

Microarc synthesis of nanostructured radiation-absorbing coatings on aluminum and titanium surfaces

T A Baranova, A K Chubenko, A E Ryabikov, A I Mamaev, V A Mamaeva and E Yu Beletskaya

National Research Tomsk State University, 36 Lenina ave., Tomsk, 634050, Russia

E-mail: konstantinova.ta9@gmail.com

Abstract. The article is devoted to the investigation of radiation-absorbing properties of the coatings formed on aluminum and titanium surfaces. Microarc oxidation in aqueous solutions was considered as a method of the coating formation. It was shown that the coatings obtained in iron-containing solutions were homogeneous, porous and had high absorption factor of electromagnetic radiation within the terahertz range (up to 70 %), which made this material extremely promising in terms of intensive development of terahertz technologies as well as stealth technologies. Investigations of elemental composition of the coatings were carried out by the X-ray fluorescent method, and the morphology of the surface was represented by the results of raster scanning electron microscopy. Absorption factors were measured using a TDS-21 terahertz spectrometer by «KDP» OJSC.

1. Introduction

The devices that use or produce concomitant electromagnetic radiation (ER) within the microwave range are widely used in modern practice. For example, various electronic devices, communication equipment and radar stations work in this way. The presence of such radiation requires solving the emerging accompanying problems, such as environmental protection of biological objects from its harmful effects, suppression of communication equipment interference, procuring of electromagnetic compatibility of radio electronic equipment, prevention of information leakage through the radio channel, etc. Protection of the equipment and strategic facilities from the radar detection is topical in military activity. Modern advances in electronics production allow the new ranges of radiation with high energies to be used. One of the most promising ranges is the so-called terahertz range. In general, it still remains poorly understood as well as protection from this radiation.

One way of protection from this kind of radiation is using the radiation-absorbing coatings and materials (RAM). The existing materials contain magnetoactive components. Fe, Co and Ni in their metallic forms are widely known and used as well as their mixed oxides – ferrites and organic nanostructural polymeric materials also containing the above-mentioned magnetoactive particles in their dispersed form. These components are either applied in different ways as films to the surface to be protected or integrated by alloyage.

Most modern developed RAM have a sufficient level of ER absorption, but other parameters do not always satisfy the operating conditions. Thus, most of these coatings have low adhesion to the substrate that reduces the operating time. Most of these coatings are also superimposed with several layers on each other to increase the absorption efficiency (sometimes this condition is necessary), so



the coatings are quite thick (1-10 mm). Such properties as wear resistance, heat resistance, dielectric strength and others do not always meet the requirements of the operation properties.

In the present paper the production of RAM on aluminum and titanium alloys was carried out in the microplasma mode in aqueous solutions of electrolytes.

2. Materials and methods

In the RAM synthesis the composition and homogeneity of the coatings are of particular importance since the coatings of different composition have different functional properties including the ability to absorb ER. The formation of the coatings in the microplasma mode provides wide opportunities of controlling and changing the composition of the material. Selecting the modes of nanostructured materials formation ensures suitable absorption of ER. The formation of coatings in the microarc mode provides a complex of functional properties in addition to radiation-absorbing ones (wear resistance, corrosion resistance, heat resistance, etc.) due to the variation of the electrolyte compositions and the mode of electrochemical processing. The distinctive features of the obtained coatings are the gradient structure (uniform variation of the concentration of different phases along the thickness), the controlled porosity, the presence of magnetoactive phases in the nanostructured form and the controlled coating thickness (from 10-100 μm).

The formation of the radiation-absorbing coatings was carried out in a homogeneous alkaline electrolyte containing complex compounds of Fe and Co. The homogeneity of such electrolytes was ensured by the ability of these metals to form stable complex compounds with a series of anions (CN^- , EDTA^{4-}) even in an alkaline medium without undergoing hydrolysis. Such soluble anion complexes approach the metal surface (which is an anode) during the microplasma process and are inserted into the coating as nanoparticles of the metal while participating in chemical and plasmachemical reactions or form crystal structures of spinels.

The process of microplasma oxidation of the samples was carried out in one step with polarizing voltage of 310 V and 20 minutes of processing time. The samples served as anodes, and plates of stainless steel served as cathodes. The electrochemical cell was continuously cooled during the processing.

The ability of the process to form high-temperature oxide modifications is confirmed either by a number of published sources [1–8] or in the present study.

Based on all of the above, the main purpose of the study is obtaining the coatings that absorb the terahertz radiation range in homogeneous alkaline electrolytes based on anion complexes of iron and cobalt.

