

REGULAR ARTICLE



Features of Oxidation and Annealing of Iron Nanoparticles, Obtained
by the EB-PVD Method on a Rotating Substrate

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Microlayered composite materials (CM) containing nanoparticles of iron oxides have obtained by the method of electron-beam physical vapor and deposition in vacuum (EB-PVD) on a rotating substrate. The size of the particles of the obtained iron oxides in aqueous colloidal solvents/systems (CS), prepared from the obtained CM have determined. For the preparation of CS $\text{Fe}_3\text{O}_4\text{-H}_2\text{O}$ and $\text{Fe}_2\text{O}_3\text{-H}_2\text{O}$ used samples of micro-layered CM NaCl-18.5 wt. % Fe, including made from just obtained CMs, after long-term exposure (607 days) and annealing in air at temperatures of 350 °C and 650 °C. The oxidation kinetics of the obtained micro-layered CM NaCl-18.5 wt. % Fe have studied by the method of thermogravimetric analyses (TGA) in air. Structural transformations occurring during an annealing in air of microlayered CM NaCl-18.5 wt. % Fe at the temperature of 350 °C was determined the growth process of crystallites in layers with oxidation of the metal component of the iron layers to Fe_3O_4 magnetite with a size of particles 5-7 nm. Upon further heating to 650 °C during the annealing in air in the studied CMs was noted the partial post-oxidation of magnetite Fe_3O_4 to hematite – $\alpha\text{-Fe}_2\text{O}_3$ (up to 20 % by mass) due to physically adsorbed oxygen, with simultaneous recrystallization and growth of NaCl crystallites. The results of determining the sizes of Fe_3O_4 and Fe_2O_3 particles of the investigated CS $\text{H}_2\text{O-Fe}_{3(2)}\text{O}_{4(3)}$ at temperatures of 25-80 °C by the method of dynamic lights scattering (DLS) have confirmed the stabilization of the dispersions degree of the obtained iron nanoparticles with the temperatures grow. In particular, the dispersion of the obtained CS, the parameters of the average hydrodynamic diameter of the particles and their index of polydispersity – have high values and a wide dispersion (interval), which characterizes them as polydisperse with the presence of particles aggregates. The results of the study of the phase composition, oxidation kinetics and residual magnetization of the studied CMs have confirmed the post-oxidation of iron in them, including due to physically adsorbed oxygen during the duration of storage and annealing in air.

Keywords: EB-PVD, Micro-layered composite materials, Nanoparticles, Annealing, Phase composition, Microstructure, Iron oxides, Thermogravimetric analyze, Dynamic lights scattering.

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1. INTRODUCTION

Electron-Beam Physical Vapor and Deposition (EB-PVD) currently is one of the promising method for the obtaining/synthesize of nanomaterials.

During the simultaneous evaporation in a vacuum of materials of the NaCl-Fe double system, which significantly difference in terms of the partial pressure of the saturated vapor and with subsequent condensation of the mixed vapor flow [1] on a rotating substrate - are formed NaCl-Fe layered composite materials (CM), the structure and properties of which significantly depend on technological parameters of their production [2, 3]. The conducted studies of microlayered NaCl-Fe CMs, obtained by the EB-PVD method on a rotating substrate was revealed that iron in such CMs is mainly in the form of oxides – nanoparticles of magnetite Fe_3O_4 ($\text{FeO:Fe}_2\text{O}_3$) and also was proved the possibility and prospects of using the EB-PVD method for production/synthesis of iron nanoparticles [2, 3].

The purpose of this paper is the investigation of influence of the previous long-term exposure and annealing in air of microlayered CMs NaCl-Fe, obtained by the EB-PVD method on a rotating substrate on their oxidation, as well as to assess the possibilities of further improvement and increasing the efficiency of this method of obtaining iron nanoparticles.

2. EXPERIMENTAL

At the first stage of the experiment at the laboratory electron-beam installation UE-150 (Paton Institute for Electric Welding) was obtained NaCl-Fe microlayered CMs by the EB-PVD method on a rotating substrate. The uniformity of the thickness distribution of microlayers, the chemical composition, structure, and properties of such CMs are sensitive to a number of controlled technical parameters of the EB-PVD process: the relative location (geometry) between the crucibles and the substrate, the temperature of the working surface of the deposition and the rate of the substrate rotation [2, 3].

