A review of chromium free passivation process for aluminum film with high protective properties

Yuanyuan Hu,
Ningguo Education Bureau
Ningguo, 242300
PR China

Shuqi Li, Zhimin Song,Fan Yang, Lin Hu*
School of Materials Science and Engineering,East China JiaoTong University
Nanchang, 330013
PR China
hulin21@hotmail.com

***Abstract*— Because of its unique properties such as light weight and corrosion resistance, aluminum and its alloys have become one of the most widely used and economical materials. This also promotes the research of corrosion resistance methods of aluminum and its alloys. At present, the most commonly used method to improve the corrosion resistance is to use chromate to form chromate passivation film on the aluminum surface, but chromate contains hexavalent chromium ions, which are extremely harmful to the environment and human body. Therefore, finding a new passivation technology that can replace chromate passivation has become the top priority. By analyzing the advantages and disadvantages of various passivation systems, with the goal of environmental protection, no pollution to the environment, good corrosion resistance and simple passivation process operation, the optimal passivation solution formula and passivation process conditions can be obtained by studying the influence of passivation solution composition and passivation process on the corrosion resistance of passivation samples.**

Keywords—aluminum passivation,passivation film, corrosion potential,

I. INTRODUCTION

The content of aluminum in the crust is 8.3%, ranking the third after oxygen and silicon, and it is the most abundant metal element in the crust. Pure aluminum is soft and has poor strength, which has been greatly limited in making structural materials. Therefore, people have studied and explored to increase the strength of aluminum by adding alloy elements, and obtained a high-strength aluminum alloy with multiple functions and mixed alloy characteristics. Aluminum alloy has many superior properties, such as low density, high plasticity, good conductivity, corrosion resistance, easy recycling, weldability, easy surface treatment, etc. It is one of the metal materials with the largest amount of use and the widest application in nonferrous metals. Aluminum alloy has high "specific strength" and is an ideal structural material. It is widely used in machinery manufacturing, automobile industry, aviation industry and other industries. It is the most widely used nonferrous metal structural material in industry [1].

Aluminum is an amphoteric metal with low electrode potential and high chemical activity. It is easy to corrode under acidic, alkaline and neutral conditions. According to the principle of corrosion, aluminum corrosion can be divided into chemical corrosion and electrochemical corrosion.

In addition to the overall corrosion of aluminum and its alloys in a few media (such as the corrosion of aluminum in alkaline solution and phosphoric acid solution), local corrosion generally occurs. The corrosion forms are mainly divided into spot corrosion, intergranular corrosion, stress corrosion and galvanic corrosion [2,3].

After corrosion of aluminum and its alloys, their structure, performance, color and other aspects will be greatly weakened, which will cause deformation and damage of products made of aluminum alloys, and sometimes cause irreparable losses.

II. CORROSION PROTECTION TREATMENT OF ALUMINUM AND ALUMINUM ALLOY

Due to the wide use of aluminum and aluminum alloys in the national economy and national defense construction, it has become an indispensable link in the use of aluminum and aluminum alloys to protect them so as to extend their service life, and it is also a research hotspot and difficulty in the field of metal anti-corrosion treatment.

According to the different treatment principles, the surface treatment technologies of aluminum and its alloys mainly include anodic oxidation technology and chemical passivation technology.

A. *Anodic oxidation technology*

Anodizing is a method of generating an oxide film on the surface of aluminum or aluminum alloy as anode, stainless steel, lead, or carbon as cathode in an appropriate electrolyte solution [4]. There are many anodizing methods for aluminum and its alloys. The properties of anodic oxide film are different with different electrolyte and process conditions. The main anodizing methods used in production include sulfuric acid anodizing, oxalic acid anodizing, chromic acid anodizing and hard anodizing.

- Sulfuric acid anodizing is to take aluminum as the anode and place it in the sulfuric acid electrolyte to form an anodic oxide film on the aluminum surface by electrolysis. At present, sulfuric acid anodizing is the most widely used in industry. At present, sulfuric acid DC anodizing is widely used at home and abroad. Compared with other acid anodizing, it has the following obvious advantages in terms of production cost, oxidation film characteristics and performance: low production cost, low price of sulfuric acid used in electrolyte, less electricity consumption in electrolysis, simple waste liquid treatment, and is the cheapest process compared with other anodic oxidation; The transparency of the film is high [5].

