ABSTRACT

«Electroplatingininstrumentation engineering. Development of technology of anodizingparts of aluminum alloy us ing chromium-containing fillers»

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The project has developed a technology ofanodizingaluminumalloyparts D16 with sealing in chromium-containing substances.

In modern technology, porous aluminum oxides are widely used in microelectronics, the creation of solarpanelsandotherindustrialsectors, suchas in strumentation engineeringandaircraftengineering.

Duralumin D16 has the composition: Al - 92.7%, Cu - 3.8%, Mg - 1.2%, Zn - up to 0.3%, Mn - 0.9%, Si - 0.5%, Fe - 0.5%, Ti 0.1%. Itis a material which has highstrength and it’s also lightweight.However, ithas a drawback - lowcorrosionresistance, soin order toprotectitmustbeelectrochemicallyanodized.

The standard electrode potential of aluminum is -1.66 V, its value is quite negative so the metal itself is thermodynamically unstable. The surface of aluminum and its alloys, due to the propensity to passivation, is constantly covered with a natural oxide film. Its thickness depends on the ambient temperature and usually reach 2-5 nm. The corrosion resistance and mechanical strength of aluminum and its alloys can be increased in hundred times, by carrying out the processof anodic oxidation (anodization) due to the formation a certain thickness of a porous oxide film and the operation of filling this film.

In all cases, the films consist of two layers - without a porous barrier layer with thickness 0,01-0,03 microns and a porous layer with thickness from a few microns to several hundred microns.

Itisimpossibletoaccuratelycalculatethethicknessoftheanodefilm, duetotheoccurrenceofadversereactions - thereleaseofoxygenandthedissolutionofaluminum, sothethicknesswaschosenaccordingtothereferencedata. Undertheseconditionsitispossibletoget a filmwith a thicknessof 6 microns.

Chemical and electrochemical methods can be used to form an oxide film. Chemical oxidation can be achieved by treating products in a solution containing 50 g/l soda and 15 g/l sodium bichromate for 3-5 minutes at a temperature of 80-100 °C. The products oxidized in this way need and additional operation, it should be dipped for 2-5 seconds in a 2% solution of chromic acid at room temperature. These films have less thickness (2-3 microns) than films that are formed by the electrochemical method, and they are considerably inferior to the protective properties of those. Due to the disadvantages of the chemical method it can be concluded that the production of an oxide film from solutions by the electrochemical method is the most efficient and controlled process, that's why it was chosen for this diploma project.

Thickness, porosity and presence of impurities are decisive factors that determine the properties of films. Their hardness is greater when the porosity is lower, but the adsorption capacity is higher in porous films. The presence of impurities significantly reduces the hardness of oxide layers.

An important stage before the main stage ofany galvanic process, in this case anodizing, is the preparation of the surface.It consists of the following operations:

1. chemicaldegreasing:
2. etching;
3. lightening;
4. several stages of washing.

Degreasing is a necessary operation because the surface could be polluted with different kind of fats after mechanical processing. The solutions used for the degreasing operation must comply with a few requirements: to remove fat

contamination, not to cause corrosion of parts and to wash off easily from the surface.

For the treatment of the surface of aluminum and its alloys, a solution of the following composition is used:

sodium carbonate (Na_2CO_3) - 15 ... 20 g/l;

threenatrium phosphate ($Na_3PO_4 \cdot 12H_2O$) - 25 ... 30 g / l;

sintanol DC-10 - 3 ... 4 g / l.

Th temperature of electrolyte is 60 ... 70 °C, processing time is from 3 to 5 minutes.

To remove the defects of the surface, conduct the etching process. Aluminum is readily soluble in acids and alkalis, especially at elevated temperatures. This process is carried out in a solution of composition:

sodium hydroxide (NaOH) - 50 ... 150 g / l.

Temperature of electrolyte is 45 ... 80 °C, the processing time from 0,5 to 1,5 minutes.

The chemical lightening is carried out in order to remove dark spots, which remaining after etching and worsen the appearance of the details. Lighting is carried out in a solution:

nitric acid (HNO_3) - 100 ... 140 g / l.

