound cores having mass about 12-15 g ($\mu_{20}$ is a value of effective magnetic permeability at room temperature at field strength 1 A/m and frequency 10 KHz).
The plots of the temperature dependences of $\mu/\mu_{20}$ are presented in Figure 1. Their behavior is similar to ones obtained by Kekalo I.B. et al [3] at investigation of amorphous Co$_{70}$Fe$_5$Si$_{15}$B$_{10}$ ribbons with essentially different silicon / boron ratio.

![Figure 1. Temperature dependence of relative effective magnetic permeability for alloys in initial state.](image1)

![Figure 2. Temperature dependence of relative magnetic permeability for the alloy No.9 in initial state and after preliminary HMT at 330°C, 1 hour.](image2)

Temperature dependences of effective permeability for as-cast specimens of ribbons are typical for systems where processes of stabilization and destabilization of domain boundaries (DB) occur under heating: $\mu_e$ (respectively, $\mu/\mu_{20}$) at first decreases with temperature increase (DB stabilization) and then, passing minimum, it increases (DB destabilization). The Hopkinson type maximum is observed near $T_C$ for all the alloys [4]. DB stabilization according to [5] occurs due to atomic composite directed ordering stimulated by a gain of magnetic component of free energy. Increase of $\mu_e$ under heating above 250°C may be connected with structural relaxation accompanied by free volume decrease [5]. The considerable drop of all $\mu/\mu_{20}$ curves is observed at temperature increase above 100-120°C, magnetic permeability drop being smaller at temperature increase up to 300-320°C and minimum temperature being higher for the alloys with increased Mn content and small Ni content (No.7, 6) that can indicate relative difficulty of composite ordering under heating of these alloys. Since they are not distinguished by increased metalloid content unlike, for example, the alloy No.5, one can logically suppose that DB stabilization degree decrease for Mn enriched alloys and Ni depleted alloys occurs in them due to slower composite ordering of main magnetic atom pairs. The abrupt $\mu/\mu_{20}$ drop occurs after achieving a maximum that indicates approaching to paramagnetic system state (achieving Curie temperature). Besides, a rather abrupt drop of relative magnetic permeability, as it was earlier noted in [6] for saturation magnetization of Co70Fe5Si4B16 alloy with $T_C>T_{x1}$, may be related to the development of primary crystallization processes. Additionally the $T_{x1}$ measurement results obtained by three different methods (resistometry, magnetometry, DTA (Table 1)) argue for it. The good coincidence of $T_{x1}$ values allows speaking with certainty about primary crystallization onset at this temperature.

$T_{x1}$ like $T_C$ noticeably decreases for the alloys with high nickel and low manganese content. The determination of temperature ranges of crystallization and Curie temperatures as well as behavior of temperature dependences of $\mu/\mu_{20}$ enables adequate selection of treatment temperatures for alloys of different chemical compositions for ensuring maximum HMT efficiency. Optimum HMT temperature for every alloy corresponds to $\mu/\mu_{20}$ increase after passing a minimum, i.e. it is DB destabilization onset temperature.
Heat treatment of cores in solenoid transverse dc magnetic field of 46 kA/m strength under conditions of DB destabilization onset can result in relatively simple inducing of uniaxial magnetic anisotropy along force lines of an external magnetic field, i.e. transversely to a ribbon axis.

The obtained results on heat stability and temperature dependence of \( \mu/\mu_0 \) could suggest easy inducing of desired anisotropy just for alloys with high manganese content (No. 6, 7, 9), which are characterized by higher \( T_{x1} \) and \( T_C \) values and, respectively, their heat treatment is possible at higher temperatures without formation of primary crystals, where atoms are more mobile. However the experiments have shown that transverse anisotropy is induced most easily in alloys with high nickel and iron content (No. 9, 10) that may be connected with more complex ribbon component redistribution processes, which are determined by atom chemical interaction, exchange energy and alloy electron structure.

Figure 2 shows the temperature dependences of \( \mu/\mu_0 \) for tape wound cores of the alloy No.9 in initial state and after HMT at 330°C. It can be seen that the relative magnetic permeability drop is more abrupt that for annealed specimen, and “dip” depth of \( \mu/\mu_0 \) dependences for these specimens differs by nearly order of magnitude. Sharp \( \mu/\mu_0 \) increase for a core (after HMT) under heating above 280°C is obviously related to induced anisotropy decay processes and again, respectively, to DB destabilization. Magnetic permeability, as a result of this magnetic structure disordering, increases at peak temperature up to a value typical for as-cast (without HMT) ribbon. The investigation of the cores subjected to HMT in a transverse field has shown that a decrease of effective magnetic permeability and its practically steady temperature behavior up to 160-180°C is typical for all the alloys. Moreover, it was found that at heating and short exposures at \( T=200-220°C \) (up to a minimum point of \( \mu/\mu_0 \) dependence (Figure 1)) magnetic permeability of the cores subjected to HMT is characterized by absolute reversibility, i.e. no hysteresis of \( \mu \) is observed.