3. Results and discussion

3.1. Structural investigations of the coatings

Topographic and qualitative phase analysis of the surface of A1 and A2 samples was carried out using the SEM 515 scanning electron microscope (Philips, Netherlands), and semi-quantitative elemental analysis was performed as well. Secondary or reflected back-scattered electrons were used to investigate the surface structure (Figures 1 and 2).

The presented coatings were dark gray, homogeneous and had developed porous structures with clear outlines of pore boundaries in both cases. However, the pores were small, and this fact was typical for undercoating layers. The phenomenon was indicated also by small thickness of the coatings (15-30 μm). Such result could be explained by complex equilibrium processes established in the electrolyte only over a period of time (a freshly prepared electrolyte was used to form these coatings). Due to the lack of complexation the deposition rate of the components from the electrolyte to the film decreased and this was reflected both in the color of the coating (a notable gray tint appeared with the increase of the deposition rate which indicated a small amount of iron), and in the pore size reducing.

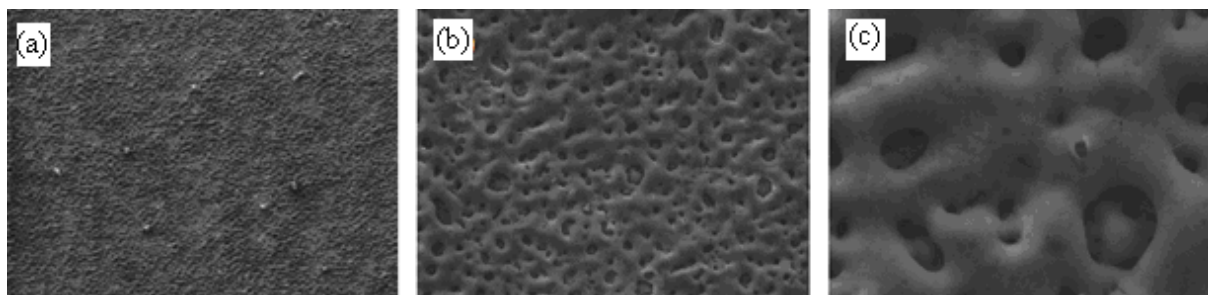


Figure 1. Approximations of the coating surface on titanium using the SEM. (a) – approximation x100, (b) - approximation x500, (c) - approximation x2000.

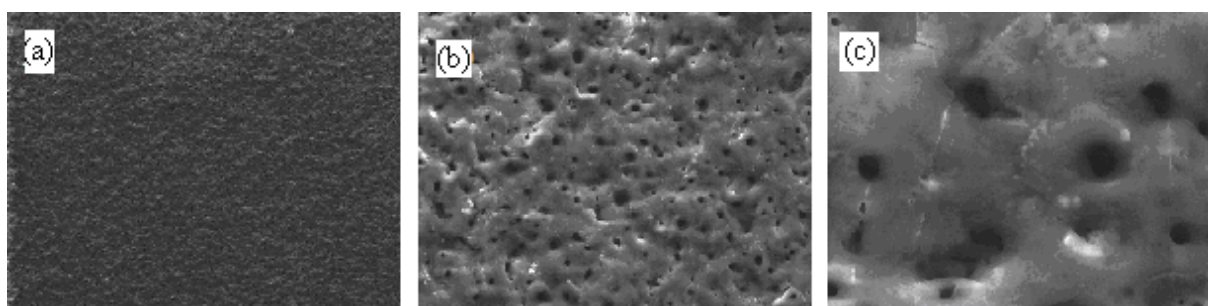
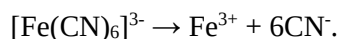
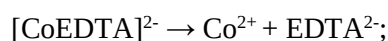


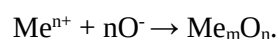
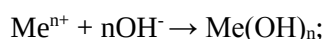
Figure 2. Approximations of the coating surface on aluminum using the SEM. (a) – approximation x100, (b) - approximation x500, (c) - approximation x2000.

It should be noted that the amount and size of pores on titanium substrate was larger than on aluminum one, which was connected with the different behavior of the substrate metal during the microplasma process, different process modes and compositions of the electrolytes. The presence of silicates in the solution for aluminum oxidation reduced the porosity of the coating and made it more smooth and homogeneous.

