

Titaniferous protective coatings on aluminum alloys

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Recent trends in world practice are toward more often use of nanoscale adhesive coating obtained from hexafluorotitanic acid solutions as an alternative to chromate layers on aluminum and aluminum alloys. The present article is devoted to the development of technology of obtaining such coatings.

There was worked out a process of titaniferous coatings depositing on aluminum and AMg6 (AMr6) and AK12 (AK12) alloys, which are comparable with chromate coatings by corrosion stability and defense capability and may serve as an alternative of the latter. The solution comprises, g/l: H_2TiF_6 — 1–2; Mn^{2+} — 0.06–0.12; tartaric (citric) acid — 0.3–0.4; $(NH_4)_2MoO_4$ — 1–3. It was found that permissible PH values of solution lie in the range of 4.5–5.0 units. It has been revealed that introducing 0.3–0.4 g/l of tartaric or citric acid into operating solution not only stabilizes pH value of the solution, but also brings to the growth of defense capability of the generated coatings. Chemical composition of coatings has been determined by methods of X-ray photoelectron spectroscopy. It has been assumed that composition of a protective film can be described by the following formula: $Al_2O_3 \cdot 4AlOF \cdot TiOF_2$. Solution temperature influence on properties of the coating has been studied. It was revealed that heating of a solution to 40 °C doesn't results in essential changes of outward appearance and defense capability of coatings, while at higher temperatures (>40 °C) their defense capability has been reduced. That's why an interval of 18–25 °C has been chosen as a working range, and it was noted that the solution heating up to 40 °C (in a summer-time, for example) is admissible.

A TS-1 non-toxic passivating composition for impregnating (sealer) was developed. It has been established that the defense capability of titaniferous alloys imbued for 40–60 s in a water solution containing 2–3 g/l of TS-1 at pH = 4 and 18–30 °C, is rising almost two times more and runs up to 110 s.

Key words: corrosion proofing, surface treatment, nanoceramic coatings, titaniferous coatings, hexafluorotitanic acid, nanostructural adhesion coatings, passivating composition.

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Introduction

Aluminum alloys are widely used as a structural material in various technical and everyday spheres: in industrial and civil engineering for making buildings frame, farms, window-frames, stairs; in motor-car construction; in shipbuilding; in aeronautical and space-system engineering; in electrical engineering; in nuclear reactor building, etc. Aluminum and aluminum alloys usage took the second place after steel and cast iron [1].

Wide application of aluminum and alloys in different lines of practical activities is connected with the whole complex of physical, mechanical and chemical properties, such as: small density, corrosion stability in atmospheric air, high thermal- and electroconductivity, plasticity and relatively high durability. Besides, aluminum and aluminum alloys are easy treated by different means: hot forging, closed-die forging, rolling etc.

Thanks to thin natural oxide spot, surface of aluminum and its alloys is quite corrosion-resistant, there-

fore in some cases they may be used without special anticorrosive protection addition. However, through low thickness, the natural spot on aluminum surface frequently can't guarantee its effective corrosion protection, for example, in damp industrial atmosphere or in sea-water.

For corrosion protection of aluminum and alloys according to alloy grade, design of product, its purpose, operating conditions and other factors, protective-decorative electrochemical oxidation (anodic treatment), laquer and paint coats, as well as complex coats consisting of oxide film with laquer and paint coat (LPC) applied over it are employed. Chemical oxide coatings have less (lower) protective and adhesive properties than electrochemical and doesn't have wide practical application. Chemical oxide coatings have lower protective and adhesion properties as compared to electrochemical, so they don't find wide practical application.

However, for the parts subjected to periodic load, on numerous occasions it is worthwhile completely exclude

surface preparation by standard methods of anodic oxidation, for “on the surface of specimens anodized in sulfuric electrolyte for a 10 mkm thickness, cracks in the coating appear at a flare angle of 4° only; as thickness of an oxide film decreases to 5 mkm, cracks appear at a flare angle of 30° . Cracks on the film obtained in chromate electrolyte appear under the same conditions, but their number is less. On the surface of materials with conversion chromate-phosphate films with thickness between 0.1 and 0.3 mkm, there are no cracks even at a flare angle of 180° ” [2, 3]. In such cases, thin-coat methods of the aluminum alloy surface treatment for (LPC) are used. Conversion chromate coatings are widely used as a thin-layer adhesive layers under LPC before colouring of aluminum and its alloys. Chromate adhesive coatings are preferable for colouring of profilecomposite products as well, because their anodic treatment is connected with difficulties and requires additional technical contrivances and expenditures.