- Oxalic acid anodizing is a method that uses oxalic acid as electrolyte and uses DC or AC electricity for oxidation. The anodic oxidation of aluminum alloy with oxalic acid can obtain 8-20um oxide film. Because oxalic acid has a weak solubility in aluminum alloy and its oxide film, the porosity of the oxide film is low, and the corrosion resistance, wear resistance and electrical insulation of the film are better than those of the sulfuric acid film. Generally, it is only used in the case of special requirements, such as the surface decoration of daily necessities such as aluminum pots, aluminum pots, aluminum pots and aluminum lunch boxes and the protective layer of electrical insulation. In recent years, it has also been widely used in building materials, electrical industry, shipbuilding, daily necessities and machinery industry [10].

- Chromic acid anodizing is an anodizing method for aluminum and its alloys invented by Bengough and Stuart in Britain in 1923. The chromic acid oxide film is much thinner than the sulfuric acid oxide film and oxalic acid oxide film, with a general thickness of only 2-5 μ m. It can maintain the accuracy and surface roughness of the original parts. The film is soft and has good elasticity, and there will be no obvious fatigue strength degradation during application. However, the wear resistance of this film is not as good as that of the film produced by sulfuric acid anodizing. Therefore, the use is limited [6].

- Phosphoric acid anodizing was first used as a pretreatment process for aluminum alloy electroplating, and was first studied and adopted by Boeing Company in the United States. At present, phosphoric acid anodizing is rarely used as electroplating pretreatment, but replaced by zincate or stannate pretreatment.

- Hard anodizing is also called thick film anodizing. The hard anodic oxide film of aluminum has been widely used and developed because of its film thickness, high hardness, corrosion resistance, wear resistance and good adsorption [8,9].

Although the anodic oxide film has obvious protective effect on aluminum and its alloys, the oxide layer is hard and easy to break when bending. In addition, a large amount of electric energy will be consumed in the anodic oxidation process, and the cost is high, and the process of anodic oxidation is complex, which limits its application in some aspects [7].

B. Chemical passivation technology for aluminum and alloy

At present, the simplest and most effective technology used in aluminum alloy corrosion protection treatment is metal surface passivation treatment. In fact, it is to separate metal from corrosive medium by generating a passivation film, so as to prevent corrosive medium from penetrating into metal matrix, thereby reducing the metal corrosion rate. The technology is easy to operate, energy saving, simple equipment, and has been widely used in many fields [11].

- At present, most industrial metals and coating metals (such as aluminum, tin, magnesium, iron, zinc, lead and other metals and their alloys) can be protected by chromate passivation. Chromate passivation technology has been widely used in household appliances, aviation, steel, manufacturing and other industries. The chromate passivation solution is composed of chromate and other compounds. A passivation film with excellent corrosion resistance is formed on the surface of the metal through treatment. This thin film is a mixed oxide film, which contains trivalent chromium and hexavalent chromium elements, of which trivalent chromium is mainly used as the framework of the passive film, while hexavalent chromium has a self repairing effect.

Common treatment methods of chromate passivation technology include chemical methods (immersion, brushing, spraying) and electrochemical methods. Electrochemical methods are not commonly used. Immersion method is widely used in chemical methods, and brushing and spraying are occasionally used. Brushing is mainly used in situations where the film needs to be repaired, and the conversion film obtained by spraying is generally difficult to be satisfactory. During chromate passivation, chromate will react with metal, and some Cr^{6+}in the passivation solution will be reduced by metal to produce Cr^{3+}, which will form a passivation film skeleton and finally produce a dense passivation film. The passivation film can largely prevent the oxygen in the air from entering the metal surface and prevent the metal from corrosion. Once the passivation film is damaged, the Cr^{6+}not reduced by the metal will migrate to the metal surface, oxidize the exposed aluminum alloy matrix, and generate $Cr^{3+}$to repair the passivation film and restore its protective performance. The conversion between hexavalent chromium and trivalent chromium makes the chromate passivation film have good self repair performance.