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To assess the influence of the mutual location of the crucibles and the distance to the substrate on the thickness distribution of the CM NaCl-Fe along the radius of the substrate surface (R_s) first monolayers of NaCl and iron were obtained separately. In order to obtain NaCl and Fe layers of equal thickness, some changes were made to the previously described technological scheme for obtaining CM NaCl-Fe with a peripheral location of the crucibles for the evaporation of the initial materials [2] relative to the axis of rotation of the substrate (Fig. 1): the distance from the crucibles to the substrate L – was increased to 300 mm, the temperature of the substrate preheating for vapor flow deposition T_s – was reduced till 50 °C, its rotation rate V_s – increased to 35 rpm⁻¹.

The vapor flow of NaCl was directed by the channels of special reactor to the middle of the substrate's radius (110 ± 30 mm from axis of rotating). The reactor's channel system prevents the electron-beam from hitting the surface of the evaporated table salt when it is heated, providing a directed output of NaCl vapor stream to the

rotating substrate. The power of the electron-beam W during NaCl evaporation was – 1.6 kW, evaporation time τ – 900 s.

Iron layers were obtained by its direct evaporation from the second crucible located near to the crucible-reactor for salt evaporation. An area of effective use of the metal vapor flow is limited by a cone with an angle at the top of $\sim 60^\circ$, therefore the vapor flow of iron was oriented to the edge of the substrate. Also, this arrangement of the crucible was reduced the angle of the meeting of the iron vapor flow with the surface of condensation (substrate) from 60° to 30° and enhanced the "shadowing" effect and obtaining microporous, which participate in the mechanism of particles formation during the layers destruction in microlayered CM NaCl-Fe. The "shadowing" effect increases in case the angle of meeting the vapor flow with the condensation surface is less than 90° [4]. The time of obtaining a monolayer of iron τ – 900 s at the power of the electron-beam W_b – 7.7 kW.

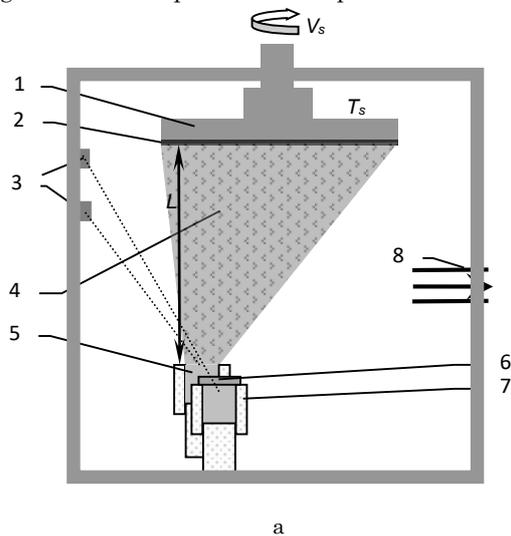


Fig. 1 – The technological scheme of obtaining of CM NaCl-Fe by the EB-PVD method (a) and technological chamber of the laboratory EB-installation UE-150: 1 – substrate; 2 – condensate (CM); 3 – EB-guns; 4 – vapor flow; 5 – Fe-ingot; 6 – NaCl-tablet; 7 – reactor for NaCl evaporating; 8 – input tube of vacuum system (to vacuum pump)

The obtained CM NaCl-Fe have a developed porous surface/structure and a significant adsorption capacity. Therefore, when the vacuum chamber is opened, moisture and oxygen from the air penetrate into the CM NaCl-Fe and are adsorbed, oxidizing the iron with the subsequent partial delamination of the obtained CM. Also, during the rapid depressurization of the vacuum chamber, the heating of condensate of the obtained CM till the temperature of 100 °C and higher due to the exothermic effect of the oxidation reaction have noted.

An annealing of the obtained CM NaCl-Fe was carried out at temperatures of 350 °C and 650 °C in air and in a vacuum for comparison. Temperature's unevenness during isothermal exposure at annealing was maintained at the level of ± 10 °C.

Investigations were carried out on samples of NaCl-18.5 wt. % Fe CM, separated from the substrate, in the dry state, including after their long-term (607 days) exposure in the air and their colloidal systems/solvents (CS) in the distilled water.

