ABSTRACT

of dissertation paper for the degree of Phylosophic Doctor (PhD) in the educational programme 8D05302 - Technical Physics

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«Modified composite films based on CuBi/$CuBi_2O_4$ as protective shielding materials»

General description of the paper

The dissertation covers the process of production of modified **CuBi/$CuBi_2O_4$** composite films by partial substitution of copper with cobalt or nickel and the study of their properties. The paper outlines the performed experiments and their analysis. Furthermore, it evaluates the applicability of the films used as protective materials against ionising radiation.

Rationale

In the last few years, more and more attention has been paid to the problem of protection against negative impact of ionising radiation, in particular X-ray and gamma radiation, which has a high penetrating ability, unlike heavy ions. The creation of protective shielding materials of new generation is due to a great pace of development of technologies that utilize sources of ionising radiation (generating type) very often now, as well as by the development of equipment designed for the use in the space whereas it is exposed to direct impact of ionising and electromagnetic radiation. At the same time, the nature of interaction of X-ray and gamma radiation with materials and living organisms that is based on ionisation processes may result in negative consequences. Prolonged exposure of living organisms to ionising radiation results in DNA mutations, causing formation of cancer cells or tumours, which can be fatal. Ionising radiation generated by microelectronic devices can lead to equipment failure or malfunction through electrical breakdowns or failure of transmitting or coupling electronic assemblies that is induced by radiation damage. Nowadays, the problem of protection against ionising radiation becomes urgent year after year due to the expanding range of applications of various types of ionising radiation in everyday life, as well as the increase in the number of radiation generating facilities used for medical purposes and within the energy sector, etc. In most cases, use of ionising radiation sources, including electromagnetic radiation, also has direct or indirect impact on living organisms, which in turn requires compliance with safety rules and regulations for operation of ionising radiation sources as well as reduction of the time of interaction with them which is impossible in some cases.

In this connection, large resources of leading scientific organisations all over the world are directed to search for new ways of protection from negative impact of ionising radiation. Creation of protective materials aimed to reduce negative impact of ionising radiation is based on the key principles of “As Low As Reasonably Achievable” (ALARA) principle adopted by the International Commission on Radiological Protection. It is generally aimed to minimise the negative impact of radiation and various types of ionising radiation. The concept is based on the principle of reducing the impact of ionising radiation by any possible means, as well as possibility of optimising protection with the use of various types of protective materials. While searching for new types of protective materials, great attention is paid to various composite films that contain various elements, including light elements, heavy or rare earth elements, as well as their mixed compositions. Interest in these materials is due to the possibility of combining the composition of resulting films, allowing to increase the shielding efficiency due to differences in absorption capacity of various elements, as well as possibility of variation of film thicknesses by changing the conditions of their production. The use of various polymeric materials, in particular polyimide and polycarbonate films as substrates that have good flexibility and heat resistance to heat, allows to create protective composites with good flexibility. These provide possibilities for covering complex-profile surfaces that are typical for a large number of microelectronic devices with such protective materials.

According to the previous studies, it was established that composites containing copper and copper oxides, despite high shielding efficiency, have rather low corrosion resistance when interacting with aggressive media. In this connection, one of the solutions to the said corrosion problem is the addition of nickel or cobalt to $CuBi/CuBi_2O_4$. It partially substitutes copper in the sites of the lattice and increases the resistance to corrosion degradation of composites. The formation of substitution or introduction phases contributes to an increase in oxidation resistance by reducing the penetration of oxygen into the near-surface layer of the composite film. This way it reduces the rate of formation of oxide inclusions, leading to strength loss of the coatings and their destruction. At the same time, the change in elemental composition of the films at partial replacement of copper or bismuth with nickel or cobalt may lead to a change in the structural and strength features, which further have a positive effect on resistance of the films to external influences, including corrosion or aging.

The purpose of the paper is to develop a technology for production of composite films based on compounds of copper, bismuth, nickel, cobalt and their oxides, as well as for evaluation of their application as shielding materials used against the negative effects of ionising radiation.

In order to achieve the aforesaid goal, the following **objectives** have been formulated:

1. Study of formation of composite films based on $CuBi/CuBi_2O_4$ compounds with partial substitution of copper by nickel or cobalt in the electrolyte solution.

2. Study of phase composition, structural and strength properties of $CuBi/CuBi_2O_4$ composite films depending on the variation of production conditions and substitution of copper with nickel or cobalt.