In the past years, chromate has been widely used in metal surface treatment industry as an excellent corrosion inhibitor. The chromate passivation process is very mature. The metal surface after chromate treatment has excellent corrosion resistance, beautiful appearance, low cost, and convenient use. It has been widely recognized and used. However, because hexavalent chromium is carcinogenic, it will pose a fatal threat to biology and human body.

Therefore, although chromium passivation technology has many advantages, considering its high hazard and high pollution factors, it has become an inevitable development trend in the field of metal surface treatment that this technology is finally prohibited from use, and the new chromium free passivation technology has become a research hotspot in the surface treatment of aluminum and its alloys today [12].

- Molybdenum and chromium belong to VIA group with similar properties, but they are low toxic inorganic salts. Therefore, molybdate is commonly used as metal corrosion inhibitor or passivator. Relevant scholars have made relevant research on molybdate passivation process.

Xu Linchao et al. [13] used the environment-friendly molybdate process to replace the chromate process to passivate the surface of 7075 aluminum alloy, and discussed the effects of the composition of the passivation solution, pH value, treatment temperature and time on the corrosion resistance of the passivation film. It is concluded that the optimum range of molybdate passivation process is: 7-10g/L, sodium fluoroborate 10-30g/L, acetic acid drill 5-8g/L, appropriate amount of? Phosphoric acid, pH 3-4.5, passivation temperature 60-70 □, time 10-15min. Within the process range, the higher the concentration of molybdate, sodium fluoroborate and cobalt acetate, the faster the film formation. The longer the passivation time is, the thicker the passivation film is. Maria A Osipenko [14] and others studied the corrosion inhibition of Na2MoO4 on Mg – xLi – 3Al (x=4 – 15%) of magnesium lithium aluminum alloy in 0.05 M NaCl solution. The inhibition mechanism of molybdic acid aqueous solution was characterized by electrochemical measurement, hydrogen evolution, Raman spectroscopy and SEM-EDX. Molybdate was found to be a highly effective corrosion inhibitor and passivator for aluminum alloys. Dmitry S. Kharitonov [15] and others studied the corrosion performance of aluminum alloy AA6063-T5 in molybdate NaCl solution. The corrosion inhibition mechanism of molybdate was studied by electrochemical, microscopic and spectroscopic experiments. It is found that molybdate passivation is more advantageous than chromate passivation.

- The passivation solution obtained by silicate passivation technology is non-toxic and pollution-free, has good stability and can be stored for a long time. Therefore, silicate passivation technology is also popular.

Xu Lu et al. [16] used a silicate solution containing 5% (mass fraction) SiO_2 to passivate the hot-dip Zn-5% Al alloy coating, and studied the effects of solution modulus (i.e. the molar ratio of SiO_2 to Na_2O), passivation temperature, time and drying temperature on the neutral salt spray corrosion resistance of the passivation film. The optimum technological conditions of silicate are: modulus 4.0, passivation temperature 80 □, passivation time 60s, drying temperature 125 □. Scanning electron microscopy (SEM) and electrochemical impedance spectroscopy (EIS) were used to characterize the surface morphology and corrosion resistance of the film obtained under the optimal process conditions. It is concluded that the silicate conversion film obtained under the optimal process is uniform, complete and transparent, and can effectively improve the corrosion resistance of hot-dip Zn-5% Al alloy coating. Li Xiaojie [17] studied the influence of the composition of silicate conversion solution on the aluminum alloy surface and the operating conditions on the film forming reaction, and found that the best film forming reaction conditions were 15g/L silicate and 25g/L disodium EDTA. At pH 11.5,65 □, the reaction time was 10min, and the neutral salt spray time could reach 10 hours. The reason why the corrosion resistance of aluminum alloy is improved after sodium silicate treatment may be that the aluminum alloy surface is covered by aluminosilicate formed by the combination of sodium silicate and aluminum ions on the metal surface. The experimental results show that appropriate pretreatment and post-treatment can further improve the corrosion resistance of aluminum alloy.