It is known that solutions for chromate treatment are very toxic because ions of hexavalent chrome are part of them. Conversional coatings formed in such solutions also contain up to 200 mg/m^2 of Cr(VI) toxic compounds. Problem of chromate treatment replacement became more sharp in 2000 after adoption of a 2000/53/EC European Directive, which restricts presence of Cr(VI) compounds in conversion coatings. An addition to this directive accepted in 2002 have completely prohibited presence of Cr(VI) compounds in conversion coatings used in motor-car construction since July, 2007 [4]. In China similar directives came into effect since March 1, 2007; in South Korea — since July 1, 2007. In the Russian Federation analogous instruction has not been accepted yet, but a task to substitute hexavalent chrome containing solutions is quite urgent, because current standards (СанПиН 2.1.5.980–00) regulates maximum allowable concentration of Cr(VI) compounds in manufacturing water at the level of 0.02–0.05 mg/l, which is an order lower than the limit of 0.1–0.5 mg/l for countries of European Union.

Recent trends in world practice are toward more often use of nanoscale adhesive coating obtained from hexafluorotitanic acid solutions as an alternative to chromate layers on aluminum and aluminum alloys. World leading companies in the surface preparation field have been deeply involved in developing technologies of obtaining such coatings.

No results of domestic research in the field of deposition of protective adhesive titanium-oxide coatings can be found in the published literature. German companies take first place in the corresponding investigations. They manufacture and supply to the Russian market finished compositions for realization of technologies in question, but their components have not been disclosed.

In connection with the mentioned above, developing technology of coatication of titaniferous coatings on

aluminum and its alloys is an important scientific and application problem, to the solving of which the present paper is devoted.

Experimental technique

Plates of A95 aluminum as well as AMg6 (AMr6) and AK12 (AK12) aluminum alloys were used as specimens. Solutions for experiments were prepared using chemicals of laboratory reagent grade “ch” (“ч”) and analytical reagent grade “chda” (“чда”) and distilled water.

For accelerated estimation of protective capacity of coatings a drop method was used in accordance with GOST 9.302–88 Russian State standard (ГОСТ 9.302–88) using Akimov’s reagent, i. e. solution containing: $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ — 82 g/l; NaCl — 33 g/l; 0.1 normality of a HCl solution — 13 ml/l. According to Akimov’s method, defense capability of a coating is estimated in seconds as a time during which the colour of the test area under drop of solution has changed from grey to red-brown.

Thickness of coatings has been determined by ellipsometric method by use of a Gartner ellipsometer on a LSM-S-111 solid-state laser with green colour filter.

Chemical compound of coatings has been studied by method of X-ray photoelectron spectroscopy. RFE spectrums have been obtained by means of a CLAM 100 special camera installed on the HB100 Auger microscope (Vacuum Generators, GB).

For estimating water-resistance of coatings, specimens with a coating have been putted into water for 10 minutes. Then the specimens have been dried, whereupon a defense capability has been determined by Akimov’s drop test. The received data have been compared with defense capability values of the specimens not tested for water-resistance.

Corrosion diagrams have been obtained by use of an IPC-Pro MF potentiostat in potentiodynamic mode of operation. Plates of aluminum alloy without coatings and with titaniferous or chromate coating were used as main electrodes. Electrode potentials have been measured comparatively silver-chloride electrode, and their values have been converted to normal hydrogen scale. Polarization curves have been read at a speed of potential scanning (1 mV/s).

Colouring of aluminum specimens with adhesive titanium-oxide precoat by Ecocolor PE RAL 9016/P (Ecocolor ПЭ RAL 9016/P) powder polyester paint has been fulfilled by use of a START-50 (СТАПТ-50) spray gun with subsequent burning-off in a ShC-80-01 SPU (ШС-80-01 СПУ) drying oven at 180°C during 5 min.

Corrosion testing of AMg6 (AMr6) aluminum alloy specimens with adhesive titaniferous coatings and with coatings-analogue, which have been coloured by powder polyester paint has been carried out in an Ascott S120iP salt spray chamber in accordance with ASTM B117 international standard (so called SCAB test) accepted in

the motor-car industry and in accordance with GOST 9.401–91 Russian State standard (ГОСТ 9.401–91) as well. As per procedure, the principal criterion for estimating defense capability of phosphate coating in conjunction with the laquer coating was an average width of expansion of an underfilm corrosion caused by notch. Parallel with this value, adhesion of a laquer coating has been determined by use of an Elcometer 107 adhesion analyser by the latticed notch technique in accordance with ASTM D3359 international standard and GOST 15140–78 Russian State standard (ГОСТ 15140–78).