The microstructure of the obtained CMs was studied

on the CamScan 4D scanning electron microscope.

The determination of the chemical composition was studied on EDX micro-X-ray spectrum analyzer for the CamScan 4D.

X-ray diffraction analysis (XRD) was performed on a DRON-UM1 diffractometer in filtered Co-K α radiation. The analyze of the obtained results was carried out by using "Powder Cell" software. The average crystallite size was estimated according to the Scherer equation.

Samples of microlayered CM NaCl-18.5 wt. % Fe were used for preparing of their colloidal systems (CS) in the distilled water the initial state and after their aging and annealing in air at temperatures of 350 °C and 650 °C. For this purpose, distilled water was added to the powder of CM previously crushed in an alund mortar. The obtained aqueous mixture was actively stirred, followed by complete settling of the sediment and removal of the salt solvent above it.

This procedure was repeated at least 5 times for maximum purification of the obtained solvent from the salt. The aqueous iron precipitate thus purified from salt was

dried. Its chemical composition was studied using a Philips Analytical X-Ray micro-X-ray spectrometer. The average size of CS particles was estimated by the Dynamic Lights Scattering (DLS) method.

The oxidation kinetic of microlayered CM NaCl-18.5 wt.% Fe – initial, after their long-term storage and annealing in air were studied using a TGA7 Perkin Elmer thermogravimetric analyzer with sensitivity up to 0.1 μg and a heating/cooling rate – 0.17 $^{\circ}\text{C}\cdot\text{s}^{-1}$ in the range of heating/cooling temperature 20-650 $^{\circ}\text{C}$.

3. RESULTS AND DISCUSSION

The thicknesses distribution of NaCl, Fe monolayers and the CM NaCl-Fe layers along the radius of the rotating substrate according to the accepted scheme of conducting the experiment is shown on the Fig. 2.

The thickness of the NaCl monolayer at a distance of 20-130 mm from the edge of the substrate was $85 \pm 1 \mu\text{m}$, with its increasing to 91 μm on the axis of rotation. Such an even distribution of the thickness of the salt condensate along the radius of the substrate was due to the orientation of the reactor's holes to the rotating substrate, which ensured a fairly uniform condensation of the vapor flow on its surface during the evaporation of NaCl.

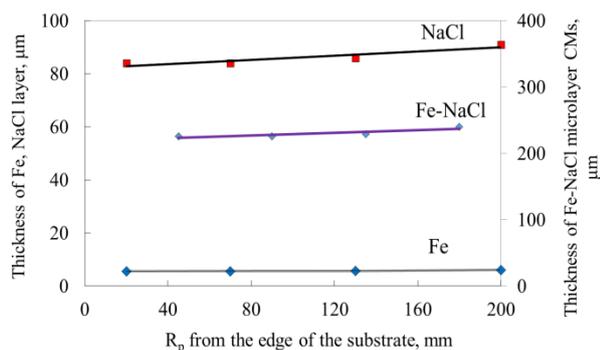


Fig. 2 – The thickness distribution of Fe, NaCl monolayers and CM Fe-NaCl microlayers along the substrate radius

The thickness of the iron monolayer also practically did not change along the radius of the rotating substrate and was $7 \pm 1 \mu\text{m}$. Such a uniform thickness distribution can be explained by the different linear rate of passage of the substrate's segments over the vapor flow of iron under the accepted scheme of mutual arrangement of the crucible and the substrate. That is, all points on the radius of the substrate from the axis of rotation have equal angular rate, period and frequency of rotation, but different linear speed [2]. Thus, the further the point of the substrate is from the axis of rotation along the radius, then faster it moves under the vapor flow of iron.

In particular, at $V_s = 35 \text{ rpm}^{-1}$ – the edge of the substrate above the effective vapor flow of iron moves with a linear speed of $0.53 \text{ m}\cdot\text{s}^{-1}$. At the same time, the linear speed of the points on the substrate's surface near the axis of rotation of the substrate is $0.06 \text{ m}\cdot\text{s}^{-1}$, so their stay under the vapor flow is almost an order of magnitude longer. As a result, a general "equivalent" of the thickness of the obtained condensed iron layer is noted.