Kazemi et al. [18] soaked 2024 aluminum alloy in potassium silicate solution, and after heat treatment, a silicon rich aluminum oxide film was formed on the surface. The principle may be that silicon penetrates into the pores of alumina to form a dense corrosion resistant layer. The experimental results also show that the concentration of the film forming solution has an important influence on the film formation. Kazemi et al. [19] also found that anodizing pretreatment plays an important role in the formation of silicate film on aluminum alloy. The passivation film after anodizing pretreatment has better corrosion resistance. The longer the anodizing time, the better the corrosion resistance of the film.

- Zirconium titanium salt passivation process has many advantages, such as non-toxic and pollution-free passivation solution, low overall cost, simple and controllable passivation process, and different colors of zirconium titanium passivation films can be prepared by controlling the parameters of passivation process. Zirconium titanium salt passivation is a kind of passivation treatment technology with both decorative and high corrosion resistance, so the current academic research on Zirconium titanium salt passivation technology is more extensive.

In order to develop a chromium free passivation process with high corrosion resistance and conductive passivation film, Fu Ming et al. [20] developed a chromium free passivation process for 2A-12 aluminum alloy with high corrosion resistance by using zirconate as the main component, adding copper salt mixed accelerator and vanadium salt filler, and optimized the composition of passivation solution and passivation process parameters, obtaining the following better process specifications: 2.0 g/L zirconate, 0.2 g/L copper salt mixed accelerator, 0.1 g/L vanadium salt filler, 4.5 g/L coordination agent, 3.0 ～6.0 g/L pH buffer, pH 4.0, temperature 55 ℃, time 8 min. The morphology and comprehensive performance of the passivation film obtained by the optimum process were analyzed. The results showed that the passivation film formed was light white, uniform and fine, belonged to the amorphous structure transformation film without cracks, and had good corrosion resistance, conductivity and coating adhesion, which was suitable for the aluminum alloy surface protective layer, the spraying bottom layer and the electromagnetic shielding protective layer of the electronic product shell. Huang Yaning et al. [21] developed a chromium free passivation formula for A356 aluminum alloy die castings through orthogonal tests: fluorozirconic acid 1.5g/L, fluorotitanic acid 0.7g/L, hydrogen fluoride 0.05g/L, cobalt nitrate 0.1g/L, allyl thiourea 0.2g/L, cerium chloride 0.1g/L, pH 4.0. Uniform, complete, colorless and transparent passivation film can be obtained by passivating 120 s at 25 □ with this formula. The resistance to potassium dichromate drops can reach 200 s, and the corrosion area fraction is only 9% after 168 h of neutral salt spray test. Kolesnikova A et al. [22] developed a process for depositing titanium and zirconium coatings on 5556 aluminum alloy. In the process of this work, the basic mode of coating formation was determined. The solution composition and process parameters were optimized, and its physical and chemical properties were studied. The results show that passivation of 5556 aluminum alloy in solution containing titanium and zirconium can improve its pitting resistance. These coatings have good corrosion resistance and can replace chromate coatings. Ren Yubao et al. [23] found that the titanium/zirconium passivation film of 6063 aluminum alloy has uniform and dense microstructure, and its surface is full of regular microcracks. The titanium/zirconium passivation film has a strong corrosion resistance. The surface is only slightly corroded after 128 h of neutral salt spray test, and the duration of chromate drop test is 75 s. The corrosion resistance is slightly lower than that of chromium passivation film, but much higher than that of other similar passivation films. The adhesion between titanium/zirconium passivation film and substrate is good. The adhesion rating is 0 according to the test results of Baige experiment. After the cupping test, the film has no cracking and falling off, which is close to the adhesion of chromium passivation film. Compared with chromium passivation of aluminum alloy, titanium/zirconium passivation is more convenient, environmentally friendly and safe, and can be used as an alternative process for chromium passivation.

- The rare earth metal salt passivation process is a chromium free passivation technology that has emerged in recent years. In essence, the inorganic salts of lanthanide rare earth elements are used to passivate metals. The principle is that the inorganic salts of lanthanide metals can react with metals to generate a layer of rare earth chloride or hydroxide film on the metal surface. This film acts as a protective layer to prevent oxygen in the air and other impurities from contacting the metal surface, and can effectively prevent the transfer and transfer of electrons between the metal surface and solution in the system, playing a role in corrosion resistance.