Corrosion testing of aluminum as well as AMg6 and AK12 aluminum alloy specimens with independent adhesive titaniferous coatings with subsequent TS-1 inhibitory impregnating has been also carried out in an Ascott S120iP salt spray chamber in accordance with ASTM B117 international standard accepted in the motor-car industry and in accordance with GOST 9.401–91 Russian State standard (ГОСТ 9.401–91) as well.

Experimental results and their consideration

According to literary sources, main components of solutions for obtaining titaniferous coatings are a hexafluorotitanic acid and ions of heavy metals, which being precipitated on the surface of metallic base in contact or in the form of compounds, initiate subsequent formation of protective coatings [5–10]. In view of this, the H_2TiF_6 -based solutions in our experiments were supplemented with ions of heavy metals, such as Fe^{3+} , Cu^{2+} , Co^{2+} , Cr^{3+} and Mn^{2+} . Ions of metals have been introduced into solution by way of nitrate or sulphate salts: $Fe(NO_3)_3 \cdot 9H_2O$, $CuSO_4 \cdot 5H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Cr_2(SO_4)_3 \cdot 6H_2O$ and $MnSO_4 \cdot H_2O$.

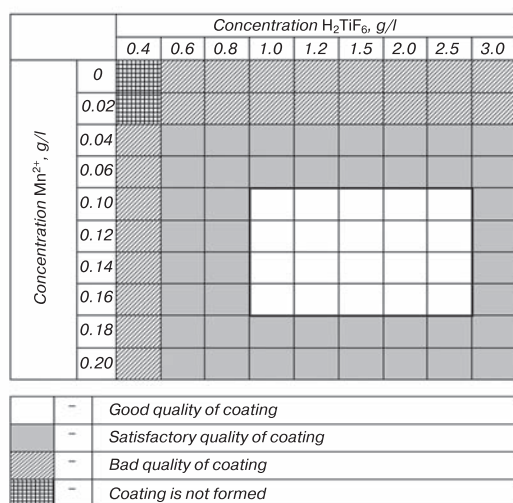


Fig. 1. Outward appearance of titanium-oxide layers depending on H_2TiF_6 and Mn^{2+} concentrations. Base — A95, AMg6 and AK12 alloys

There were determined intervals of concentration of ions of the listed metals within which it has been possible to obtain the continuous coatings with the highest possible defense capability on the aluminum alloy surface. As indicated in the diagram represented in Fig. 1, the highest defense capability (23–25 s) is observed, if the ions of manganese concentration in the solution lie within the range of 100–160 mg/l.

As to other metals, the allowable concentrations of their ions in the solution vary in the range of 60–120 mg/l, while defense capability is present between 10 and 15 s. Thus, the defense capability of coatings obtained in the Mn^{2+} ions presence in solution is higher as against the ions of other metals.

It might be well to point out that the coatings generated on the aluminum alloy surface by solutions without ions of heavy metals, possess broken structure and quite low defense capability.

Studies made it clear that allowable PH values of solution are present between 4.5 and 5.0 units. Outside this range, coatings are either not generated at all ($pH \leq 4.5$), or they are nonuniform and broken ($pH \geq 4.5$).

We sampled, as additive agents, such hydroxycarbon acids like malic, citric, tartaric and lactic ones. Their pH values are present between 3.5 and 5.5 units. In the course of experiments it has been revealed that introducing 0.3–0.4 g/l of tartaric or citric acid into operating solution not only stabilizes pH value of the solution, but also brings to the growth of defense capability from 25 to 35 s (Fig. 2) as well as to an increased homogeneity and uniformity of generated coatings.

