Construction of layered structures on valve metal alloys by microplasma oxidation

T A Baranova, A K Chubenko, A I Mamaev, V A Mamaeva and Ya B Kovalskaya
National Research Tomsk State University, 36 Lenina ave., Tomsk, 634050, Russia
E-mail: konstantinova.ta9@gmail.com

Abstract. Process of layered structure materials creation based on aluminum alloys is presented. Microplasma texturing method, microplasma oxidation method and chemical metallization method were used to create these structures. Non-conductive nonmetallic inorganic coatings were produced by microplasma oxidation method. Obtained structures showed high durability under thermal stress loads due to substrate metal – non-conductive nonmetallic inorganic coating phase boundary texturing.

1. Introduction.
Construction of laminated functional materials that are able to work under mechanical and thermal loads is an actual issue nowadays.

In this connection relatively new class of coatings – nanostructured non-metallic inorganic coatings – represents specific interest [1, 2]. These coatings can be obtained under conditions of high energy flows localization at the metal – electrolyte solution interface usually followed by microarc charges.

Based on this non-metallic inorganic type of coatings there is a capacity to create laminated composite materials with different constitutions and applications.

Applying these materials as construction materials appears to be very perspective for electronics, microelectronics, micromachines and also for space equipment, military equipment and general engineering.

Melting point of nanostructured non-metallic inorganic layers formed under microplasma influence is 2680 °C for zirconium oxides and 1780 °C for titanium oxides. Besides, such coatings can be classified due to their structure as microporous that allows to consider these coatings as practically ideal sublayers.

Imposition of successive layers like metals, for example, on local places of the surface provides functional properties of obtained coatings.

Real operating conditions of proposed materials applications require ensuring of maximum adhesion to the substrate metal surface as well as durability of the formed structures under mechanical and thermal loads.

Paper [3] based on mathematical modeling shows that texturing of substrate metal surface provides increase of nanostructured non-metallic inorganic coatings and successive connected layers’ adhesion to substrates.

Mechanical loads result in laminated materials deformation and cracks formation. The way of cracks distribution depends on texture type: cracks can be orthogonal or circular. Circular cracks formation on the textured coating surface leads to elimination of loads and prevents trunk cracks...
formation and exfoliation of laminated non-metallic inorganic coating material. As a result, durability of the coating material itself under deforming conditions significantly increases.

Valve metal surface texturing can be achieved using microplasma discharge effects [1, 2]. Microplasma texturing contains significant amount of regulating factors including electrolyte composition, duration of exposure and methods of process installation.

Let us consider formation of non-metallic inorganic coating with textured metal-coating phase boundary using formation of such coating on aluminum.

2. Materials and methods

Samples produced in form of plates of D16 aluminum alloy were initially grinded to 10th class of roughness in order to eliminate oxide layer and to get unique surface. Then organic contaminants were removed from the surface by rinsing with 1 M Na₃PO₄ solution at a temperature not lower than 60 °C. Treated samples were washed with distilled water, then with ethanol and with distilled water again.

Microarc coatings deposition was carried out for all aluminum samples in fluorine–phosphate solution with the following composition:

- NaF – 5 g/l,
- Na₂B₄O₇·10H₂O – 7 g/l,
- HBO₃ – 10 g/l,
- Na₃HPO₄ – 18 g/l.

Treated aluminum alloy sample served as anode; stainless steel tub with water cooling casing served as cathode.

Coatings obtained in electrolyte of described composition predominantly consisted of aluminum oxide and aluminum phosphate:

\[ \text{Al} - 3e \rightarrow \text{Al}^{3+}, \]
\[ \text{Al}^{3+} + \text{PO}_4^{3-} \rightarrow \text{AlPO}_4, \]
\[ 2\text{Al}^{3+} + 3\text{O}_2 \rightarrow \text{Al}_2\text{O}_3. \]

Coatings were chemically etched with 3 % NaOH solution for 5 minutes at a room temperature, then thorough and intensive rinsing with distilled water was carried out. Process was conducted repeatedly in order to determine influence of deposition and etching cycles amounts on metal texture.