Hu Bo [24] selected nitrate solution of cerium element in rare earth element as passivation treatment solution and alkaline NaCl solution as corrosion medium to passivate 7075 aluminum alloy test piece by chemical immersion process. In order to obtain the best corrosion resistance of the passivation film under alkaline conditions, the author conducted a single factor experimental analysis on the concentration of $Ce(NO_3)_3$, passivation time and drying time by using the drop test and corrosion medium immersion test, and obtained the optimal scheme. In the subsequent experiments, electrochemical methods and corrosion weight-loss experiments were used to test 7075 aluminum alloy after rare earth passivation in alkaline corrosion medium containing Cl^-. It was found that the CeO_2 element in the passivation film on the surface of 7075 aluminum alloy after rare earth passivation treatment accounted for more than 95%. The self corrosion current density in alkaline Cl corrosive medium decreased significantly, the self corrosion potential increased, the corrosion weight loss rate decreased, the electrochemical impedance increased, and the corrosion inhibition performance improved significantly. Liu Wei [25] used $Ce(NO_3)_3$ and $La(NO_3)_3$ as additives respectively and doped them in the film to improve the corrosion resistance of the passive film. The best addition amount of rare earth salt obtained through single factor experiment is: cerium nitrate 0.5g/L or lanthanum nitrate 0.3g/L. According to the electrochemical test results and scanning electron microscope pictures, the addition of rare earth salt has a very positive effect on improving the corrosion resistance of the film. The corrosion current of the passive film doped with cerium nitrate is $1.35 \times 10^{-7} A \cdot cm^{-2}$, polarization resistance is 5712.61 k Ω· cm-2; The corrosion current of the passive film doped with lanthanum nitrate is $3.16 \times 10^{-7} A \cdot cm^{-2}$, polarization resistance 3446.91 k Ω· cm^{-2}. The impedance is one order of magnitude higher than the basic film.

BREN et al. [26] observed the surface micro morphology of the film by means of scanning, EDS and other analysis methods; The micro morphology and corrosion resistance of rare earth conversion coatings produced by different processes, types of film forming solutions and concentrations were studied. The results show that the solid solution+artificial aging treatment and short time alkali washing activation pretreatment are beneficial to the deposition of rare earth conversion film. When the content of $CeCl_3 \cdot 7H_2O$ in the film liquid is 0.05 mol/L, the aluminum alloy with rare earth conversion film has the strongest corrosion resistance. Zhang Mingshen et al. [27] used Ce $(NO_{3)}$ $_3$ as the main film forming agent to study the rare earth conversion film forming process of 6061 aluminum alloy by orthogonal test and single factor test, and analyzed the surface morphology, composition and corrosion resistance of the conversion film. The results showed that the conversion film was brown yellow; The conversion film contains cerium and manganese elements; The copper sulfate dropping test of aluminum alloy with rare earth conversion treatment reached more than 340 seconds. The electrochemical test showed that the self corrosion current density was 2 orders of magnitude lower than that of aluminum alloy substrate, and the polarization resistance was about 93 times of that of untreated aluminum alloy, effectively improving the corrosion resistance of aluminum alloy. Peter Rodi č et al. [28] explored the use of cerium conversion coating as a substitute for chromate conversion coating for corrosion protection of aluminum alloy 7075-T6. The conversion coating was formed in a conversion bath of 0.05 M cerium salt and 0.25 M hydrogen peroxide at room temperature. Various cerium salts are used: Ce (III) acetate, Ce (III) nitrate and Ce (III) chloride. The conversion process from $Ce^{3+}$to $Ce^{4+}$is followed by ultraviolet visible spectrophotometer. The conversion of cerium coating on the alloy surface was monitored by measuring the open circuit potential. In order to study the corrosion properties of uncoated and coated samples, linear polarization and electrochemical potential kinetic curves were recorded in 0.1 M NaCl. In addition, salt spray chamber tests were carried out. The samples were characterized by scanning electron microscope The results show that the conversion rate and corrosion resistance of cerium depend on the type of cerium salt in the conversion tank and the conversion time. The densest and uniform cerium conversion coating is produced from cerium acetate (III) solution, but due to the thicker coating, it is better protected in nitrate, especially chloride solution.

