

Practice Aspects of Deposition of Nanostructured Composite NaCl-Fe Films by EB-PVD on a Rotating Substrate

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EB-PVD combines the feasibility of controlled intensive evaporation of nonorganic materials in vacuum with subsequent deposition of vapor on the substrate/product. This method is characterized by wide capabilities of various technological setups and precise control of technological process parameters. The paper considers peculiarities of the EB-PVD technological setup for obtaining nanostructured NaCl-Fe materials for medical applications. A technological setup with a peripheral to the substrate rotation axis arrangement of vapor sources is employed. The use of a disk with a complex of inclined vapor channels on a vapor source ensures a uniform thickness distribution of thick NaCl films along a rotating substrate with an average thickness deviation of $\pm 5\%$. The geometric ratio of the directions of vapors of source materials on a rotating substrate allows to obtain qualitative nanostructured NaCl-Fe materials. The relative deviation of the concentration of the metal component does not exceed 8-10%. The peripheral arrangement of vapor sources made it possible to reduce the distance between the sources of evaporating materials and the substrate deposition surface to 230 mm. Thus, an increase in the film thickness up to 300-400 μm is achieved. The structure of composite NaCl-Fe films by EB-PVD on a rotating substrate is an alternation of NaCl and Fe enriched layers of different thickness that depends on the rotation speed of the substrate. An increase in the substrate rotation speed decreases the thickness of the deposited film layers. The results of X-ray phase analysis of the deposited composite NaCl-Fe films reveal that Fe in the form of magnetite oxide Fe_3O_4 ($\text{FeO}\cdot\text{Fe}_2\text{O}_3$) is included in the NaCl matrix. The size of the obtained Fe_3O_4 crystallites in the analyzed composite NaCl-Fe films, obtained on a rotating substrate for an Fe content of 16.4-19.0%, does not change with the thickness of the Fe layers and is 8 ± 1 nm. The presented results of experimental studies demonstrate the effective application of EB-PVD for obtaining various composite nanomaterials on rotating substrates.

Keywords: Nanomaterial, EB-PVD, Structure, Rotating substrate.

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1. INTRODUCTION

The method of electron-beam physical evaporation of various materials in vacuum with subsequent vapor deposition on a substrate (EB-PVD) has capabilities to construct new materials in the form of thick films (up to 1 mm and higher), possesses high productivity and is capable of obtaining metal nanoparticles in different matrixes [1, 2, 5-7].

Microporous sodium chloride (NaCl) formed by EB-PVD is often used as a matrix for dispersed metal phase containment. The pressure of NaCl vapor allows its simultaneous deposition even with refractory materials. Such composites are promising for the production of various drugs due to their biocompatibility, minimal toxicity, and good solubility in water [1, 2].

The properties of Fe nanoparticles differ from those of macrocrystalline Fe. The melting point, electrical conductivity and energy of electron activation transitions – all depend on the size of Fe particles. The final size of the obtained Fe nanoparticles is also associated with their oxidation [3].

NaCl-Fe materials with nanoparticles of Fe_3O_4 ($\text{FeO}\cdot\text{Fe}_2\text{O}_3$), Fe_2O_3 oxides in a microporous matrix of NaCl show high efficiency in practical applications. For example, in medicine for targeted drug delivery and treatment of blood diseases.

The experimental data [1-3] confirm the possibility

of obtaining NaCl-Fe materials by EB-PVD on stationary substrates. The geometrical arrangement of the stationary substrates with respect to the vapor sources leads to the formation of a gradient elemental composition of NaCl-Fe films, increases the heterogeneity of their structure and limits the productivity of the deposition process.

The use of rotating substrates for the production of nanosized porous materials and metal nanoparticles is more promising, productive and technological. The rotation of the substrate changes the "shadowing" mechanism because it changes the angle of encounter of vapor and the deposition surface, which determines the formation of pores with micro- and nano-dimensions. The effect of "shadowing" is enhanced if the angle of vapor with the deposition surface is less than 90° , while the formation of the matrix phase affects the process of nucleation and growth of the second phase particles on the substrate surface [4, 5].

The goal of the present work was to study the technological aspects of production of nanostructured NaCl-Fe materials (thick films) by EB-PVD on rotating substrates, their structure and some properties.