In the obtained microlayered CMs NaCl-18.5 %wt.

Fe by the X-ray phase analysis was determined a content of the metallic phase was until 1 % wt. It is obvious that the size of the obtained iron oxides particles is beyond the sensitivity of the used XRD-method.

The results of the study of the obtained CMs NaCl-18.5 %wt. Fe after annealing in air at 350 $^{\circ}\text{C}$ (Fig. 3b) - oxidation of the metal component of the iron layers to magnetite (Fe_3O_4) with a size of particles of 5-7 nm was ascertained. At the same time, the layers of NaCl have a porous microstructure, consisting crystallites with a mean size – 32 nm.

Analyze of the chemical composition of transverse chipping samples of micro-layered CMs NaCl-18.5 wt. % Fe (Fig. 4) was showed the relative uniformity of the distribution of Fe, Na, Ca and O along of the substrate radius. The mean content of iron in the obtained CM is 18.5 % wt., oxygen – 16 % wt.

It is known the adsorption capacity of nanoparticles to oxygen and water vapor increases with a decrease in their size [5]. In the obtained CMs NaCl-Fe, the decreasing of oxygen/iron ratio is noted with an increasing of oxygen content, which is confirmation of the participation of adsorbed by CM oxygen in the process of oxidation of Fe_3O_4 to Fe_2O_3 .

Measurement of the distribution by size of iron particles in the colloidal solvents/systems (CS) obtained by the dissolution of obtained CM in distilled water was provided at the temperatures: 25, 40, 60 and 80 $^{\circ}\text{C}$. The main parameters, characterizing the particle's distribution by size, used for the investigation by the method of Dynamic Lights Scattering (DLS) are: the average hydrodynamic diameter of the particles (Z-Average) and the polydispersion index (PDI). PDI is the dimensionless parameter, characterizes the width of the particle dispersion distribution and is sensitive to the content of particle's aggregate in the CS. For monodispersion CS, the PDI parameter does not exceed 0.1 [1].

The obtained results (Table 1) indicate that the PDI parameter for the studied CM samples varies from 0.413 to 1.0, which characterizes them as polydisperse with the presence of aggregates. Increasing of the heating temperature of the CM helps to stabilize the dispersion of iron particles.

The size of the iron particles corresponding to the maximum of the distribution of the dispersion can be considered as a characteristic average size of the iron particles in the CM. Increasing of the annealing temperature of CM, the average size of iron particles decreased in them (Table 2).

Table 1 – Estimated parameters of quality of dispersion of powders/particles $\text{Fe}_{3(2)}\text{O}_{4(3)}$ -NaCl

Samples	Temperature of the tests			
	25 $^{\circ}\text{C}$	40 $^{\circ}\text{C}$	60 $^{\circ}\text{C}$	80 $^{\circ}\text{C}$
	PDI (Z-average, nm)			
initial	0,638 (1348)	1,000 (3469)	1,000 (5027)	0,681 (19764)
annealing at 350 $^{\circ}\text{C}$	0,413 (2632)	1,000 (4233)	–	1,000 (3418)
annealing at 650 $^{\circ}\text{C}$	0,841 (1031)	1,000 (5220)	1,000 (3690)	–

