Synthesis of non-metallic inorganic radiation-absorbing coatings on the surface of VT1-0 titanium alloy

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Abstract. The paper is devoted to the microplasma synthesis of radiation-absorbing coatings on VT1-0 titanium alloy surface. This method allows the formation of thin nanostructured non-metallic inorganic films. The process is carried out in an electrolyte solution. Iron and cobalt compounds in forms of potassium hexacyanoferrate and cobalt (II) acetate are added to the solution in the present work. It is shown that the formed coatings have high coefficients of electromagnetic radiation absorption in the terahertz range and in the near-infrared spectrum.

1. Introduction
Radiation-absorbing (RA) materials have a wide range of applications, and the production of materials for RA coatings is one of the most relevant areas in modern material science. RA coatings are used nowadays to solve the problems of electromagnetic compatibility of radioelectronic devices, protect biological objects from electromagnetic radiation and are an instrument of reducing the radar visibility of military equipment [1-2].

It was shown recently that iron-containing oxide coatings with RA properties could be obtained by the method of valve metals surface microplasma oxidation in solutions. Even so, microplasma synthesis is rarely used for RA coatings formation nowadays [3-5].

The core of the method is electrochemical oxidation of metal surfaces under the influence of spark and arc electric discharges developing in the near-surface area. At the same time, various components can be introduced from the solution into the coating formed by this method. As a result, the coating may contain dispersed particles such as metal iron, nickel, cobalt, their oxides and other compounds with ferromagnetic properties. These particles are synthesized during the coating formation process in specific quantities in order to achieve the target magnetic properties of the coating [6-7].

The present work is devoted to the microplasma synthesis of nonmetallic inorganic RA coatings on the surface of VT1-0 titanium alloy in aqueous solutions containing iron and cobalt.

Coating composition and uniformity are important properties at the end of RA coatings synthesis. The microplasma coating formation is carried out in an electrolyte solution, and this feature allows to control and change the coating composition. Combinations of electrolytes define the element composition of the synthesized coating. It should be noted that the coatings formed in the microplasma mode have a number of valuable functional properties: wear resistance, corrosion resistance, thermal stability, etc. The gradient structure, specific porosity and thickness are also the distinctive features of the obtained coatings [8].

High-frequency radiation absorption by the coating occurs due to the superposition of alternating magnetic and electric fields. This fact causes molecular vibrations and microcurrents in the coating
that in turn leads to the energy dissipation by transferring it into the heat. Thus, the external energy is absorbed by the coating and dissipated due to either dielectric or magnetic losses. This mechanism is defined as non-resonant absorption. Non-resonant magnetic RA materials as a rule contain magnetic particles (for example, ferrite particles) as well as particles with high electrical conductivity (graphite particles, fullerenes) which are distributed in the polymeric material layer.

Analysis of the literature data shows that the currently used RA materials are formed by the distribution of a magnetically active phase in an organic polymer or an inorganic material. Therefore, the purposeful forming of this phase in the form of magnetically active particles (mixed iron oxides) in the coating layer is the primary task.

The paper [9] shows the positive effect of iron and molybdenum compounds in electrolyte solutions for RA coating microplasma synthesis. Iron and titanium mixed oxides as well as iron and cobalt mixed oxides are proposed in the present work to use as a magnetically active phase. It is known that cobalt-containing spinels have sufficiently high magnetic activity values and their formation in the coating composition can result in an increase of the coating absorption ability.

2. Materials and methods

Widely used in engineering, VT1-0 titanium alloy was chosen in the present work as the base material for the coating formation.

Alkaline solutions containing compounds of iron and cobalt (solution 1 and solution 2 respectively) were developed for the coating formation. Solution 1 included \( \text{H}_3\text{BO}_3, \text{Na}_3\text{PO}_4, \text{NaOH}, \text{Co(}\text{CH}_3\text{COO})_2, \) Trilon B, \( \text{K}_3[\text{Fe(CN)}_6] \) (5 g/l for each component). The pH value of the solution was stabilized at 8.69 by using a buffer mixture. Solution 2 included \( \text{K}_3\text{P}_2\text{O}_7 \) (10 g/l), \( (\text{NH}_4)\text{MoO}_4 \cdot 4\text{H}_2\text{O} \) (1 g/l), \( \text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O} \) (30 g/l), \( \text{K}_3[\text{Fe(CN)}_6] \) (15 g/l), \( \text{Co(}\text{CH}_3\text{COO})_2 \) (1 g/l) and \( \text{KOH} \) (1 g/l).

Compositions of these solutions were developed due to the fact that phosphorus ions supported the barrier film formation on the metal surface and also increased the electrochemical polarization and porosity of the formed film. In addition, phosphorus ions increased the hardness of the coating while being injected into it in the form of oxygen-containing ions [10].

Boric acid was introduced into the electrolyte composition in order to control the rate of the coating formation and maintain the solution pH value. High voltage and high temperatures developing in the zone of microplasma discharges led to the formation of solid and heat-resistant boron-containing oxides.

\[
\begin{align*}
4\text{H}_3\text{BO}_3 & \rightarrow \text{B}_2\text{O}_7^{2-} + 5\text{H}_2\text{O} + 2\text{H}^+, \\
\text{Na}_2\text{B}_4\text{O}_7 \rightarrow 2\text{B}_2\text{O}_3 + \text{Na}_2\text{O}, \\
\text{Na}_2\text{O} + \text{H}_2\text{O} & \rightarrow 2\text{NaOH}.
\end{align*}
\]

The presence of silicate ions in the solution composition contributed to the rapid formation of the barrier film and the emergence of silicon oxide in the coating:

\[
\begin{align*}
2\text{SiO}_3^{2-} + 4\text{H}^+ & \rightarrow \text{H}_2\text{SiO}_3, \\
\text{H}_2\text{SiO}_3 & \rightarrow \text{SiO}_2 + \text{H}_2\text{O}.
\end{align*}
\]

It should be noted that silicate-containing compounds are widely used in the microplasma oxidation process.