2. EXPERIMENTAL

Ingots of NaCl tablets and Fe were used for evaporation. NaCl tablets were prepared from 99.9% pure

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sodium chloride powder by pressing. Fe ingots for the experiments were obtained by double electron beam melting of 99.8 % pure iron.

The technological setup for the deposition of composite NaCl-Fe materials (thick films) on a rotating substrate is presented in Fig. 1.

The surface of the evaporated Fe ingot, located in the water-cooled copper crucible, was heated by an electron beam (EB) gun. In case of NaCl, a graphite disk with a complex of vapor channels placed on the crucible with a NaCl tablet was heated by an EB-gun [2]. The deposition of NaCl vapor was oriented by the inclination of vapor channels to the middle of the radius (110 ± 10 mm) of the rotating substrate ($V_s = 1 \text{ rpm}^{-1}$). The system of channels in the reactor at an angle of 30° to the normal to the horizon prevents the direct contact of the electron beam with the surface of the NaCl tablet when the disk is heated, providing vapor to the substrate.

The resulting vapors are condensed on the rotating substrate with a diameter of 400 mm located above the crucibles. The vacuum level in the process chamber during evaporation was $(1-2) \cdot 10^{-2}$ Pa. The substrate temperature of $50-70^\circ \text{C}$ was measured by thermocouples. The distance between the crucibles and the substrate was 230 mm, the distance between the axes of the crucibles was 115 mm. One composite NaCl-Fe composite layer with a total thickness H , μm consisting of NaCl and Fe enriched layers is deposited during one rotation period of the substrate over the mixed vapor. The speed of substrate rotation V_s was varied within 1, 2, 5, 20 and 25 rpm^{-1} .

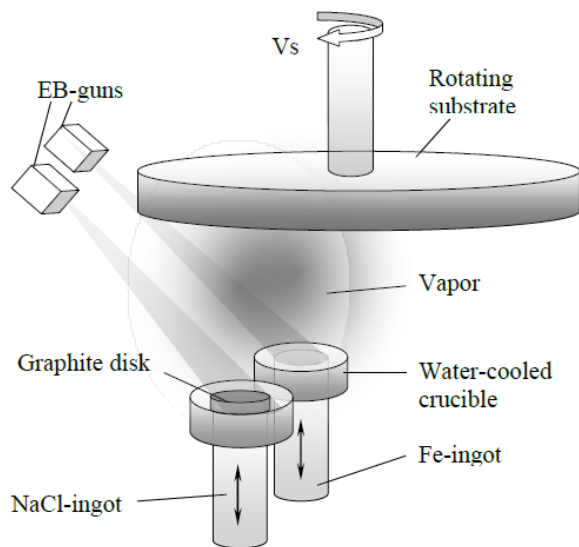


Fig. 1 – Setup for the deposition of composite NaCl-Fe films on a rotating substrate

The concentration of Fe in the obtained films varied from 11 to 35 at. %. The thickness of the NaCl, h_{NaCl} , and Fe enriched, h_{Fe} , layers in the composite varied from 0.56 to 1.43 μm and from 0.11 to 0.64 μm , respectively, see Table 2. The thickness of the composite layers and the concentration of Fe in the film were adjusted by the speed of substrate rotation and material evaporation intensity. The vapor deposition speed (V_k) was $6-9 \mu\text{m} \cdot \text{min}^{-1}$, the total thickness of the obtained

films was 80-400 μm .

The microstructure of the deposited films was studied on cross-sections by SEM. Energy dispersive X-ray analysis was used to determine the elemental composition of NaCl-Fe films. X-ray phase analysis of NaCl-Fe films was carried out in filtered ($\text{Co-K}\alpha$) radiation with the Bragg-Brentano geometry in the angular range $10-85^\circ$. The average crystallite size was estimated by the Scherrer equation. Semi-quantitative phase analysis of the diffraction of the samples was completed using the Match program.

3. RESULTS AND DISCUSSION

For effective application of EB-PVD to a rotating substrate, geometry arrangement of the crucibles and the rotating substrate should be considered. To assess the influence of the geometrical parameters of the arrangement of vapor sources on the distribution of the thickness of the resulting film along the substrate radius R_s (from the axis of rotation to the edge of the substrate), NaCl and Fe films were first deposited separately and their thickness distributions along the radius were measured.