Revealed range of optimal pH values of solution between 4.0 and 5.0 units is well matched with a coating generating mechanism described in the literature. It is deemed that within this pH value area, the natural oxide film presented on aluminum surface has been dissolved in accordance with the reaction [11]:

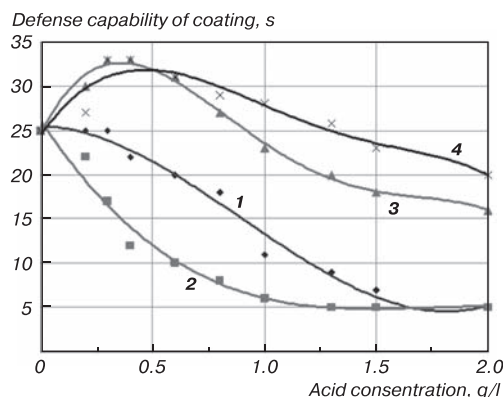
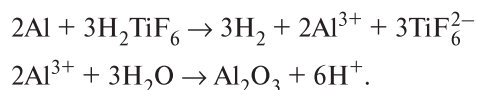


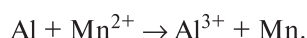
Fig. 2. Influence of hydroxycarbon acids concentration on defense capability of obtained coatings: 1 — malic; 2 — lactic; 3 — citric; 4 — tartaric

Next hexafluorotitanic acid catalyses aluminum oxidation according to the following reactions:



Aluminium and titanium oxyfluorides arise as a result of these reactions. First of all, they are absorbing on the surface of contactly precipitated heavy metal (manganese), then they are spreading up generating the coating.

Chemical compound of coatings has been studied by method of *X*-ray photoelectron spectroscopy. General RFE spectrums have been uncovered titanium, aluminum, fluorine and oxygen compounds in the coating. Besides, it was established that manganese may be observed in the first layers of the coating (up to 10 nm thick) only. The following layers are manganese free. These facts agree with the coating generating mechanism described above. Apparently, manganese makes active centers by precipitating on separate parts of aluminum surface. Then titanium and aluminium oxyfluorides have been absorbing there, enlarging into the coating as follows:



Taking into account aforecited reactions and results of *X*-ray photoelectron spectroscopy, one might surmise that composition of a protective film generated on the aluminum alloy surface can be described by the following formula: $\text{Al}_2\text{O}_3 \cdot 4\text{AlOF} \cdot \text{TiOF}_2$.

As we might expect, the defense capability of coatings depends on duration of their obtaining: it is increasing during first 30 seconds of the process and then stabilizes. Being in solution more than 5 min is undesirable for coatings, because it results in deterioration of their defense capability. These data correlate with results of ellipsometric examination (Fig. 3). Thickness of coating both on aluminum and its alloys is rising during 30 s of the process and then stabilizes. We notice that difference in thicknesses of coatings generated on A95,

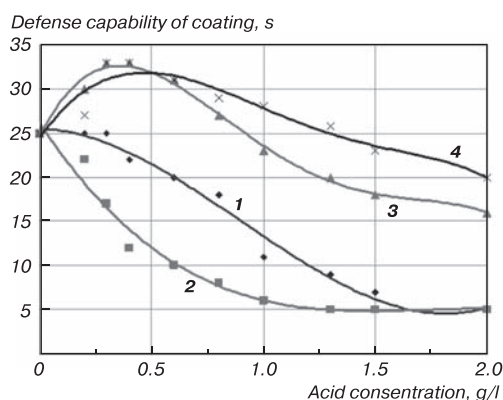


Fig. 3. Dependence of the thickness of titaniferous coatings (*d*) on the process duration:
1 — aluminum; 2 — AMg6 alloy; 3 — AK12 alloy

AMg6 and AK12 alloys are not essential: 62, 67 and 70 nm respectively.

To improve coatings for greater defense capability, nitrogen-containing compounds which have made a good showing in phosphatization processes have been introduced into solution. Among them are sodium metanitrobenzosulphonate, hydroxylamine sulphate, ammonium molybdate. It has been revealed that introducing into solution up to 3 g/l of ammonium molybdate raises defense capability of coatings from 35 to 60 s. Other additions introduced into solution have been of no positive effects. From 1 to 3 g/l of ammonium molybdate have been included in composition of the solution in view of obtained results.

Studied is a solution temperature influence on properties of coatings. It is found out that solution heating up to 40 °C doesn't results in essential changes of outward appearance and defense capability of coatings, while at higher temperatures (>40 °C) their defense capability has been reduced. That's why an interval of 18–25 °C has been chosen as a working range, and it was noted that the solution heating up to 40 °C (in a summer-time, for example) is admissible.

It is known that defense capacity of conversion coatings, both adhesive under lacquering and merely anti-corroding ones, may be increased by their passivation in chrome anhydride diluted solutions. Such passivating treatment raises the defense capability of conversion coatings by three to five times [12].