Potassium hexacyanoferrate and cobalt (II) acetate were used as additives responsible for the magnetically active phase formation. The advantage of using potassium hexacyanoferrate is its high water solubility as well as the presence of iron in the form of a complex anion that simplified the injection of iron into the coating composition:

\[
\begin{align*}
[\text{Fe (CN)}_6]^{3-} + 3\text{H}_2\text{O} & \rightarrow 6\text{CN}^- + \text{Fe(OH)}_3 + 3\text{H}^+, \\
\text{Fe(OH)}_3 & \rightarrow 4 \text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O}, \\
\text{Fe}_2\text{O}_3 + \text{FeO} & \rightarrow \text{Fe}_3\text{O}_4.
\end{align*}
\]
Mixed iron and titanium oxides were formed from simple iron and titanium oxides as a result of melting under the high temperature effect.

2.1. Preparation of samples
VT1-0 titanium alloy samples were cleaned from organic impurities by washing the samples in 0.5% NaOH solution at a temperature about 20-25°C.

2.2. Formation of the coatings
The processed samples served as anodes and a water-cooling stainless steel bathtub served as a cathode. The temperature in the bathtub did not exceed 40°C. The electrical impact was applied by voltage pulses with 310 V amplitude and 500 μs duration using the Corund Power Source developed by Sibspark LLC. The coating formation process lasted for 30 minutes. The formed coatings were uniformly dark gray, almost black, rather dense and had sufficient adhesion to the substrates. Figure 1 shows the appearance of the samples with the obtained coatings.

Figure 1. Appearance of the coatings formed on the surface of VT1-0 titanium alloy (a – electrolyte 1, b – electrolyte 2).

3. Results and discussion
The eddy current thickness gauge QuaNix 1500 was used to control the coating thickness. The thickness of the formed coatings was 19 μm for electrolyte 1 and 25 μm for electrolyte 2. The coating morphology analysis by the method of scanning electron microscopy showed the uniformity and high porosity of the obtained coatings at the microscopic level (figure 2). High porosity of the coatings contributed to the increase of RA characteristics [11].

Figure 2. Micrographs of the coatings formed on the surface of VT1-0 titanium alloy (a – electrolyte 1, b – electrolyte 2).
The element composition of the obtained coatings was determined by the X-ray fluorescence method (table 1).

**Table 1. Element composition of the coatings formed on the surface of VT1-0 titanium alloy.**

| Element | Electrolyte 1 Mass fraction (%) | Electrolyte 2 Mass fraction (%) |
|---------|-------------------------------|-------------------------------|
| O       | 41.71                         | O                             | 41.78 |
| Ti      | 38.02                         | Al                            | 25.13 |
| P       | 11.03                         | Si                            | 17.89 |
| Fe      | **6.03**                      | P                             | 4.28  |
| Co      | **2.13**                      | Fe                            | **5.89** |
| other   | 1.08                          | Co                            | 1.35  |
|         |                               | Mo                            | 0.03  |
|         |                               | other                         | 3.65  |

It should be noted due to the obtained data that the microplasma treatment in the proposed solutions resulted in magnetically active phase formation. The coatings included iron and cobalt which were capable of forming the magnetically active compounds. Iron and cobalt oxide mixtures melted thereby forming crystalline ferrite spinels as a result of exposure to the microplasma discharges under the high temperature effect:

\[
\text{Fe}_2\text{O}_3 + \text{CoO} \rightarrow \text{CoFe}_2\text{O}_4,
\]

\[
\text{Fe}_2\text{O}_3 + \text{FeO} \rightarrow \text{Fe}_3\text{O}_4.
\]

Some fraction of these oxides also deposited on the metal surface due to the oxide film perforation. The base metal was able to reduce iron and cobalt from their oxides during the process under the high temperature effect thus forming the metallic phase of iron and cobalt:

\[
\text{Me}_n\text{O}_m + \text{mTi} \rightarrow \text{TiO}_2 + \text{mMe}^{n+}.
\]

Absorption coefficients for all samples were measured on an STD-21 terahertz spectrometer developed by KDP OJSC in the frequency range from 428 to 973 GHz. The electromagnetic radiation absorption coefficient oscillated from 0.7 to 0.8 within the specified frequency range that was extremely high for thin films with a thickness of less than 30 microns.

Reflection spectra for the near-infrared area were also obtained by means of the Nicolet infrared spectrometer with normal incidence of electromagnetic radiation (figure 3).

![Figure 3. Reflection coefficient (R) dependence on the frequency (VT1-0 titanium alloy).](image-url)
The obtained dependence demonstrated high absorption ability of the synthesized coatings in the near-infrared spectrum. Differences in the absorption ability of the coatings could be noted only in the frequency range of 250 THz.

**Conclusion**

Thus, it is shown in the present paper that radiation-absorbing coatings can be formed by the microarc oxidation method on the surface of VT1-0 titanium alloy. Potassium hexacyanoferrate and cobalt (II) acetate are added to the electrolyte composition and form magnetically active compounds. Electromagnetic radiation absorption coefficients of the obtained coatings oscillate from 0.7 to 0.8 within the frequency range from 428 to 973 GHz that is extremely high for thin films. At the same time, such coatings are also effective electromagnetic radiation absorbers in the near-infrared spectrum with absorption coefficients 0.78-0.95.

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