NaCl films were obtained by evaporation through a graphite disk with a complex of vapor channels [2]. In this case, the direction of channels also determines the opening angle of vapor spreading. The electron beam power W_i during the evaporation of NaCl was 1.8 kW. A constant evaporation rate of the source material was ensured by its constant supply of $1.7 \text{ g} \cdot \text{min}^{-1}$. The evaporation time amounted to 15 min. The distribution of the NaCl film thickness over the radius of the rotating substrate is shown in Fig. 2.

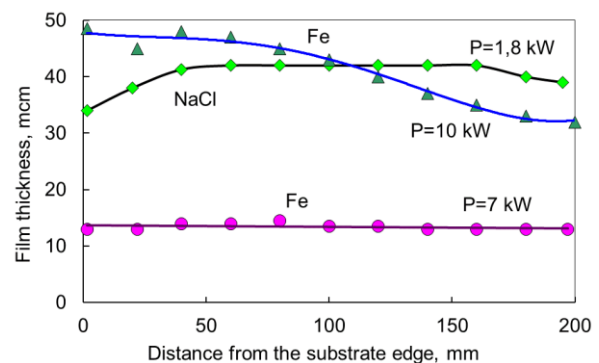


Fig. 2 – The thickness distribution for Fe and NaCl films along the substrate radius (R_s)

The thickness of the NaCl layer along the radius of the substrate ranges from 37 to 41 μm , i.e., its uniformity deviation is $\pm 5\%$. This confirms the effectiveness of the inclined orientation of the graphite disk vapor channels towards the rotating substrate that ensures uniform deposition of the NaCl vapor.

Fe films were obtained by evaporation from another crucible located near NaCl crucible. Fe vapor was oriented directly to the edge of the rotating substrate by geometrical positioning of the crucible (Fig. 1). It is known that the area of effective use of the metal vapor is limited by a cone with an apex angle of 60° [6]. This positioning of the crucible relative to the substrate also changed the angle of encounter of Fe vapor with the

deposition surface in order to enhance the "shadowing" effect during the formation of micropores.

The Fe film was obtained in a 30 min technological process at an electron beam power $W_1 = 7.0$ kW. The Fe film thickness 14 ± 1 μm was practically uniform along the radius of the rotating substrate ($V_s = 1$ rpm $^{-1}$), Fig. 2. Using the discussed deposition rates of NaCl and Fe, composite films with a maximum Fe content of up to 14 % were obtained.

To increase the Fe concentration in the composite NaCl-Fe film and the overall productivity of the process, the electron beam power (and the corresponding Fe evaporation rate) was raised to 10 kW ($V_s = 2$ rpm $^{-1}$). In the high-intensity vapor region, the rate of Fe deposition increased from 0.47 to 1.5 $\mu\text{m}\cdot\text{min}^{-1}$. It was experimentally determined that at an electron beam power $W = 10$ kW in a 30 min technological process, the thickness of the Fe film from the edge to the middle of the substrate radius increased by 30 % to 45 ± 1 μm and decreased to 33 μm closer to the axis of rotation.

Studies of the conditions of Fe vapor deposition on a rotating substrate revealed that the structure of a film is largely determined by the temperature of the substrate surface and depends both on the technological setup geometry and on the parameters of the technological process. A decrease in the distance between the evaporation surface of melted Fe with a temperature above 2000 $^{\circ}\text{C}$ and the rotating substrate from 400 to 230 mm leads to an increase in the substrate temperature from 40-45 $^{\circ}\text{C}$ in case of a stationary one to 55-70 $^{\circ}\text{C}$ in case of a rotating substrate. It is confirmed by theoretical and experimental studies by authors [7].

Table 1 – Speed of rotation along the substrate radius

V_s , rpm $^{-1}$	Substrate radius R_s , m		
	0.20	0.14	0.02
	Fe content, at. %		
2	16.2	19.2	20.9
5	27.9	31.8	31.7
20	14.1	12.7	16.4
25	21.1	22.7	22.4

The relatively uniform thickness of Fe films along the radius of the substrate can be explained by different linear velocities of different substrate deposition regions (Table 1). Substrate points located at different radii from the axis of rotation have the same angular velocities, periods and frequencies, but different linear speeds. The farther a point is from the axis of rotation, the faster it moves above the Fe vapor. Wherein the substrate region distant from the rotation axis moves with a linear velocity of 0.05 m·s $^{-1}$, the linear velocity of the substrate region near the rotation axis is 0.005 m·s $^{-1}$, i.e., its periodic presence in Fe vapor is an order of magnitude less. This results in a uniform thickness of the film.