Temperature of electrolyte is 18 ... 25 °C, the processing time from 0,5 to 1,5 minutes.

After degreasing the parts washes in warm and cold water, after etching and lightening only in cold water. The operation of washing is needed to remove completely the reagents that last there after previous operation.

Industrial anodizing of aluminum and its alloys is most often produced in sulfuric, chromic and oxalic acids.

For anodizing aluminum as an electrolyte, 15 - 20% solution of sulfuric acid is used. The bath temperature is maintained at 15 - 23 °C. The process is carried out at anode current density of 1.5 - 2 A / dm^2. The duration of the process is 40-50 minutes.

Anodizing in sulfuric acid is a universal method of processing aluminum and allows to obtain dense and solid films that have a high adsorption capacity and corrosion resistance.

The advantages of this electrolyte include:

1. Ability to anodizing in it almost all aluminum alloys.

2. Electricity costs are 30-50% lower than other electrolytes.

3. Diluted sulfuric acid is also the cheaper than chromic and oxalic acids.

Disadvantages of anodizing in sulfuric acid are:

1. The need to cool the electrolyte at work.

2. Some complexity of the technological process is caused by the need to fill the film

Considering the advantages of sulfate electrolyte, it is expedient to choose the electrolyte composition for execution of this project:

H_2SO_4 - 180 ... 200 g / l

The temperature 18 ... 25°C,current density is 1,0 ... 1,5 A / dm^2, duration 40 ... 50 minutes.

The main reactions that took place in the process of anodizing are:

onthecathode:

$$H^+ + 2e \rightarrow H_2$$

on the anode:

1. $2Al + 3H_2O \rightarrow Al_2O_3 + 6H^+ + 6e$
2. $2H_2O \rightarrow O_2 + 4H^+ + 4e$
3. $Al \rightarrow Al^{3+} + 3e$

Films obtained from the electrolyte of this composition are characterized by high corrosion properties and have a strong adhesion to the surface of the substrate.

Sealing of a film is one of the final operation after anodization. It is carried out in a solution of chromium in a stationary bath that has local ventilation. Seals are made in a solution of the composition:

Potassium tartaric acid ($K_2Cr_2O_7$) - 80 ... 100 g / l

Temperature is 80 ... 90 ◦C, processing time 20 ... 25 min.

After anodization and sealing there is reclaim dip for a more complete removal of the electrolyte after the operations and for saving the electrolyte.

A warm dip is provided before the drying operation.Drying is carried out by blowing hot air for 10 - 25 minutes at a temperature of 50-60 °C.

Quality control is performed on the following parameters:

1. film thickness;
2. film porosity;
3. the quality of sealing the film.

Gravimetricmethodisusedtodeterminethethicknessofthefilm. Itisbasedonweightingcoatingmassesbeforeandafterdissolvingonanalyticalscales. Thismethodisusedtodeterminethethicknessofsingle-layercoatingswithknowndensity. Therelativeerrortomeasurethismethodisnotmorethan 10%.

The porosity can be determined by applying a dropof a solutioncontaining 3 g of $K_2Cr_2O_7$, 25 ml ofHCl (ρ = 1.16 g / cm3) and 75 ml of H_2O to the anodized aluminium. Ifthefilmisdamagedorifitssealdoesnotoccur, thecolorofthesolutionchangesfromorangetogreenduetotheinteractionofthesolutionwiththemetal. As a result, hydrogenisreleasedandionsofhexavalentchromiumarerestoredtotrivalent. Themorefilledporesandthickfilm, theslowerthedissolutionprocessis, whichisanindicatorofitsprotectiveproperties.

Theprotectivepropertiesoftheoxidefilm are satisfyingwhenthetimeofgreening thedropoccursat 8 minutes of the experimentat a testtemperatureof18 ... 21 °C.