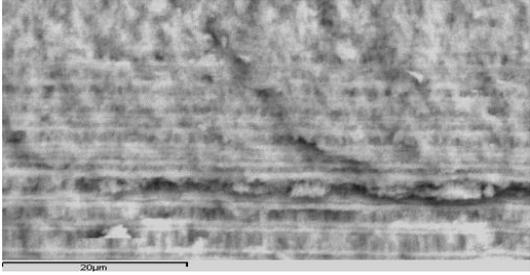
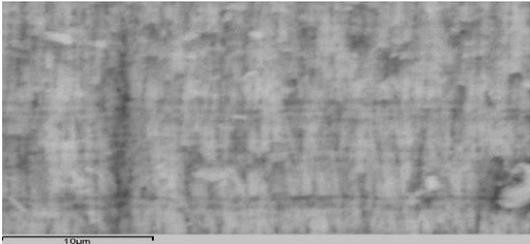
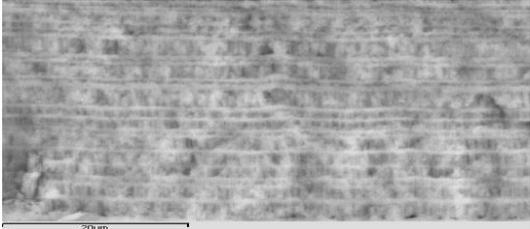
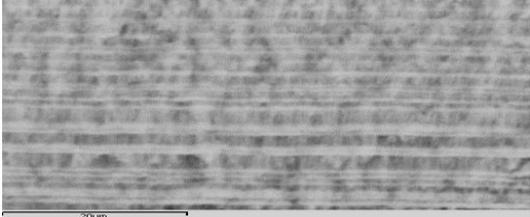
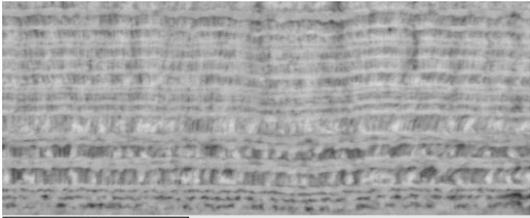
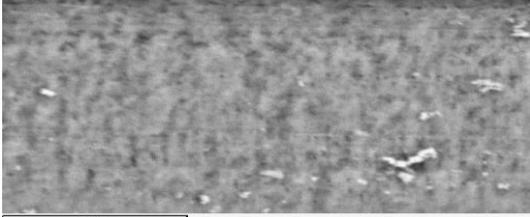
Microstructure	Phase's composition (annealing environment)	Size of the crystallites, D, nm (mean)	Chemical composition, %wt.
	NaCl Fe ₃ O ₄ -traces (air)	30 –	99 1
	NaCl Fe ₃ O ₄ -traces (vacuum)	29 –	99 1
	NaCl Fe ₃ O ₄ (air)	32 5-7	96.5 3.5
	NaCl Fe ₃ O ₄ (vacuum)	33 13	94 6
	NaCl α-Fe ₂ O ₃ (air)	46 46	80 20
	NaCl Fe ₃ O ₄ (vacuum)	37 34	78 22

Fig. 3 – Microstructure and phase's parameters of microlayered CMs NaCl-18,5 % wt. Fe: a – initial; b – after annealing at the temperature 350 °C; c – after annealing at the temperature 650 °C

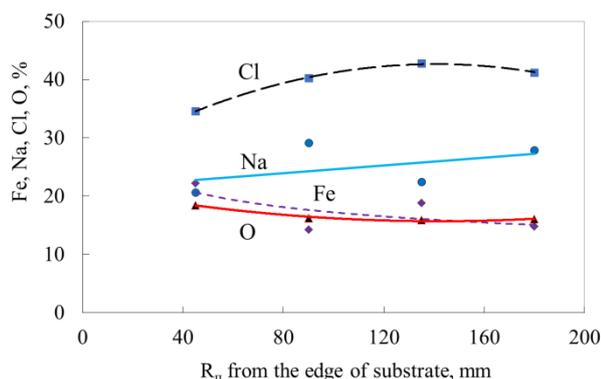


Fig. 4 – The distribution of elemental composition of Fe, Na, Cl, and O in the cross-section samples of microlayered CM NaCl-18.5 wt. Fe along the substrate radius

Thermogravimetric analysis (TGA) upon heating in air of CM samples just obtained immediately after EB-PVD revealed a non-monotonic increase in their mass (m/m_0) with increasing temperature. On the other hand, the mass of CM samples after their long-term storage during TGA decreased monotonically (Fig. 5).

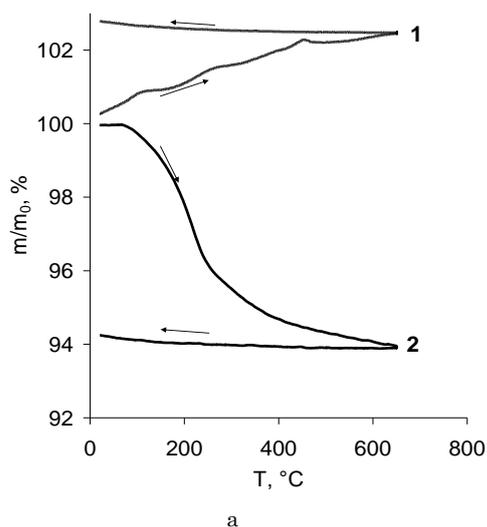


Table 2 – The range of size and average size of particles Fe_3O_4 and Fe_2O_3 at CM $H_2O-Fe_{3(2)}O_{4(3)}$