- As early as the early 1990s, silane began to be used in metal surface treatment. Compared with the traditional chromate passivation process, the organic silane passivation process is simpler, has little difference in corrosion resistance, and is non-toxic and pollution-free. The adhesion between the silane treated metal surface and the organic coating is more excellent.

Yu Haiqing et al. [29] carried out silane treatment on 7075 aluminum alloy, and analyzed the thickness, water absorption, composition, morphology and corrosion resistance of silane film. The silane treatment solution forms Si-O-Al covalent bond through hydrolysis and condensation reaction, covering the aluminum alloy surface to form silane film. The results show that the surface of silane film is uniform and dense, the water absorption is only 0.763 ‰, and the thickness is about 4 μ m; After the aluminum alloy is silane treated, the film resistance increases by at least two orders of magnitude, the self corrosion potential moves forward -0.331 V, the self corrosion current density decreases by nearly two orders of magnitude, and the corrosion resistance is significantly improved. In order to further improve the corrosion resistance of silane conversion film on the surface of aluminum alloy, Jia Fengchun et al. [30] used fluotitanate to modify silane to form a composite conversion solution, and prepared silane fluotitanate conversion film on the surface of 6061 aluminum alloy. The corrosion resistance of the conversion film was evaluated by polarization curve, $CuSO_4$ drop test, salt water immersion test and salt spray test; The effect of fluotitanate content on the corrosion resistance of the composite film was studied, and the corrosion resistance of single conversion film and composite conversion film was compared. The results show that the optimum dosage of fluotitanate is 1.0 × 10^{-3}mol/L, at this time, the self corrosion current density of the composite film is the smallest, the polarization resistance is the largest, the corrosion area is the smallest, and the resistance to CuSO4 drops is the longest. Under the optimal amount of fluotitanate, the self corrosion current density of the modified silane composite film decreases by an order of magnitude compared with the silane conversion film. After 24h of neutral salt spray, there is almost no white rust on the surface, and the corrosion rate of salt water immersion is the smallest.

Peng Sha et al. [31] prepared a layer of hybrid silane film on the surface of 7N01 aluminum alloy by dip coating method, and characterized and analyzed its corrosion resistance by electrochemical test. The test results show that the corrosion resistance of silane film can be enhanced by doping cerium nitrate into silane film, and the corrosion current density of the sample without any treatment is 1.35 × 10^{-4}A/cm^2, low frequency impedance about 3.98 × 10^3Ω/cm2; Corrosion current density after single silane treatment 1.71 × 10^{-6}A/cm^2, low frequency impedance about 105 Ω/cm^2; The corrosion current density of doped cerium nitrate reaches 4.41 × 10^{-8}A/cm2, low frequency impedance about 2.51 × 10^5Ω/cm2; The corrosion current density after doping zeolite is 6.28 × 10^{-7}A/cm^2, low frequency impedance about 2.51 × 10^4Ω/cm^2。 YuchaoDun et al. [32] added the pre hydrolyzed FAS-17 solution to the GPTMS solution, and mixed the heptafluorodecyl trimethoxysilane (FAS-17) γ- Hybrid silane graphene films (FG/rGO) were prepared on 2024 aluminum alloy surface in (2,3-epoxypropoxy) propyltrimethoxysilane/graphene (GPTMS/rGO). Compared with GPTMS/rGO films, FG/rGO films show better thermal shock resistance, good adhesion and higher microhardness. In neutral

3.5 wt% NaCl solution, the corrosion current density of FG/rGO film is about one fifth of the GPTMS/rGO membrane sample. In acidic and alkaline NaCl solutions, FG/rGO films also show better corrosion resistance than GPTMS/rGO films.

III. Discussion and Conclusion

In this paper, several kinds of chromium free passivation systems for high protective aluminum films are briefly analyzed and compared. It is hoped to find out all kinds of passivation systems that can perfectly replace chromate passivation systems that do great harm to the environment. By comparing and analyzing the advantages and disadvantages of all kinds of passivation systems, the goal is to be green, pollution-free, good corrosion resistance, simple and easy to operate passivation process, and by studying and comparing the effects of passivation solutions with different components and different processes on the corrosion resistance of passivation samples, It is hopeful to find the optimal passivation solution formula and passivation process conditions. The in-depth research in this field not only provides a more advanced technology for the aluminum metal surface treatment industry, promotes the development of chromium free passivation technology, but also improves the independent innovation ability of scientific research, thus showing significant economic and social benefits.