3. Study of influence of the phase composition of produced films on corrosion resistance to aggressive media.

4. Assessment of prospects of application of produced composite films as shielding materials for protection against X-ray and gamma radiation.

The main points of the paper to be defended:

1. It was established that addition of cobalt sulfate or nickel sulfate to the electrolytes solutions in the percentage of at least 15 % results in formation of a well-structured phase of tetragonal $CuBi_2O_4$ with spinel structure.

2. It was established that partial substitution of copper with cobalt or nickel in CuBi2O4 films causes an increase in hardness from 20% to 80% when compared to $CuBi/CuBi_2O_4$ films; tear and wear resistance also increased in tribological tests.

3. It was established that the substitution of copper with cobalt or nickel in $CuBi_2O_4$ films leads to an increase in resistance to corrosion within aggressive

environment as well as to preservation of stability of strength features by more than 2.0 - 2.5 times in comparison with Cu, Cu(Bi), $CuBi_2O_4$ films.

4. It was established that formation of films with tetragonal phase of $CuBi_2O_4$ with content of cobalt and nickel of about 15 - 20 at. % in the composition at a film thickness of about 10 μm allows shielding of X-ray radiation with a wavelength of 1.54 Å with efficiency of about 90 - 95 %.

Scientific novelty of research works conducted within the framework of the dissertation is as follows:

1. The developed technology for production of $CuBi/CuBi_2O_4$ composite films with partial substitution of copper with nickel or cobalt provides possibilities for making protective films with high flexibility and use them for protection of complex materials exposed to ionising radiation.

2. The results of study of phase composition, mechanical and strength properties of the obtained $CuBi/CuBi_2O_4$ composite films depending on synthesis conditions, variation of difference of applied potentials, and electrolyte solutions, have shown the promising use of the electrochemical deposition method for obtaining flexible films with high strength properties.

3. The achieved results on increased resistance to degradation and oxidation during corrosion tests due to substitution of copper with nickel and cobalt show prospects and possibilities for the use of composite films under the conditions of exposure to aggressive environments during long-term operation.

4. The results of studies on evaluation of the future perspectives of the obtained $CuBi/CuBi_2O_4$ composite films used as shielding materials showed that the substitution of copper for nickel or cobalt leads to increased shielding efficiency and decreased intensity of X-ray and gamma radiation when compared with unmodified films (by 1.5 - 2 times).

CuBi/CuBi2O4 composite films with copper substitution by nickel or cobalt were chosen as the **object of research**. They have great prospects for their use as protective materials for shielding the negative impact of ionising radiation, in particular, X-rays and gamma radiation that have high penetrating ability. Electrochemical deposition method was selected as the main one for obtaining composite films due to its ability to vary the phase composition and mechanical characteristics of films by changing the conditions of synthesis, as well as the variation of electrolytes solutions used for deposition of films. Substitution of copper with nickel or cobalt in the composition of films is due to possibilities of increasing mechanical strength, as well as resistance to corrosion degradation and oxidation in the process of interaction with various media.

The subject of the research is to conduct systematic study aimed at gaining new data on the properties of $CuBi/CuBi_2O_4$ composite films with partial substitution of copper by nickel or cobalt, used for protection from negative impact of ionising radiation by reducing its intensity during shielding. The established dependences of corrosion resistance and biocompatibility of obtained $CuBi/CuBi_2O_4$ composite films with partial copper substitution by nickel or cobalt allowed estimation of the area of effective practical application. Within the framework of the thesis research Comparative analysis of shielding efficiency of various types of ionising radiation with the use of obtained $CuBi/CuBi_2O_4$ composite films with partial copper substitution by nickel or cobalt was carried out with other types of shielding materials as part of the thesis research.

Research methods

Assessment of structural features of synthesised composite films under variation of synthesis conditions and electrolyte solutions was carried out using the method of X-ray phase analysis. Its use allowed determination of phase composition of the films and changes in the structural characteristics. Determination of morphological features of obtained films was carried out with the use of method of atomic force microscopy, by constructing 3D images of the surface of the samples depending on the conditions of the production. Determination of influence of changing the synthesis conditions on stoichiometric ratio of elements was carried out by evaluating elemental composition with the use of energy-dispersion analysis. The strength features of synthesised films were determined by indentation and dry friction coefficient determination. Corrosion resistance was assessed by evaluating changes in the degree of structural ordering (degree of crystallinity) of samples after exposure to aggressive media, as well as by changing the strength features of the films before and after exposure to aggressive media. Determination of gamma and X-ray radiation shielding efficiency was carried out by carrying out full-scale experiments with ionising radiation sources, as well as by detecting changes in radiation intensity before and after the use of shielding materials.