The presence of magnetoactive elements (Fe and Co) in the form of metallic nanosized particles and in crystalline mixed oxide forms (Fe_3O_4 and CoFe_2O_4) was discovered during the X-ray phase analysis. The formation of such phases was possible due to the specificity of the microarc oxidation process. Microplasma discharges occurred during the disruption of the anodic oxide film, and these discharges were characterized by high temperature values (2000-8000 K). The expected mechanism of the process was based on high-temperature dissociation of the anion complexes of magnetoactive particles while approaching the anode surface:



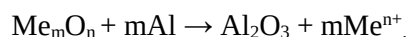
Then the metal ions were deposited on the surface of the coating in the form of oxides by the following reactions:



Mixtures of the resulting oxides under the influence of high temperature were able to melt, thereby forming crystalline spinel ferrites:



Some part of those oxides was also deposited on the surface of the metal due to the disruption of the oxide film. The substrate metal was able to reduce Fe and Co from the oxides during that process under the influence of high temperature with forming metallic phase of Fe and Co:



3.2. Determination of the elemental composition of the coatings

The X-ray fluorescent method was used to determine the elemental composition of the obtained coatings. The X-ray fluorescent sequential wave-dispersive spectrometer Shimadzu XRF-1800 was used in the Material science collective research center of Tomsk State University.

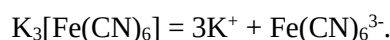
Investigations of the phase composition were carried out using PDF 4+ databases with POWDER CELL 2.5 full-profile analysis program.

The results of elemental analysis are presented in Table 1.

Table 1. The results of elemental analysis of the coatings on titanium and aluminum substrates.

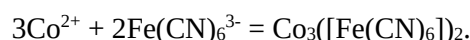
Substrate	Ti (% wt)	Al (% wt)	Fe (% wt)	Co (% wt)	O (% wt)	Si (% wt)
Al	-	20.1	6.9	0.02	48.6	19.9
Ti	38	0.07	6	2.1	41.7	0.06

One could see from the obtained data that magnetoactive Fe and Co had been inserted into the coatings as a result of the microarc processing. Speaking of Fe, it should be noted that despite the difference in the processed metals, modes and compositions of the electrolyte, the Fe percentage in those two coatings was quite close (the difference was about 0.9 %). This fact probably indicated that the potassium hexacyanoferrate (III) used as a Fe-containing substance acted well in the electrochemical process. This complex at pH 7–10 was really stable in the solution, and the complex salt completely dissociated according to the equation:



The anion Fe complex subsequently participated in the transformations described above.

As for Co, its percentage in the coatings sharply differed depending on the oxidized metal. The reason was, first and foremost, in different compositions of the electrolytes. A miscalculation happened during the development of electrolytes for oxidation, namely, the presence of Co^{2+} and $\text{Fe}(\text{CN})_6^{3-}$ in the solution that gave an insoluble deposition was not taken into account:



The insoluble deposition was discovered after preparation of both electrolytes.

The electrolyte contained Trilon B ($\text{Na}_2\text{H}_2\text{Y}$) during the microarc oxidation of titanium, and Trilon B partially bound Co^{2+} ions into a stable chelate complex thus increasing the percentage of Co ions soluble form, and the resulting CoY^{2-} complex anion took part in the electrochemical process through its migration to the anode. The electrolyte for the microarc oxidation of aluminum did not contain Trilon B, so the percentage of Co in the solution was apparently rather small, that resulted in the

elemental composition of the obtained coating. The percentage of the potassium hexacyanoferrate (III) was either much higher (15 g / l versus 1 g / l cobalt acetate in the electrolyte for the microarc oxidation of aluminum) or equal (5 g / l $[\text{Fe}(\text{CN})_6]^{3-}$ and CoY^{2-} in the electrolyte for the microarc oxidation of titanium), so that Fe was inserted into the coatings and was quite close in percentage values.

3.3. Measurements of the reflection factors

Measurements of the reflection factors for samples A1 (coating on the titanium substrate) and A2 (coating on the aluminum substrate) were carried out using a TDS-21 terahertz spectrometer within the frequency range from 428 to 973 GHz. Two oscillators based on backward-wave tubes (BWT) were used as radiation sources.

The absolute value of the reflection factor was calculated as the ratio of the power received by the detector when the sample was in the holder to the power at the detector when the sample was absent in the path, and the reflection emerged from the reference metal mirror.

The dependencies of the reflection factors on frequency were obtained on the basis of the measurement results (Figures 3 and 4).

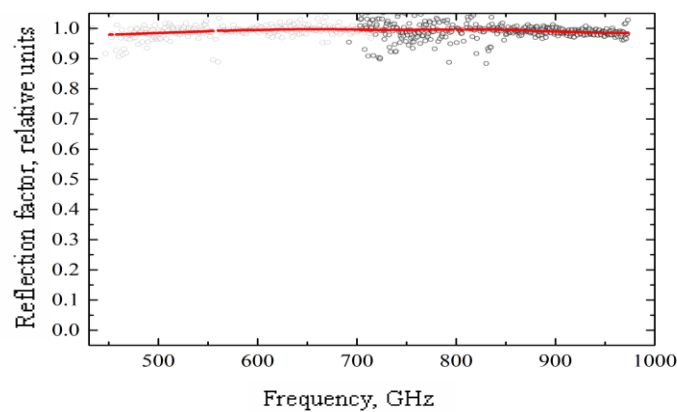


Figure 3. The dependence of the reflection factor on frequency for A1 sample (aluminum).

