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Ferromagnetism of Iron-copper Nanocomposites

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The magnetic characteristics of thin films in massive samples are considered and realized in present paper. Multilayer nanocomposite materials from both iron and copper powders, and iron powders with multilayer carbon nanotubes were obtained in two ways. The first method is that a mixture of heterogeneous metal powders with the size of 4-100 microns was rolled, sintered and compressed with a total 99% reduction. In a second method, the powders mixtures were previously treated in a planetary mill before sintering. It is shown that the microstructure of the samples obtained is, as a rule, layered. Due to deformation, in particular, rolling, the thickness of the layers can be reduced to nanoscale. The properties of such massive materials, despite the possible heterogeneity of the continuity of the layers during rolling to nanoscale thicknesses and their fragmentation into nanoflakes, are similar in most to the properties of thin films. The relation between the microstructure, which is determined by the method of processing the powders mixture, the thickness of the layers/scales and the coercive force of the obtained materials, is established. The optimal processing parameters are determined for the realization of practically attractive magnetic characteristics of such materials.

Keywords: Thin films, Magnetic characteristics, Coercive force, Layered nanocomposite materials, Structure.

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1. INTRODUCTION

The electrophysical, in particular, magnetic characteristics of thin films (TF) are fundamentally different from those of massive samples [1-6].

Recent TF technologies allowed to obtain them with given crystalline, quasicrystalline or amorphous structures and create the fundamentally new magnetic materials, multi-layered structures, superlattices, etc. on their basis. Such magnetic films and multilayered structures on their basis have a number of features, which are either completely absent or almost not observed in massive materials. The obtaining of massive samples with magnetic characteristics of TF allows to significantly increase their functionality. Therefore, the search for ways to implement in macro-samples the level of magnetic characteristics inherent in the TF is an important task for researchers.

Physical-mechanical [7, 8], electrophysical, and magnetic characteristics inherent in TF can be realized in massive samples by creation of multilayer nanocomposite materials (MNCM) [9]. The development of new ways of MNCM obtaining, manufacturing and investigation of samples of such nanocomposites opens opportunities for creating materials with preassigned characteristics. Grinding of structural elements to nanoscale results in improving the majority of practically important characteristics. There is the possibility of combining a number of characteristics in the compositions, which is impossible to obtain in homogeneous massive samples. If in ordinary massive crystalline materials, the size factor is the average cross-sectional size of grains or crystallites, in MNCM this is also the thickness of the layers [9].

The purpose of the present work was to establish the regularities of magnetic characteristics changes (in particular, the coercive force) of the ferromagnetic iron-copper composition during the transition of the structural elements of its components to the thin-film state.

2. EXPERIMENTAL

A number of methods were developed to obtain MNCM. For example, they can be obtained by rolling a package of heterogeneous foils of metals, or by rolling a pseudo-alloy or a mixture of powders. Two manufacturing methods of MNCMs from powders were used. The first one traditional method [9] is that a mixture of 4-100 microns dissimilar metal powders is rolled, sintered and compressed with a total compression of 99%. The annealing process was carried out at a temperature of 75-85% of the melting point of the more fusible component. This technology allows to obtain the structure of rolled particles with a thickness of about 20 nm. This method is used only to obtain metal MNCMs that do not form intermetallic compounds between themselves and soften the material during the rolling process. In the second method, powders mixtures from iron and multiwall carbon nanotubes (MWCNT), iron and copper were pre-treated in a planetary mill [10] before the sintering. After sintering of powders compositions in both methods, their cross-section will consist of nanofilms in the form of flakes, which arbitrarily alternate with each other. This provides an opportunity to obtain massive materials with specified characteristics similar to TF.

X-ray powder diffraction data were collected with DRON-4 automatic diffractometer (CoK_α-radiation). The diffraction patterns were obtained in discrete mode under the following scanning parameters: observation range $2\theta = (40\text{-}130)^o$, step scan of 0.05^o, counting time per step at 3 s. The peak position and integral intensities of the observed reflections were determined using full profile analysis.

The original software package elaborated for the au-

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tomated DRON equipment including full complex of the Reitveld refinement procedure (qualitative and quantitative phase analysis, lattice parameter refinement, crystal structure determination) was used [11, 12].

The average grain size (d) of the α-Fe phase forming after mechanical alloying was estimated by the Debye-Scherrer formula $d = \dfrac{K\lambda}{\beta\cos\theta}$, were K is the crystallite shape factor (a good approximation is $K = 0.9$), λ is the X-ray wavelength; β is the full width at half maximum of the peak in rad; θ is the Bragg`s angle in degrees.