Roughness and sample’s profilograms after texturing were scrutinized by contactless 3D Micro Measure Station produced by STIL. Maximum roughness (Ra = 1.015 μm) was achieved after 3 cycles of coating/etching (Table 1).

| Table 1. Aluminum samples surface roughness |
|--------------------------------------------|
| Coating/etching cycle quantity | Ra, μm |
|--------------------------------|--------|
| 1                              | 0.787  |
| 2                              | 0.962  |
| 3                              | 1.015  |
| 4                              | 0.815  |
| 5                              | 0.797  |

Obtained surface texture data were used in order to form laminated structures with predetermined textured phase boundary on aluminum substrates.

Next stage of laminated material forming was introducing of metal copper on non-metallic inorganic coating oxide layer surface. Metallization was provided by chemical method.

Chemical deposition of the metal results in sewing the oxide layer along its longitudinal and transverse pores with formation of monolithic composite metal-oxide coating. This fact also provides
smoothing of oxide layer imperfections and thus friction coefficient decreasing. Surface conductivity increases, that makes it possible to deposit subsequent metal layers using electroplating techniques.

Moreover, the given approach allows to equalize thermal stresses under thermal loads and to increase the whole durability of laminated material in case of local thermal loads. Melting of copper layers with the following filling of micropores and microcracks under significant thermal loads is permitted and leads to the «healing» effect in relation to re-appeared imperfections.

Sensitization and activation operations were successively conducted within the framework of preparing the surface for copper deposition [4]. Chemical deposition of copper was carried out in tartrate copper solution. Formalin served as reducing agent. Copper was reduced during the copperplating process [4]:

$$2\text{H}_2\text{CO} + \text{Cu}^{2+} + 4\text{OH}^- \rightarrow \text{Cu} + \text{H}_2 + 2\text{HCOO}^- + 2\text{H}_2\text{O}.$$  

Thickness of chemically deposited copper layer was 1 - 3 \(\mu\)m. Obtained samples were investigated by semi-quantitative elemental composition assessment using EDAX Genesis microanalyzer. Results of investigation showed that percentage of copper on the surface layer amounted from 98 to 98.8 wt.%.

3. Results and discussion

Micrograph of layer material surface which has copper outer layer has been obtained by raster scanning microscopy method (Figure 1).

![Figure 1. Surface micrograph of three-layered laminated structure on aluminum alloy](image)

Coating destruction process was analyzed on obtained samples of three-layered laminated structures with predetermined metal-coating phase boundary texture. Texturing influence on destruction character was revealed under thermal stress loads. Thermal stress tests were carried out within temperature values from - 60 °C to + 360 °C. Exposure time at extreme temperature values was 2 hours, 10 test cycles were carried out.

Scanning electron microscopy results presented in Figure 2 confirmed that thermal loads exceeding the material breaking point led to successive load removal by microcracks formation in porous coating. Circular microcracks relaxed and eased down on themselves during their growth. Emergence of circular microcracks eliminated the load within the coating and prevented trunk cracks resulting in coatings exfoliation. Further increase of the load caused macrocracks and then exfoliation of the upper part of the coating [3].
4. Conclusions
Thus, microplasma oxidation method allowed to obtain nanostructured non-metallic heat-resistant coatings with predetermined phase boundary texture on valve metal alloys. Metal – coating phase boundary texturing provided durability of the coating, also coating exfoliation and deformation under external impacts was not generated.

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References
[1] Lukiyanchuk I V, Rudnev V S, Tyrina L M and Chernykh I V 2014 Applied surface science 315 481–489
[2] Nawrat G, Wierzbinska M, Wieczorek T, Nieuzyla A, Krzakala A, Maciej A, Simka W and Raga R 2015 Solid state phenomena. International Scientific Conference Corrosion 227 151–154
[3] Konstantinova T A, Mamaev A I, Chubenko A K, Mamaeva V A and Beletskaya E Yu 2015 Procedia chemistry 15 174–179
[4] Melashchenko N F 1987 Galvanic coating of dielectrics: Directory (Minsk: Belarus’) 176

Figure 2. Surface micrograph of three-layered laminated structure on aluminum alloy substrate after critical thermal loading