Table 2 presents the main research results on magnetic characteristics of the cores made of the best complexly doped alloys after their optimum heat-magnetic treatments.

| Alloy No. | \( \Delta e \) | \( B_{1300°C} \), T | Field of constant \( \Delta e \), A/m | Linearity, \( K_m \) | \( H_C \), A/m (1 kHz) | \( H_C \), A/m (10 kHz) | \( T_C \), °C |
|----------|----------------|-------------------|----------------|-----------------|-----------------|-----------------|-------|
| 4        | 3000 ± 2000    | 1,008             | -              | >0,167          | >26,1           | >47,1           | 460   |
| 5        | 2500 ± 1000    | 1,00              | <100           | 0,09-0,11       | >16,6           | >32,6           | 458   |
| 6        | 1700 ± 400     | 0,93              | 450            | 0,03-0,06       | 10-16,5         | 23-32,2         | 459   |
| 7        | 1300 ± 80      | 1,066             | 550            | 0,01-0,06       | 3,4-12,8        | 9,8-22,1        | 445   |
| 8        | 1000 ± 40      | 0,965             | 650            | 0,01-0,043      | 1,3-9,8         | 6,1-17,7        | 447   |
| 9        | 670 ± 30       | 0,94              | 1100           | 0,003-0,02      | 1,3-6,4         | 5,7-10,4        | 417   |
| 10       | 550 ± 20       | 0,84              | 1300           | 0,002-0,02      | 1,0-12,6        | 4,5-17,7        | 417   |

The following conclusions can be drawn from the values \( \mu_e \), \( K_s \) (hysteresis loop squareness ratio at frequency 1 kHz) and \( H_C \) (dynamic coercive force at frequencies 1 kHz and 10 kHz) determined for...
each alloy: all magnetic characteristics after HMT improve more and more with more strong $T_C$ decrease and that is evidence of easier process of inducing transverse anisotropy for alloys, which are characterized by lower Curie temperature; both remagnetization loop linearity and $\mu_c$ bias resistance increases monotonously with increase of doping components in an alloy. It was revealed that higher iron content doesn’t result in desired saturation induction increase – it remains on the level of $B_S = 1 T$ and $B_{1300} = 0.84-0.94 T$. Field stability was shown to be strongly dependent of chemical composition and average value of effective magnetic permeability.

The dependence of $\mu_c$ on $H$ in Figure 3 shows that magnetic permeability stability increases with decrease of average value of $\mu_c$.

The most linear loops with record low values of $K_s$ and $H_c$ were obtained after optimum HMT for alloys high-doped with Ni (No. 9, 10). At the same time, we didn’t practically succeed in obtaining more or less stable field dependence of $\mu_c$ for low-doped alloys No. 4 and 5.

From the point of view of practical use the alloys No.7 and 8 with magnetic permeability after HMT 1300 and 1000, respectively, are also very promising. Just these alloy compositions can compete with cut magnetic cores with high field stability of $\mu_c$ in current measuring transformers of electron electricity meters.

Magnetic cores made from the alloys No.9 and 10 with lowest effective magnetic permeability can be used successfully both in filter chokes of pulse power supply units and matching minitransformers of telecommunication systems, which must ensure high efficiency and precision of signal transmission, including high-frequency pulses at steady dc bias influence.

Thus, the performed experimental investigations enabled to determine the best promising compositions of complexly doped Co based alloys with nearly zero magnetostriction, where formation of induced magnetic anisotropy is easiest and effective magnetic permeability remains constant in a wide field range.

References
[1] Kohmoto O, Ohya K, Yamaguchi N, Fujishima H and Ojima T 1979 J. Appl. Phys. 50 5054
[2] Kohmoto O, Ohya K, Yamaguchi N, Fujishima H and Ojima T 1980 J. Appl. Phys. 51 4342
[3] Kekalo I B, Stolyarov V L and Tsvetkov V Yu 1983 FMM 55
[4] Tikadzumi S 1987 Fizika ferromagnetizma. Magnitnye kharakteristiki i prakticheskie primeneniya Moscow Mir 419
[5] Kekalo I B, Tsvetkov V Yu 1985 FMM 59
[6] Makino Y, Aso K, Uedaira S, Hayakawa M, Ochiai Y and Hotai H 1981 J. Appl. Phys. 52 2477