Samples	Temperature of the tests			
	25 °C	40 °C	60 °C	80 °C
	The range of size (average size) of particles, nm			
initial	295-1281 (615)	190-342 (255)	44-91 (58,8)	12-22 (15,7)
annealing at 350 °C	825-2305 (1281)	79-164 (105,7)	–	68-142 (105,7)
annealing at 650 °C	295-615 (459)	28-51 (37,8)	18-33 (24,4)	–

For samples of CM NaCl-18.5 wt. Fe after their long-term storage, a study of the influence of annealing temperature in air at temperatures (T_{an}) of 350 °C and 650 °C on the kinetics of their oxidation by the TGA method was carried out. In the fig. 6 shows the dependence of the mass change of the studied microlayered CM NaCl-18.5 wt. % Fe after their long-term storage and annealing in air.

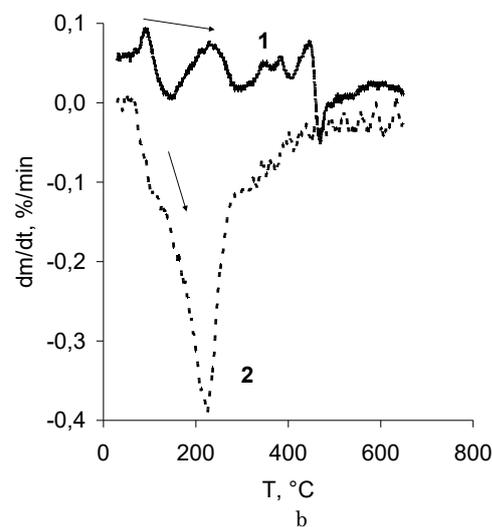


Fig. 5 – Curves TGA (a) and differential thermogravimetric analyses (DTA) (b) of CM NaCl-18.5 wt. Fe just obtained (1) and after long-term storage (607 days) on air (2)

In all experiments, a monotonous decrease in the mass of the samples was noted up to the maximum temperature of their heating of 650 °C. During the subsequent cooling of the CM samples in air, the same slight increase in mass was observed without the influence of the previous history of their heat treatment.

Analysis of TGA curves of microlayered CM NaCl-18.5 wt. % Fe found that the increase in mass of just obtained samples during TGA was almost linear with three peaks on the differential curve at temperatures: 87 °C, 229 °C and 446 °C, followed by its saturation (Fig. 5).

Oxidation of the obtained samples of CM NaCl-18.5 wt. Fe during their long-term storage and annealing in air is also confirmed by the results of X-ray phase analyses (XRD). At the same time, the loss of mass of such samples during TGA is most likely due to the desorption of moisture absorbed on the surface during their heating (Fig. 6), which is also confirmed by the view of CM samples before and after TGA. In particular, the color of such

CMs changed from pink-green-black to red (after TGA), which is a characteristic sign of oxidation of magnetite Fe_3O_4 to hematite Fe_2O_3 and is consistent with the results of XRD-analyses.

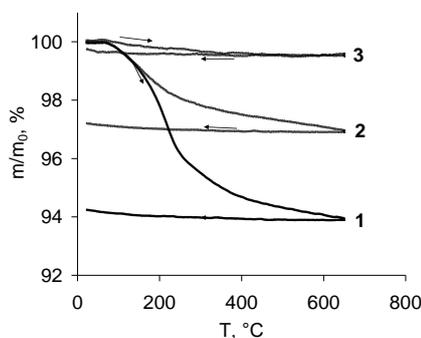


Fig. 6 – TGA curves of microlayered CM NaCl-18.5 wt. Fe initial (1) and after annealing on air at 350 °C (2) during heating till 650 °C and cooling in air (3)

A comparative analysis of the obtained TGA results for CM NaCl-18.5 wt. % Fe was carried out. Fe with the results of measuring their residual magnetization M_r depending on the annealing temperature and the period of storage of the samples in air (Fig. 7). Residual magnetization (M_r) of CM NaCl-18.5 wt. % Fe after long-term storage in air (0.29 emu/g) was significantly lower compared to the initial samples (1.8 emu/g) and exceeded the corresponding decrease in M_r for CM samples after their annealing in air. Such a decrease in residual magnetization also confirms the oxidation of hematite with an increase in the proportion of Fe_2O_3 in the composition of CM after long-term exposure and annealing in air.