References

[1] Cui Shan, An Chengqiang, Hao Jianjun. Research progress in chromium free passivation of aluminum and aluminum alloys [J] Surface technology, 2016,45 (06): 63 - 69

[2] Zhang Zengguang, Lv Wangyan, Su Wei. Atmospheric Corrosion and Protection Countermeasures of Aluminum and Aluminum Alloy in Substation [J]. Comprehensive Corrosion Control, 2016,30 (10): 36-40

[3] Xiao-guang Sun,Peng Lin,Cheng Man,Jian Cui,Hai-bo Wang,Chao-fang Dong,Xiao-gang Li. Prediction model for atmospHeric corrosion of 7005-T4 aluminum alloy in industrial and marine environments[J]. International Journal of Minerals Metallurgy and Materials,2018,25(11):1313-1319.

[4] Huang Xiaolan. Overview of Aluminum and Aluminum Alloy Anodizing Technology and Patent Analysis [J]. Chemical Management, 2017 (13): 38-39

[5] Chen Jing, Cheng Yang, Chen Dongchen, Jiang Zhiping. Development Status of Aluminum and Aluminum Alloy Anodizing [J]. Jiangxi Chemical Industry, 2019 (04): 44-46

[6] Mu Qiang, Yu Wengang, Lu Gang, Yang Zhengshan. Chromic acid anodization of aluminum and aluminum alloys [J]. Shandong Chemical Industry, 2016, 45 (05): 26-28

[7] Zou Mengting, Xiong Ju, Ma Yanlong, Wu Liang, Sun Lidong, Wu Haisheng, Deng Shengwei. Effect of pretreatment process on the structure and corrosion resistance of 5056 aluminum foil phosphoric acid anodized film [J]. Journal of Chongqing University of Technology (Natural Science), 2021,35 (11): 95-101

[8] Student, M. M.,Pohrelyuk, I. M.,Hvozdetskyi, V. M.,Veselivska, H. H.,Zadorozhna, Kh. R.,Mardarevych, R. S.,Dzioba, Yu. V.. Influence of the Composition of Electrolyte for Hard Anodizing of Aluminum on the Characteristics of Oxide Layer[J]. Materials Science,2022,57(prepublish):

[9] Student M. M., Pohrelyuk I. M., Chumalo H. V.,Hvozdetskyi V. M.. Improvement of the Functional Characteristics of Coatings Obtained By the Method of Hard Anodizing of Aluminum Alloys[J]. Materials Science,2021,56(6):

[10] Liu Changming, Zhang Di, Zhao Huaipeng, Kong Bing, Wang Shuai, Ren Yubao. Research on Oxalic Acid Anodic Oxidation Process [J]. Aluminum Processing, 2017 (04): 42-45

[11] Zi Yun Chromium free passivation process and properties of aluminum alloy [D]. Shenyang University of Technology, 2011

[12] Jiang Qin Study on corrosion resistance of chromium free organic inorganic composite passivation film on aluminum alloy [D]. Graduate School of Chinese Academy of Sciences (Institute of Oceanography), 2013

[13] Xu Linchao, Chen Xianhang, Li Yong. 7075 Molybdate passivation process for aluminum alloy surface [J]. Journal of Zhejiang Industry and Trade Vocational and Technical College, 2015,15 (02): 49-52

[14] Osipenko, M.A.; Kharitonov, D.; Wrzesi ń ska, A.; Kasach, A.A.; Kurilo, I.I. Effective inhibition of magnesium-lithium-aluminum alloys corrosion by sodium molybdate, in Proceedings of the 1st Corrosion and Materials Degradation Web Conference, 17–19 May 2021,