The investigation of magnetic hysteresis loops of materials obtained was carried out on a vibration magnetometer with a frequency of 70 Hz in a constant magnetic field with a maximum value up to 150 kA/m [10]. The magnetic moment of the samples depends on their magnetic parameters, on the mass and form. So, calibrated specimens with a ratio of their length to a diameter not less than 10 were prepared for the experiments. The magnetometer was calibrated by the nickel standard to obtain absolute values of the magnetic characteristics of the materials. The cyclic dependences of the magnetic induction (B) on the magnetic field strength (H) (magnetic hysteresis loop) were built based on experimental results. Using these dependences, the values of the specific magnetization at saturation (σ_s), residual magnetization (σ_r), coercive force (H_c) of materials were determined.

3. RESULTS AND DISCUSSION

Fig. 1 shows a typical image of the microstructure of iron-copper MNCM. The material was obtained by the first method. The figure shows that the structure of the material is layered.

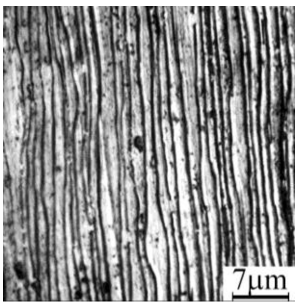

Fig. 1 – The microstructure of MNCM Fe-Cu: $h_{Fe}/h_{Cu} = 5$. Dark stripes are copper layers, light ones – iron layers

The coercive force (Fig. 2) increases with decreasing thickness of the MNCM's layers obtained by the first method or decreasing size of the grains previously dispersed in the planetary mill and compacted compositions, by the second method. This increase can be determined by different factors. The most important among them are different crystallographic anisotropies in samples, the density of defects, magnetostatic interaction of layers, etc. The dashed lines in Fig. 2 show the H_c levels for Fe and Cu alloys with 2:1 percentage ratio of Fe and Cu [9]. When comparing the H_c values for MNCM and for alloys of the same composition, it is evident that the contribution of mutual diffusion of components is absent. The maximum (almost 2.2 times) increase of the H_c value for MNCM compared to deformed alloys of the same composition was observed for curves 1-3 in Fig. 2. These data indicate the promising use of the considered compositions for the production of magnetic materials with specified characteristics. At the same time, the increase of the H_c value in these materials is determined by the combination of properties of the nanolayer ferromagnetic and diamagnetic components in the nanocomposite. An increase of H_c value with increasing processing time up to 60 min and its reduction with a further increasing of processing time were observed for composite mixtures of Fe and Cu obtained in a planetary mill. Structural studies have shown that the processing of mixtures increases the dispersion (reducing the cross section of the particles of treated mixtures) at certain time intervals. The mutual dissolution of such practically insoluble components as Fe and Cu, the conglomeration of their particles and the corresponding decrease of the H_c values are also observed at different processing time for the different materials. There are no significant changes of H_c value with increasing mechanochemical activation time of mixtures with a higher concentration of Fe. The magnetization of samples does not change significantly (Table 1 for the Fe-Cu system).

In general, a pre-saturated α-(Fe,Cu) solid solution is formed after processing of Fe-Cu mixtures in a planetary mill [10]. This solid retains the ferromagnetic characteristics inherent in pure α-Fe.

At the same time, there were no correlations between the changes of H_c value and the parameter of the crystalline lattice (a) of the solid solution α-(Fe,Cu) formed during the treatment in the mill (Fig. 3).

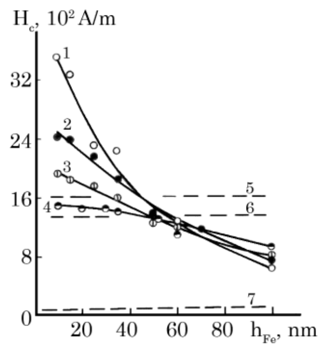

Fig. 2 – Dependence of the coercive force H_c on the thickness of layers of MCNM Fe-Cu: 1-4 for $h_{Fe}/h_{Cu} = 1$, 2, 3.3 and 5; 5 and 6 for $V_{Fe}/V_{Cu} = 2$ and 1; 7 – for 08КП steel

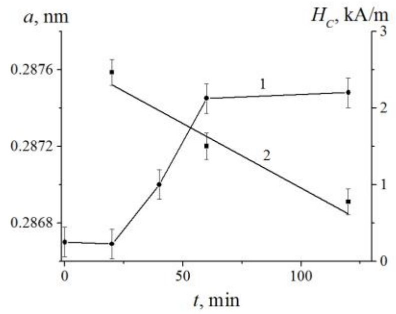

Fig. 3 – Dependence of the lattice parameter a (1) and the coercive force H_c (2) on the time t of mechanochemical treatment of NCM Fe-Cu (4:1) in planetary mill

On the one hand, the interaction conditions of the ferro- and diamagnetic components in MNCM change after processing of a powders mixture in a planetary mill, since their concentration changes and a solid solution forms. On the other hand, the conditions for the conglomeration of particles change, too. This is confirmed by that an increase in the value of H_c (Fig. 4) is observed with increasing processing time which exceeds the time that increases the dispersion of Fe and Cu mixture particles for a composition of iron and multi-wall carbon nanotubes. At the same time, H_c reduction was observed only after the formation of new carbide phases of Fe_3C, Fe_7C_3 and oxide phases of Fe_2O_3 in the mixtures [10]. In addition, there was a certain correlation between the H_c values and the size of the coherent dispersion blocks (Table 2).

