The use of magnetron sputtering to synthesis boride neutrons-absorbing coatings

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Abstract. The paper describes the development of methods for the synthesis of a neutron-absorbing coating based on the B-Ti system. It is shown that this approach can significantly reduce the thickness of the coating with a satisfactory value of the neutron absorption coefficient. The optimal modes of coating synthesis by DC-magnetron sputtering are determined.

1. Introduction

For countries with a developing nuclear industry, the solution of problems of safe management of spent nuclear fuel and radioactive waste is a priority. To date, the volumes of accumulated radioactive waste and the predictions of their growth require an increase in the level of organization of the management of radioactive waste and SNF. Depending on the degree of burnout, SNF may contain a significant amount of fissile materials. SNF is a source of neutron radiation, which can, with compacted storage, lead to the regeneration of part of the fuel and, as a consequence, an increase in total activity. It is possible to reduce the number of neutrons in a material using neutron-absorbing materials in the manufacture of transport packaging containers and hexahedral canister tubes for compacted storage of spent nuclear fuel in holding pools [1–3]. These materials must have an adequate margin of safety, corrosion and radiation resistance, the design must be technologically advanced in the manufacture and handling of low weight and overall dimensions. Optimization of the required characteristics develops in two directions: the creation of new structural steels and alloys doped with neutron-absorbing elements, and the creation of strengthening neutron-absorbing coatings [4–6]. The cost of doping increases. This makes it preferable to obtain the required performance characteristics in a more economical way. The idea of the research is a composite of a neutron-absorbing high-performance coating by DC magnetron sputtering. Considered as candidate material $^{11}$B – it has the largest thermal neutron absorption cross section and therefore it was supposed to synthesize titanium boride, the most common and studied compound of which is TiB$_2$. The fundamental difference between the proposed technology and existing methods of powder-plasma deposition is due to the fact that the density of boron distribution doesn’t depend on the distribution density of powder granules and the distance between them (about 100 nanometers), but on the interatomic distance of the resulting compound (several angstroms). This approach will allow to achieve an increase in neutron-absorbing characteristics while reducing the thickness of the coatings. Magnetron sputtering will allow to...
achieve better adhesion of coatings without changing the structure and properties of the substrate material, as well as improving the physico-mechanical characteristics.

Currently, there are methods for applying hardening coatings based on metal borides in relation to cutting tools and microelectronics [7]. As a neutron-absorbing materials, coatings based on metal borides synthesized by the magnetron method have not been previously considered. In this regard, the technology of deposition, the determination of the neutron-absorbing ability and the physical mechanical characteristics of such coatings require detailed consideration.

The main objective of magnetron coating experiments with the B-Ti system is to determine the possibility of its synthesis using a DC magnetron and determine the optimal modes of magnetron sputtering.

DC magnetrons are used to spray metals using inert gases. We have applied magnetron sputtering technology to apply neutron-absorbing coatings. The main difficulty in the implementation of this technology in relation to boron-containing coatings is that boron is a dielectric and the application of boron-containing coatings is a rather complicated task.

2. Materials and methods

Austenitic stainless steel was used as a coating substrate 12Cr18Ni9Ti. Elemental composition, according to X-ray diffraction analysis on the spectrometer S1 TITAN (Bruker AXS) and EMF analysis on a scanning electron microscope PHENOM XL (Phenom-World), presented in table 1. Samples were made in the form of a parallelepiped with dimensions of 20×2×0.3 mm³. The surface of the samples was polished, roughness is not worse than Ra = 150 nm.

| Elem. | Fe  | Cr  | Ni  | C   | Si  | Mg  | In  | Ru  | Cu  | Ti  | Mo  | V   | W   |
|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| At.%  | 71.46 | 16.88 | 8.74 | 4.23 | 1.38 | 0.49 | 0.43 | 0.38 | 0.26 | 0.14 | 0.04 | <<0.08 | <<0.08 |

In the manufacture of the cathode target for the magnetron used boron carbide B₄C. To increase the electrical conductivity, titanium was added to the target. Magnetron target was a sintered mixture of powders of B₄C and Ti with a mass ratio of 1:1. The fraction of powders from 10 to 200 microns. Obtaining a cathode target for a magnetron installation was carried out by hot pressing a mixture of powders of B₄C and Ti, in a vacuum. Compression was carried out at a load of ~ 300 MPa and a temperature of ~ 800°C. After this was carried out annealing at a temperature of 1250°C. Target diameter 40 mm, thickness 4 mm. In addition to increasing the electrical conductivity, this will eliminate the use of a second target, because in fact two targets are combined into one composite target. With simultaneous sputtering of two magnetron targets, the substrate is mounted in a holder on the lateral surface of a rotating drum, which provides alternate deposition of elements of each of the targets. Lack of rotation will reduce the synthesis time, reduce the non-target consumption of the source material and allow you to consistently receive films with a stable structure, even with repeated use of the target. This feature greatly simplifies the method of coating synthesis.