Thus, composite NaCl-Fe films with a uniform Fe layer thickness and a maximum Fe content of up to 35 % were deposited ($W_1 = 10$ kW, Fig. 2). The productivity of the synthesis of composite NaCl-Fe films was tripled because of the stable metal phase content and an increase in the film thicknesses.

By adjusting the rate of evaporation and deposition of Fe vapor on a rotating substrate at $V_s = 25$ rpm $^{-1}$, composite NaCl-Fe films of relatively uniform thickness were obtained (Fig. 3a). Thus, the technological parameters of the formation of composite NaCl-Fe films of uniform thickness with different contents of the metal phase on a rotating substrate were determined.

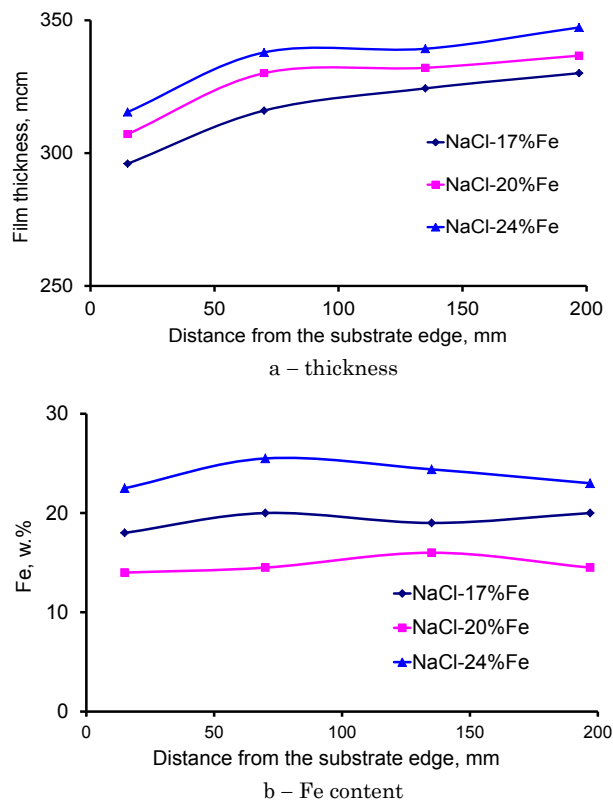


Fig. 3 – The total thickness (a) and Fe content (b) of composite NaCl-Fe films along the radius (R_s) of the rotating substrate ($V_s = 25$ rpm $^{-1}$)

The specified ratio of NaCl and Fe vapor orientation towards the rotating substrate made it possible to obtain high-quality NaCl-Fe materials with a stable Fe content within ± 5 % along the radius of the substrate (see Fig. 3b).

The dependences of the O/Fe ratio in NaCl-Fe composites along the radius of the rotating substrate ($V_s = 2, 20, 25$ rpm $^{-1}$), depending on the Fe content, as one of the characteristics of nanostructured NaCl-Fe films, is shown in Fig. 4. It is revealed that the O/Fe atomic content ratio depends on the amount of Fe and decreases with an increase in its content in the film.

High activity of composite NaCl-Fe films to oxygen can be explained by the presence of small size Fe nanoparticles in Fe enriched layers with high surface and chemical activity [8].

It was revealed that the size of the metal phase crystallites slightly increases with Fe content in the film (Fig. 5). The average size of Fe_3O_4 crystallites obtained on a rotating substrate is 60 % higher than on a stationary substrate. X-ray phase analysis of composite NaCl-Fe films revealed that sizes of Fe_3O_4 crystallites obtained on a rotating substrate are 7-9 nm, while on a