Table 1 – Magnetic characteristics of nanocompositions Fe-Cu

System	Processing time, t, min	Coercive force, H_c, kA/m	Saturation magnetization, σ_s, A·m²/kg	Residual magnetization, σ_r, A·m²/kg
Fe-Cu (1:9)	20	1.78		
	60	5.03		
Fe-Cu (1:4)	20	1.42	23.30	1.45
	60	7.49	19.40	1.12
Fe-Cu (3:7)	20	2.27		
	60	8.95		
	120	0.88		
Fe-Cu (1:1) (at. %)	20	2.64		
	60	5.94		
	120	3.00		
Fe-Cu (2:1)	20	3.25		
	60	3.58		
	120	2.86		
Fe-Cu (4:1)	20	2.46	11.90	0.61
	60	1.50	14.86	0.41
	120	0.78	14.12	0.22
Fe	20	1.54		
	60	2.18		
	120	2.19		

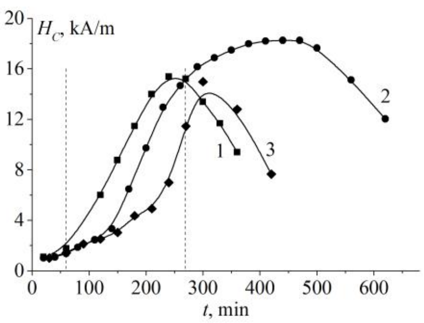

Fig. 4 – Dependence of the coercive force of NCM powders Fe-MWCNT (10 vol. %) (1), Fe-MWCNT (20 vol. %) (2), Fe-MWCNT (30 vol. %) (3) on the processing time in a planetary ball mill

The defects of the crystal lattices of ferromagnets have a significant effect on their magnetic characteristics [9, 10]. First of all, it is observed in the magnetostrictive interaction between magnetization and stress under mechanical deformation of ferromagnetic crystals. The relation between magnetostriction and dislocations for cubic crystals can be determined by the magnetoelastic energy of the volume unit [6]. In general, the interaction of domain walls with dislocation depends on dislocation density and their distribution in real crystals, and the value of coercive force is proportional to the density of dislocations [9]. For TF, the H_c value will be proportional to the density of dislocations under the condition that Bloch walls dominate them, and the defects are evenly distributed. A dimensional factor also plays its role in this case [13]. There is a critical size of the TF thickness and the particles while they exist in a single-domain state [9].

Since the boundaries of the layers and grains limit the movement of the domain walls, the decrease of layer thickness or grain size should cause an increase in the H_c value. However, achieving the indicated value of the 50 nm, which is a critical value, an increase in the H_c value does not occur. This is because the width of the domain wall for nanocrystalline iron is ~ 54 nm [14]. In contrast to Fe-Cu MNCM, the coercive force for the Fe-C composition treated during 60 min in the planetary mill practically does not change (Fig. 4). In this case, it does not depend on the decrease of the size of iron grain. With further mechanochemical treatment of the mixture, the H_c value increases rapidly. This coincides with the fact that the carbide phases are beginning to emerge in the mixtures at such processing times. However, this process competes with the process of reducing the concentration of MWCNT into the composition, from which this phase is formed and which blocks to a certain time the conglomeration of iron grains. In this regard, starting from a certain processing time, which varies for different mixtures, H_c begins to decrease (Fig. 4).

For both composite materials, whose components were pretreated in a planetary mill, and for nontreated ones, the thickness of diamagnetic (h_d) layers decreases with decreasing thickness of ferromagnetic (h_f) layers. Although the impact of h_f and h_d changes on the H_c value is different for MNCM. Simultaneous reduction of such layer thicknesses in the compositions can lead to significant changes in the values of the coercive force. Characteristic is that the forms of hysteresis curves (Fig. 5) are typical for hard magnetic materials.