In present work, a non-toxic (4th class of danger) alternative to chromate passivation solutions has been developed. Its composition represents an aqueous solution of organic compounds for final compacting of titaniferous coatings (sealer), which we have ciphered as TS-1.

It has been established that the defense capability of titaniferous alloys imbued for 40–60 s in a water solution containing 2–3 g/l of TS-1 at pH = 4 and 18–30 °C, is rising almost two times more and runs up to 110 s.

There has been studied how temperature of heat treatment of titaniferous coatings passivated in TS-1 solution effects on their protective properties. It is revealed that coatings which has been impregnated in TS-1 solutions with following heat treatment at 180 and 200 °C for 5–7 minutes possess the highest defense capabilities.

It is discovered that Akimov's defense capability of titaniferous coatings both impregnated and not impregnated in TS-1 solution is higher than that of chromate adhesive coatings on aluminum alloys as well as of foreign analogues, such as SurTec 609 and Interlox 5705 zirconium-containing coatings.

Contemporary colouring technologies often use water-thinned paints, hence adhesive layers under LPC should be water-resistant. Water-resistance of coatings were estimated by defense capability reduction after their ten-minute's holding in water. It is worked out that defense capability of specimens with titaniferous coatings

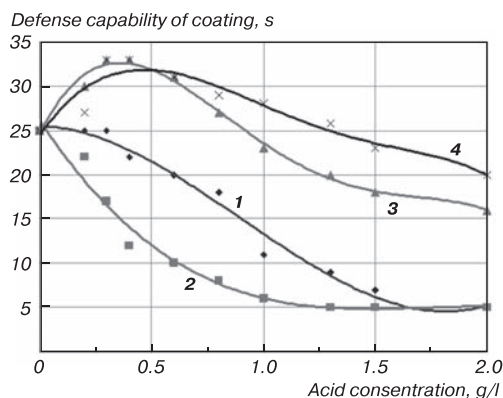


Fig. 4. Results of corrosion testing (ASTM B117) of AMg6 samples with adhesive coating with following coloring by powder polyester paint (h — width of the LPC lift-off caused by notches)

doesn't change after water-resistance testing, that is to say, coatings stay water-resistant.

To estimate passivating action of coatings, corrosion rate of AMg6 alloy specimens both non-passivated and passivated in chromate and titaniferous solutions was electrochemically determined, for which purpose corrosion diagrams in a 5% solution of NaCl were made. Comparison of corrosion rate values obtained by use of corrosion diagrams shows that the AMg6 alloy corrosion rate decreases from $6.0 \cdot 10^{-6}$ to $7.5 \cdot 10^{-8}$ A/cm² after chromate treatment and to $7.0 \cdot 10^{-8}$ A/cm² after passivating in titaniferous solution.

Corrosion testing (according to ASTM B117) of AMg6 aluminum alloy specimens with adhesive titaniferous coatings coloured by Ecocolor PE RAL 9016/P powder polyester paint has been carried out in a salt spray chamber. The testing has showed that defense capability of the developed titaniferous coatings impregnated in a TS-1 composition meets the requirements of indicated standard, for width of corrosion penetration from place of a notch in such cases doesn't exceed 2.0 mm after 750 h of testing (Fig. 4). The reported results shows that the developed titaniferous coatings are not only highly competitive with Interlox 7507 and SurTec 609 CC German analogues as well as chromate coatings by protective characteristics, but do surpass them.

Moreover, corrosion testing (according to ASTM B117) of independent anticorrosion titaniferous coverings impregnated in TS-1 solution has been also carried out in a salt spray chamber. This testing showed that coatings generated on an AMg6 alloy have maximum defense capability. First corrosion points appear on such base after 210 h of testing against 180 h on AK12 alloy and 100 h on aluminum.

Adhesion of a laquer coating with adhesive titaniferous precoat has been determined by use of an adhesion

analyser by the latticed notch technique. It has been found that the developed coatings possess a good adhesion: class 0 of ASTM D3359 standard. It doesn't deteriorate even after corrosion testing.

As a result of the performed work, process of titaniferous coatings coaction to A95 aluminum and AMg6 and AK12 alloys is developed for adhesive layers under LPC and independent anticorrosion coverings under an inhibiting impregnation which are compared to chromate coatings by defense capability and may serve as an alternative to the latter.

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