Practical significance of the paper

The technology of obtaining $CuBi/CuBi_2O_4$ composite films when copper is replaced by nickel or cobalt with the possibility of variation of phase composition, structural and strength properties has been developed.

The proposed technology of increased resistance of composite $CuBi/CuBi_2O_4$ films due to partial substitution of copper with nickel or cobalt in the composition to degradation under the influence of aggressive media in various operating conditions may further be used for development of protective anticorrosion coatings for complex devices that operate under aggressive conditions.

The obtained results of tribological tests of synthesised $CuBi/CuBi_2O_4$ films showed that partial substitution of copper with cobalt/nickel sulphate electrolytes to the composition leads to an increase in wear resistance, as well as to an increase in strength features. It further makes it possible to create high-strength wear-resistant coatings that are able to withstand heavy mechanical loads for a long time of exposure.

The results of corrosion tests of $CuBi/CuBi_2O_4$ films that depended on the temperature of the aggressive medium can be further used to extend the general theory of corrosion of thin-film materials and as a basis for design of protective coatings based on such films.

The results of evaluation of prospects of application of synthesised $CuBi/CuBi_2O_4$ films as protective shielding materials for gamma radiation and X-ray radiation can be further used for development of flexible protective films for protection of the most vulnerable parts or in creation of filters used for reduction of power X-ray radiation power.

Personal contribution of the candidate. The candidate carried out experimental works on development of modes for obtaining thin $CuBi/CuBi_2O_4$ films with the use of different types of electrolyte solutions during electrochemical synthesis, as well as characterisation of obtained results and their interpretation. Setting the goal and objectives of the dissertation research, as well as determining the vector of development of experimental works, taking into account a priori information about the properties of the selected objects for research and the primary results of shielding efficiency evaluation was carried out by the candidate in coordination with local and foreign scientific supervisors. Characterisation of samples obtained in the course of electrochemical synthesis was carried out jointly with the employees of the Laboratory of Solid State Physics, Astana Branch of the Institute of Nuclear Physics of the Ministry of Energy of the Republic of Kazakhstan. The works related to experiments to determine the effectiveness of shielding of ionising radiation were carried out by the candidate at the Laboratory of Solid State Physics, Astana Branch of the Institute of Nuclear Physics of the Ministry of Energy of the Republic of Kazakhstan.

Reliability of obtained results

The main results of the dissertation research were approved at international scientific conferences and scientific schools in the form of scientific reports.

Reliability of obtained results was proved by the use of verified and certified high-precision analytical equipment. All experimental works were performed in several stages in order to eliminate errors or methodological inaccuracies, as well as to determine standard deviation and measurement errors. Experiments related to determination of gamma and X-ray radiation shielding efficiency were carried out in compliance with the required regulations applied for the work with ionising radiation sources (including generating ones). Registration of radiation intensity was performed with the use of high-precision detection systems. The sources of ionising radiation were placed in special lead containers having holes with diameter of about 10 mm. The intensity of gamma quanta from the emitted sources was recorded through such holes.

Evaluation of the dissertation work was carried out by delivery of scientific reports at the following international scientific conferences:

1. X International Scientific Conference “ACTUAL PROBLEMS OF SOLID STATE PHYSICS”, 22-26 May, 2023. City of Minsk, Belarus.
2. 52nd International Tulinov Conference ON PHYSICS OF CHARGED-PARTICLES INTERACTION WITH CRYSTALS (City of Moscow, Russia).

Publications

7 printed works were published based on the results covered in the dissertation paper. These included 2 peer-reviewed scientific publications in the Republic of Kazakhstan recommended by Science and Higher Education Quality Assurance Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan, 2 publications in journals reviewed in Web of Science and Scopus databases, 2 publications in collections of international conferences, 1 copyright certificate.

Structure and scope of the thesis work

The dissertation is printed on 100 pages. These include 56 figures, 4 tables and 112 literature sources. The dissertation paper consists of the following: introduction that includes the relevance and novelty of the research and formulation of the main goal and objectives; four chapters that include literature review on the subject of the research, the description of methods used for production and characterisation of thin films, and main experimental works related to the study of influence of the change in variation of electrolyte compositions on production of synthesised thin films, their strength properties, and results of shielding of ionising radiation (gamma and electron radiation); conclusion that includes brief summary of performed works and also formulated findings about the research conducted.