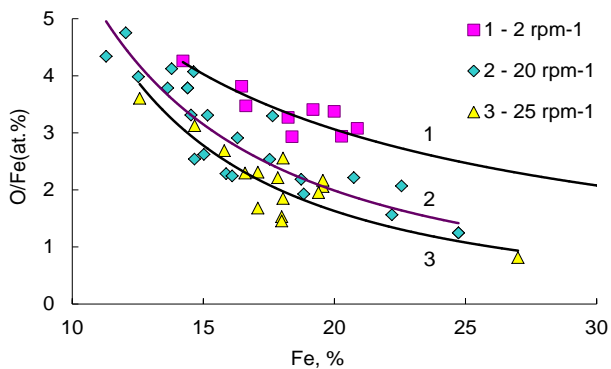


Fig. 4 – The O/Fe ratio (at. %) of composite NaCl-Fe films on the Fe content, at. %

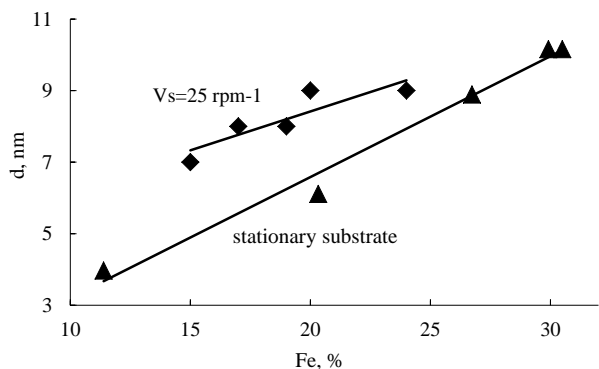


Fig. 5 – The average size of Fe₃O₄ crystallites in composite NaCl-Fe films on the Fe content, at. %

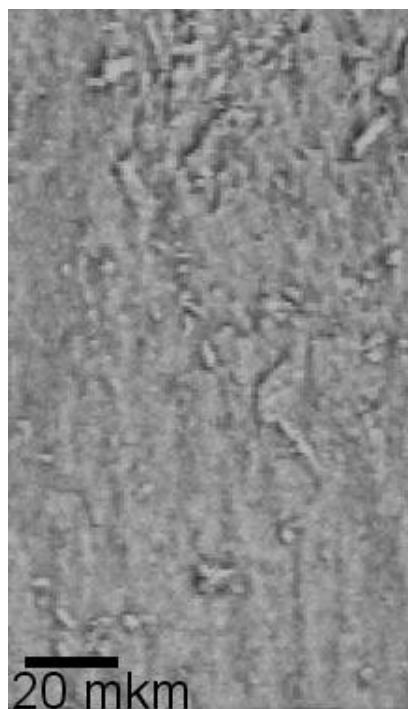
stationary substrate they are 4-10 nm. The average increase in the crystallite size is due to an increase in temperature on the deposition surface of the rotating substrate, measured at 50-70 °C in comparison with 40-45 °C of the stationary substrate. The study of the technological aspects of evaporation and deposition of Fe and NaCl vapors formed from separate sources made it possible to draw the following conclusions:

- composite NaCl-Fe films with uniform thickness can be deposited by EB-PVD on rotating substrates. It is possible to control the elemental composition (components ratio) along the radius of the substrate within ± 5 %;
- arranged geometry of a rotating substrate relative to vapor sources allows to obtain homogeneous composite materials (thick films over 300-400 μm) and triple productivity of their production by increasing the evaporation/deposition rate of raw materials and the deposition area of vapors.

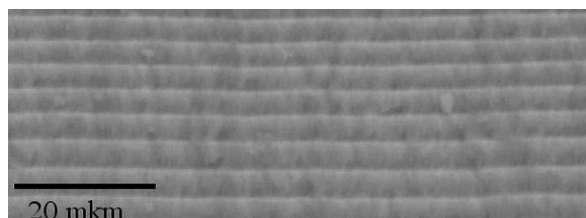
It was revealed that the structure and properties of the deposited films are determined by two main factors: the thickness of the layers and the content of the metal phase. The microstructure of composite NaCl-Fe films obtained on stationary (a) and rotating (b) substrates at a deposition temperature of 50-70 °C are shown in Fig. 6. The deposition temperature corresponds to the first structural zone $T_1 \leq 0.3T_{melt}$ NaCl and Fe [2].

The structure of composite NaCl-Fe films deposited on a stationary substrate is a microporous matrix, consisting of randomly oriented crystallites (Fig. 6a).