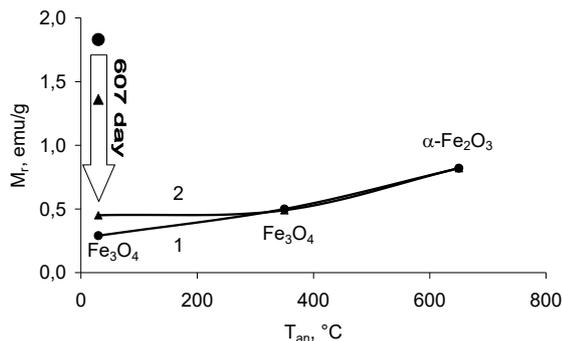


Fig. 7 – The influence of the annealing temperature (T_{an}) on the residual magnetization (M_r) of microlayered CM NaCl-18.5 wt.% Fe after long-term (607 days) storage in air

The fixed slight increase in M_r for the annealed samples when the annealing temperature is increased from 350 °C to 650 °C is within the experimental error.

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Особливості окиснення та відпалу наночастинок заліза, отриманих способом ЕВ-РВД на підкладці, що обертається

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Способом електронно-променевого фізичного осадження з парової фази у вакуумі (ЕВ-РВД) на підкладці, що обертається було отримано мікросферуваті композиційні матеріали (КМ), що містять нанорозмірні частинки оксидів заліза. Визначено розмір частинок отриманих оксидів заліза у колоїдних водних розчинах/системах (КС), приготованих із отриманих КМ. Для приготування КС $\text{Fe}_3\text{O}_4\text{-H}_2\text{O}$ та $\text{Fe}_2\text{O}_3\text{-H}_2\text{O}$ використовували зразки мікросферуватих КМ NaCl-18,5 %мас. Fe: вихідні, після довготривалої (607 діб) витримки й відпалу на повітрі за температур 350 °C та 650 °C. Кінетику окиснення отриманих мікросферуватих КМ NaCl-18,5 % мас. Fe досліджували методом термогравіметричного аналізу (ТГА) на повітрі. Структурні перетворення, що відбуваються під час відпалу на повітрі мікросферуватих КМ NaCl-18,5 % мас. Fe при температурі 350 °C визначали процес росту кристалітів у шарх із окисненням металевий складової шарів заліза до магнетиту Fe_3O_4 із розміром часток 5-7 нм. При подальшому нагріванні до 650 °C за рахунок фізично адсорбованого кисню у досліджуваних КМ відзначалось часткове доокиснення магнетиту Fe_3O_4 до гематиту – $\alpha\text{-Fe}_2\text{O}_3$ (до 20 %мас.) із одночасною рекристалізацією та ростом кристалітів NaCl. Результати визначення методом динамічного розсіяння світла (DLS)

розмірів частинок Fe_3O_4 та Fe_2O_3 досліджуваних КС $\text{H}_2\text{O}-\text{Fe}_{3(2)}\text{O}_{4(3)}$ за температур 25-80 °С засвідчили стабілізацію ступеня дисперсності отриманих наночастинок заліза. Зокрема, дисперсність отриманих КС, параметри середнього гідродинамічного діаметру частинок та індексу їх полідисперсності - мають високі значення та широку дисперсію (інтервал), що характеризує їх, як полідисперсні з присутністю агрегатів. Результати вивчення фазового складу, кінетики окиснення та залишкової намагніченості досліджуваних КМ – підтвердили доокиснення заліза в них, у тому числі за рахунок фізично адсорбованого кисню під час тривалого зберігання та відпалу на повітрі.

Ключові слова: EB-PVD, Мікрошаруваті композиційні матеріали, Наночастинки, Відпал, Фазовий склад, Мікроструктура, Оксид заліза, Метод динамічного розсіяння світла, Термогравіметричний аналіз.