The sputtering of the target was carried out on a two-channel magnetron installation VUP-5M (DC) [8]. In the working chamber, air was pumped out using two modes: deep vacuum using a diffusion pump and low vacuum using only a foreline vacuum pump. Then plasma-forming gas – Ar, was injected; its content in the working chamber was ~ 28%. A voltage of 600 V and a current of 70 mA was applied to the cathode target. Spraying time was 30 and 60 minutes.

The elemental composition of the target was monitored using a PHENOM XL (Phenom-World) scanning electron microscope. X-ray phase analysis (XRD) was performed on a D8 ADVANCE ECO diffractometer using CuKα copper tube radiation. To identify the phases and study the crystal structure, the software BrukerAXSDIFFRAC.EVA4.2 and the international Crystallography Open Database (COD) software were used. X-ray diffractogram recording conditions: Voltage – 40 kV,
Current – 25 mA, $20 = 20–82^\circ$, step, 0.03°, time at the point – 3 seconds, nickel soller was used as an absorber.

3. Results and discussion
When using a diffusion pump, plasma formation occurs only at a pressure of ~ 0.1 Pa. This is limit of steady work of the pump. In this regard, a technological solution was found – to produce sputtering during operation of the foreline pump, which ensures operation at a pressure of $\geq 1$ Pa. In this mode the coating application was stable.

As a result, experimental samples of titanium boride Ti$_2$B$_5$ coating were synthesized. This compound, according to the state diagram of the B-Ti system, is closest in its properties and structure to TiB$_5$ [9]. Coating thickness during spraying for 30 minutes amounted to 370 nm, within 60 minutes ~ 1 $\mu$m. The boron content is ~ 70%, which exceeds the calculated values. The density of the obtained compound correlates with the calculated values (table 2). We have previously shown that increasing the density of boron in the coating can reduce the thickness of the neutron-absorbing coating to 1 $\mu$m [10], at the same time, the absorption capacity will not be lower than that of existing analogues.

Table 2. The density of the distribution of elements in the model coverage.

| Element | B | Ti | N | C |
|---------|---|----|---|---|
| Density, $\times 10^{22}$ (at.cm$^{-3}$) | 6.4484 | 2.561 | 1.598 | 0.51136 |

Table 3 shows the data of the crystallographic characteristics of the coating obtained. The results of studies of the structure and composition of the synthesized coating showed that the phase composition of the coatings obtained by magnetron sputtering is a mixture of phases consisting of 66.8% of Ti$_2$B$_5$ titanium hemipentaboride and 33.2% of titanium dodecaboride TiB$_{12}$.

The average content of boron atoms in the coating is ~ 80% at a thickness of 1 $\mu$m, the value of the neutron absorption coefficient is 1.14. This value is 2 times higher than the absorption coefficient of coatings 1 mm thick, synthesized by powder-plasma spraying.

Table 3. Data crystallographic characteristics of the coating obtained.

| Phase      | Crystal lattice parameters (Å) | Density (g.cm$^{-3}$) | Integral porosity (%) |
|------------|--------------------------------|-----------------------|-----------------------|
| $\omega$-Ti$_2$B$_5$ | $a_{exp}=3.63215$, $c_{exp}=27.41830$ | 3.971 | 0.75 |
| $\beta$-TiB$_{12}$ | $b_{exp}=12.81759$, $c_{exp}=10.16583$ | 2.703 | 1.27 |

4. Conclusion
The study of the structure of the obtained samples showed that during magnetron sputtering a composite coating was formed, consisting of two phases: the matrix – Ti$_2$B$_5$ and the phase of implantation – TiB$_{12}$. During the experiments, the optimal parameters for the synthesis of this coating were determined. It is proved that such a coating can be effectively used as a neutron-absorbing protective coating during storage of radioactive waste and SNF.

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