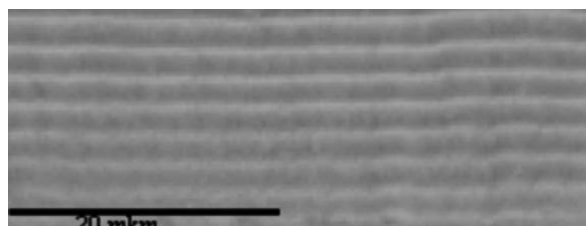
The structure of composite NaCl-Fe films obtained on a rotating substrate (Fig. 6b) represents NaCl and Fe enriched alternating layers with thickness (H , μm)



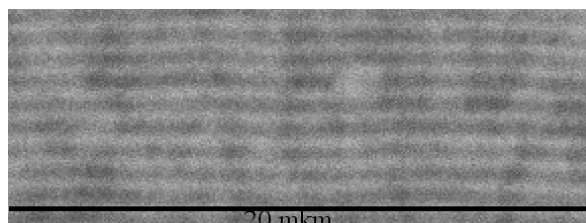
a – stationary substrate



V_s = 2 rpm⁻¹



V_s = 5 rpm⁻¹



V_s = 20 rpm⁻¹

b – rotating substrate

Fig. 6 – Microstructure of cross-sections of composite NaCl-Fe films obtained on stationary (a) and rotating (b) substrates

depending on the substrate rotation speed. A qualitative analysis of the microstructure indicates that an increase in the substrate rotation speed leads to a decrease in the thickness of the constituting layers of composite NaCl-Fe films.

Parameters of the layers of composite NaCl-Fe films deposited at different substrate rotation speeds are shown in Table 2. At the substrate rotation speed $V_s = 2 \text{ rpm}^{-1}$ the thickness of NaCl enriched layers is $3.25 \mu\text{m}$, while the thickness of Fe enriched layers is $0.64 \mu\text{m}$. The maximum average size of NaCl crystallites in the layers is about 45 nm . The maximum size of NaCl crystallites deposited on a stationary substrate at $50 \text{ }^\circ\text{C}$ is 57 nm [2].

An increase in the rotation speed of the substrate to 25 rpm^{-1} expectedly reduces the thickness of composite layers: NaCl enriched layers to $0.46 \mu\text{m}$, while Fe enriched layers to $0.09 \mu\text{m}$ (90 nm). The ratio of the thickness of NaCl and Fe enriched layers of the studied composite multilayer NaCl-Fe films remains constant at 0.2 .

Such a reduction in the thickness of NaCl and Fe enriched layers of the composite NaCl-Fe film fully corresponds to the full period of substrate rotation in vapor (Table 2).

Table 2 – Characteristics of composite NaCl-Fe films

V_s , rpm^{-1}	t_{exp} , min	Number of layers, N	H , μm	h_{NaCl} , μm	h_{Fe} , μm	$h_{\text{Fe}}/$ h_{NaCl}
2	11	24	3.89	3.25	0.64	0.2
5	2	10	1.77	1.43	0.34	0.2
20	13	260	0.68	0.56	0.12	0.2
20	20	400	0.63	0.52	0.11	0.2
25	20	500	0.55	0.46	0.09	0.2

Table 3 – Phase composition and average size of crystallite (d) of composite NaCl-Fe films

Fe, at. %	V_s , rpm^{-1}	Thickness of layers, μm		Phase characteristics	
		h_{NaCl}	h_{Fe}	Phase composition	Average size of crystallites (d), nm
16.4	25	0.46	0.09	NaCl/Fe ₃ O ₄	27/7
16.5	2	3.25	0.64	NaCl/Fe ₃ O ₄	45/8
17.5	20	0.52	0.11	NaCl/Fe ₃ O ₄	29/8
17.6	20	0.56	0.12	NaCl/Fe ₃ O ₄	34/8
19.0	5	1.43	0.34	NaCl/Fe ₃ O ₄	29/9

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The phase composition, the thickness of NaCl and Fe enriched layers and the corresponding crystallite sizes of composite NaCl-Fe films obtained on a substrate with different rotation speeds are shown in Table 3.

X-ray phase analysis of composite NaCl-Fe films revealed that Fe is contained in the oxide form Fe₃O₄ in the NaCl matrix. The size of Fe₃O₄ crystallites in composite NaCl-16.4-19 % Fe films deposited on a rotating substrate does not correlate with the thickness of Fe enriched layers and is around $8 \pm 1 \text{ nm}$.