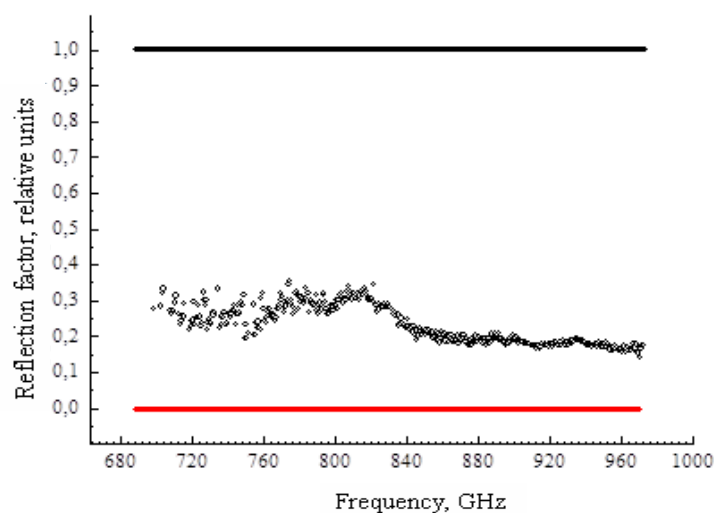


Figure 4. The dependence of the reflection factor on frequency for A2 sample (titanium).

One of the most important tasks in creating RAM was to achieve high absorption factors and low reflection factors simultaneously within a wide range of wavelengths.

The obtained dependencies showed that in the first case the reflection factor decreased rather weakly, however, for titanium this decrease amounted to 70-80 % for the given frequency range. This behavior of the coatings with respect to the given frequency range could be explained by the different percentage of magnetoactive elements, in particular, different percentage of Co and the degree of homogenization. The presence of Co (2 % wt) in combination with Fe gave a wider range of various magnetoactive phases (metallic Co, ferrite CoFe_2O_4), which apparently affected the decrease of the reflection factor.

4. Conclusions

Radiation-absorbing within the terahertz frequency range coatings were obtained on aluminum and titanium substrates. Fe and Co were chosen to serve as magnetoactive components ensuring the absorption of ER, and these metals were inserted into the electrolyte in the form of soluble anion complexes ($\text{Fe}(\text{CN})_6^{3-}$ and CoY^{2-}). Investigations showed that the magnetoactive particles were included into the coatings during the microplasma process. The obtained percentage of Fe was 6 % wt, the obtained percentage of Co was 2 % wt, and the measured reflection factor within the frequency range 450-1000 GHz was reduced by 15 % for the coating on the titanium substrate. The obtained percentage of Fe was 6.9 % wt, the obtained percentage of Co was 0 % wt for the coating on the aluminum substrate, and the measured reflection factor did not change and was 100 %. Such result could be explained by the complex character of the processes occurring at the stage of the electrolyte formation.

On the one hand, the formation of complex compounds was an equilibrium process characterized by quite long settling time (for Co). On the other hand, some features of the interaction of individual components ($\text{Co}^{2+} + \text{Fe}(\text{CN})_6^{3-}$) were not taken into account. This phenomenon affected the percentage of the required elements in the solution, and, consequently, the percentage of these elements in the coatings. At the same time, the electrochemical process of the coating formation on aluminum in the presence of EDTA showed the harmful effect of this component on the formed coating during the cycle of experiments on model samples of pure aluminum. Aluminum that was dissolving during the microplasma process, on the one hand, bound into poorly soluble compounds ($\text{Al}(\text{OH})_3$, AlPO_4 , Al_2SiO_3 , etc.) and deposited on the surface of the metal, which contributed to the formation of the coating. On the other hand, the released Al^{3+} ions were able to bind into soluble stable compounds and to be ejected from the reaction zone into the solution since their concentration in the said solution was extremely small. This process was exactly the one that caused etching, since there was no solid phase deposited on the surface of the substrate. Al-EDTA^- complex was characterized by high stability ($\lg\beta = 18$), therefore it could be one of the mechanisms of the negative influence of such complexing agent on the process of the coating formation.

Acknowledgement

The results were obtained in the framework of the state assignment by the Ministry of Education and Science of Russian Federation, project № 16.9621.2017/8.9

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