Table 2 – Phase composition and parameters of the crystal structure of the Cu-Fe nanocomposites obtained in a planetary ball mill at different processing times

Processing time t, min	Phase composition	Lattice parameter a, nm (Cu, Fe)	Lattice parameter a, nm α-Fe	Size of coherent scatter blocks d, nm
Cu-Fe (1:9)				
20	(Cu,Fe) (82) + α-(Fe) (18)[1)]	0.36143(2)	0.28665(3)	60
60	(Cu,Fe) (96) + α-(Fe) (4)	0.36184(5)	0.28664(2)	54
120	(Cu,Fe) (100)	0.36214(5)	–	60
Cu-Fe (1:4)				
20	(Cu,Fe) (78) + α-(Fe) (22)	0.36143(2)	0.28661(2)	60
60	(Cu,Fe) (89) + α-(Fe) (11)	0.36187(3)	0.28658(4)	54
120	(Cu,Fe) (100)	0.36255(2)	–	64
Cu-Fe (7:3)				
20	(Cu,Fe) (73) + α-(Fe) (27)	0.36143(4)	0.28651(2)	50
60	(Cu,Fe) (81) + α-(Fe) (19)	0.36212(1)	0.28657(3)	53
120	(Cu,Fe) (99) + α-(Fe) (1)	0.36281(2)	0.28660(1)	53
Fe-Cu (4:1)				
20	α-(Fe,Cu) (83)[1)] + Cu (17)	0.36436(4)	0.28669	31
60	α-(Fe,Cu)	–	0.28749	26
120	α-(Fe,Cu)	–	0.28748	14

1) Phase composition, wt. %

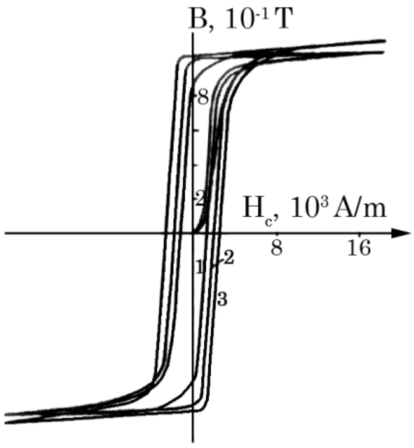

Fig. 5 – Magnetic hysteresis loop of MNCM Fe-Cu, $h_{Fe}/h_{Cu} = 2$; h_{Fe}(nm) = 70 (1); 35 (2); 15 (3)

Rectangularity of loops increases with a decrease of the h_f thickness and with an increase of h_d. This is connected, most likely, with the increase of fixing the domain walls on defects, the density of which increases with a decrease of h_f. The decrease of h_d causes an increase in the factor which contributes to demagnetization, which, accordingly, reduces the H_c value and the rectangularity of the hysteresis loops.

Thus, the creation of multilayer nanocomposite materials allows to obtain materials with ferromagnetic characteristics, which inherent in TF. The production of MNCM from powders under the previous mechanochemical activation of mixtures of such powders in a planetary mill allows us to obtain nanocomposites with given practically important ferromagnetic characteristics.

4. CONCLUSIONS

The creation of layered nanocomposite materials (NCM) with ferromagnetic and diamagnetic components, the microstructure of which is a combination of thin-film layers or layered flakes, allows to realize in these NCM practically important, in particular, ferromagnetic characteristics, which are inherent to thin films.

It was established that the change in the composition of MNCM and the thickness of its layers can increase the coercivity of the massive material obtained by the first method to a level which is 2.2 times higher than the H_c value for iron-copper alloys of the corresponding concentration for the compositions obtained by the second method. This excess can be 9.3 times higher, and for iron-MWNT composition, the excess can reach 20 times and more.

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Феромагнетизм нанокомпозицій залізо-мідь

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У роботі розглянуті і реалізовані магнітні характеристики тонких плівок у масивних зразках. Багатошарові нанокомпозиційні матеріали з порошків заліза і міді та порошків заліза з багатошаровими вуглецевими нанотрубками одержували двома способами. Перший спосіб полягає в тому, що суміш гетерогенних металевих порошків розміром 4-100 мкм піддають прокатці, спіканню та пресуванню з загальним обтисненням 99 %. У другому способі суміші порошків попередньо обробляють в планетарному млині перед спіканням. Показано, що мікроструктура одержаних зразків, як правило, шарувата. При цьому товщину шарів за рахунок деформації, зокрема, прокатки, можна зменшувати до нанорозмірів. Властивості таких масивних матеріалів, незважаючи на можливі розриви суцільності шарів при прокатці до нанорозмірних товщин і їх фрагментації на нанолусочки, притаманні в своїй більшості властивостям тонких плівок. Встановлено взаємозв'язок між мікроструктурою, яка визначається способом обробки суміші порошків, товщиною шарів або лусочок і коерцитивною силою одержаних матеріалів. Визначені оптимальні параметри обробки для реалізації практично привабливих магнітних характеристик таких матеріалів.

Ключові слова: Тонкі плівки, Магнітні характеристики, Коерцитивна сила, Шаруваті нанокомпозиційні матеріали, Структура.