The study of the elemental composition of cross-section samples of NaCl-Fe films revealed the presence of oxygen, which presumably interacts with Fe during depressurization of the vacuum chamber after the completion of film deposition.

The ratio of the atomic content of oxygen to Fe depends on the amount of Fe and decreases with an increase in Fe and an increase in the rotation speed of the substrate (Fig. 5), which is the result of intensive oxidation of highly active Fe enriched layers.

Oxidation of Fe to Fe₃O₄ occurs during depressurization of the vacuum chamber and during the process of film separation from the substrate in air. Its integrity is violated, so the oxidation of Fe enriched layers is accelerated. When Fe interacts with oxygen, an exothermic reaction occurs with intense heat release. In some compositions, the measured temperature rise of the films separated from the substrate reaches $100 \text{ }^\circ\text{C}$ and above.

The presented results of experimental studies demonstrate the possibility of effective application of the physical processes of evaporation and deposition of various substances on a rotating substrate in vacuum to obtain nanoscale materials.

4. CONCLUSIONS

A new efficient technological method of deposition of thick (up to $400 \mu\text{m}$) nanocomposite NaCl-Fe films by EB-PVD on a rotating substrate is proposed. Fe content is stable within $\pm 5 \%$ along the radius of the substrate and can be adjusted technologically.

Consistent patterns of change in the structural characteristics (including the thickness of NaCl and Fe enriched layers, as well as the metal phase content with the corresponding size of layer constituting crystallites) of nanocomposite NaCl-Fe films relating to the arranged geometry of the technological setup and the rotation speed of the substrate are experimentally determined.

Практичні аспекти отримання наноструктурних композитних NaCl-Fe плівок способом EB-PVD на підкладках, що обертаються

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Метод EB-PVD поєднує можливості інтенсивного керованого випаровування різноманітних матеріалів у вакуумі з наступною конденсацією отриманого парового потоку на охолоджуваній підкладці/виробі та характеризується широкими можливостями використання різноманітних технологічних схем, а також контролю та автоматизації параметрів проведення даного технологічного процесу. У роботі розглянуто деякі особливості використання технологічної схеми проведення EB-PVD процесу з периферичним відносно осі обертання підкладки розташуванням джерел випаровуваних матеріалів для отримання композиційних матеріалів NaCl-Fe, перспективних для застосування у медицині. Використання шайби з комплексом похилих парових каналів при випаровуванні NaCl забезпечило рівномірність розподілу товщини отримуваних плівок NaCl по радіусу підкладки з діаметром 400 мм, що обертається, із середнім відхиленням не більше $\pm 5\%$. Розглянуте у роботі геометричне співвідношення напрямленостей парових потоків випаровуваних матеріалів на підкладці, що обертається, дозволило отримати якісні композиційні матеріали NaCl-Fe з відхиленням концентрації металеві складової, що не перевищує 8-10%. Периферійне розташування джерел пари дозволило зменшити відстань між джерелами випаровуваних матеріалів та поверхнею осадження основи до 230 мм. Таким чином досягнуто збільшення товщини плівки до 300-400 мкм. Структура композиційних плівок NaCl-Fe, отриманих методом EB-PVD на обертовій підкладці, представляє собою чергування збагачених NaCl та Fe шарів різної товщини, яка залежить від швидкості обертання підкладки. Із збільшенням швидкості обертання підкладки відзначається зменшення загальної товщини одиничного композиту NaCl-Fe. Результати рентгенофазового аналізу отриманих композитів NaCl-Fe виявили, що залізо перебуває у вигляді оксиду – магнетиту Fe_3O_4 ($\text{FeO}\cdot\text{Fe}_2\text{O}_3$) у матриці NaCl. При цьому розмір кристалітів Fe_3O_4 в плівках NaCl-16,4-19,0% Fe не змінюється з товщиною збагачених Fe шарів та становить 8 ± 1 нм. Наведені у роботі результати експериментальних досліджень підтверджують можливість ефективного використання фізичних процесів випаровування та конденсації на підкладках, що обертаються, різних матеріалів у вакуумі для отримання нанорозмірних матеріалів.

Ключові слова: Електронно-променеве осадження, Наноматеріал, Структура, Підкладка, що обертається.