[15] Dmitry S. Kharitonov, Illia Dobryden, Birhan Sefer, Jacek Ryl, Angelika Wrzesi ń ska, Irina V. Makarova, Izabela Bobowska, Irina I. Kurilo, Per M. Claesson,Surface and corrosion properties of AA6063-T5 aluminum alloy in molybdate-containing sodium chloride solutions,Corrosion Science,Volume 171,2020,108658

[16] Xu Lu, Che Chunshan, Kong Gang, Wang Yanqi. Silicate passivation process of hot-dip zinc-5% aluminum alloy coating [J]. Electroplating and Finishing, 2017, 36 (24): 1307-1311

[17] Li Xiaojie Research on silicate passivation technology of aluminum alloy surface [D]. Xi'an University of Architecture and Technology, 2010

[18] KAZEMI M, DANAEE I, ZAAREI D. Deposition and corrosion behavior of silicate conversion coatings on aluminum alloy 2024 [J]. Materialwissenschaft and Werkstofftechnik, 2014, 45 (7): 574-581.

[19] KAZEMI M, DANAEE I, ZAAREI D. The effect of pre-anodizing on corrosion behavior of silicate conversion coating on AA2024 [J]. Materials Chemistry and pHysics, 2014, 148 (1/2): 223-229.

[20] Fu Ming, Zhang Xiang, Liu Yanming. High corrosion resistance chromium free passivation process of aluminum alloy [J]. Material Protection, 2019, 52 (07): 116-120

[21] Huang Yaning, Fan Xiaoling, Xie Jinping, Xiao Ning, Li Ning. Zirconium titanium passivation of A356 aluminum alloy die castings [J]. Electroplating and Finishing, 2019, 38 (11): 513-518. DOI: 10.19289/j.1004-227x.2019.11.001

[22] Kolesnikova A, Abrashov A, Grigoryan N. A high-performance Ti-Zr BASED conversion coating on 5556 aluminum alloy[J]. Machines. Technologies. Materials.Vol. 15 (2021), Issue 3, pg(s) 128-129

[23] Ren Yubao, Li Dan, Liu Changming, Zhao Huaipeng, Liu Fu.6063 Comparative study on titanium/zirconium passivation and chromium passivation performance of aluminum alloy [J]. Aluminum Processing, 2021 (04): 19-21+26

[24] Hu Bo Corrosion Behavior of 7075 Aluminum Alloy in Alkaline NaCl Medium and Corrosion Inhibition of Rare Earth Passivation [D]. Qinghai Normal University, 2014

[25] Liu Wei Study on chromium free passivation process and properties of cast aluminum materials [D]. Shenyang University of Technology

[26] BREN, YANG Lijuan, ZHANG Fuyi. Study on rare earth conversion film on aluminum alloy surface for automobile parts [J]. Light Metals, 2020 (01): 47-52

[27] Zhang Mingshen, Wang Xiuchun, Xu Bin, Zhou Jixue, Zhao Dongqing, Su Haitong. Research on the process and properties of aluminum alloy rare earth conversion film [J]. Shandong Chemical Industry, 2019, 48 (08): 12-15

[28] Rodič, Peter & Milo š ev, Ingrid. (2020). Corrosion resistance of cerium-conversion coatings formed from cerium(III) salts on aluminium alloy 7075-T6. Studia Universitatis Babe ș- Bolyai. Chemia. 65. 227-244

[29] Yu Haiqing, Yan Xiuxia. Research on silane treatment of 7075 aluminum alloy surface [J]. Electroplating and Environmental Protection, 2020, 40 (01): 40-42

[30] Jia Fengchun, Ma Guoyang, Li Hongling. Corrosion resistance of fluotitanate modified silane film on aluminum alloy surface [J]. Material Protection, 2018,51 (09): 70-73

[31] Peng Sha, Chen Hongwei, Sun Lin, Chen Ming'an. Preparation and corrosion resistance of hybrid silane film on aluminum surface [J]. Aluminum Processing, 2019 (06): 14-18

[32] Yuchao Dun, Xuhui Zhao, Yuming Tang, Sahib Dino, Yu Zuo,Microstructure and corrosion resistance of a fluorosilane modified silane-grapHene film on 2024 aluminum alloy,Applied Surface Science,Volume 437,2018,Pages 152-160