Themethod for controlling the seal of the oxide film isbasedontheelongationofthesampleinthesolutionofthedyeandfurtherdefinedchanges inthecolorofthecoating. Testsarecarriedouton a plotofanareaof atleast 5 cm^2. Testsareperformedbydippingin solution.First, thesampleisimmersedin a solutionofnitricacidat a concentrationof 400 g / l at a temperatureof 23 - 25 °C. After 5 minutes, thesampleistakenout, washedandfor 5 minutesimmersedinanalcoholicsolutionofmethylvioletat a concentrationof 20 g / l.

Afterthis, thesampleiswashed in wateranddried. Thefillingisconsideredas a highquality one,ifthecoatingdoesnotchangethecolorduringthetest, orthesechangesareinsignificant.

Thepoorcoverageisremovedandtheprocessisre-launched. Filmscanberemovedinsolutionsofalkalis, buttheyreactwiththemainmetal, sothesolutionthat can be used contains :

phosphoricacid (H_3PO_4) - 35 ml / l

chromicacid (H_2CrO_4) - 20 g / l

Temperature for the process is 98 ... 100 °C, the time of operation from 1 to 10 min.

Selected bath for anodizing has the following characteristics:

- length - 1250 mm
- width - 710 mm
- height - 1000 mm

Leadsheetswerechosenascathodesforthisproject.Assuspensiondevices, steelsuspensionswereselectedonwhichthepre-preparedaluminumwiresarefastened. Preliminarypreparationofaluminumwireconsistsofapplyingtothesurfaceof PVC - plastisol, whichundernormalconditionsisliquid, butheatingupto 180 °C, freezesandturnsintoplasticwithhighphysicalandmechanicalpropertiesandalsochemic alresistance. Installationiscarriedoutinsuch a waythatthepartsdonotoverlapeachotherandarenotincontactwitheachother, theyarelocatedatthesamedistancefromthecathodes.

Inthisdiplomaproject, forthepurposeofobtaininginformationonthevalueoftheinvestigatedparametersofthea nodizingprocessandautomaticadjustmentofthevaluesoftheseparameterswithinthelim itsprovidedbythenormsofthetechnologicalregime, a systemofcontrolandmeasuringdevicesandcontroldevicesisincluded.The main parameters that were controlled:

- temperature
- leveloftheelectrolyte

- concentrationoftheelectrolyte
- currentdensityandvoltage

Intheprocessofanodizingaluminumanditsalloys, suchoperationsasdegreasing, etching, lightinganddirectanodizingoccur, whichisaccompaniedby a significantamountofflushingwater. So, it's important to clear the water from the ions of heavy metals and toxic chemical products. In this project a combined method of sewage treatment has been selected, including the reagent method of the ion exchange method.

Disposal and neutralization of effluent takes place in a special building of a treatment plant containing reservoirs, where the solutions and special reagents are constantly added.

In this production sulfuric acid from the anodizing bath, sodium hydroxide from the etching bath, nitric acid from the bath of lightning and Cr^{6+} ions from the sealing bath should be neutralized.

The waste containing Cr^{6+} ions requires separate cleaning. The processing takes place in two stages:

1. Chromium recovery (□) to trivalent chromium (□), which occurs in the tank of chromium-containing wastewater using a reagent-reducing agent Na_2SO_3. Completeness of recovery depends on the pH value, which should be within 2…2,5. This usually requires acidification, which produces 10 ... 15% sulfuric acid. When processing chrome-containing effluents, the following reaction occurs:

   $$Cr_2O_7^{2-} + 3SO_3^{2-} + 8H^+ \rightarrow 2Cr^{3+} + 3SO_4^{2-} + 4H_2O$$

2. Chromium deposition (□) in the form of hydroxide in a separate tank of the neutralizer by reaction:

   $$Cr^{3+} + 3OH^- \rightarrow Cr(OH)_3 \downarrow$$

From the tank-neutralizer, the drainage enters the reservoir, where the separation of sludge and water passes, which then goes on to further purification.

In addition, the flocculant is added to the settling tank to facilitate the process of depositing particles. Polyacrylamide acts as a flocculant.

From the solution of degreasing to the sewage also fall aluminum ions AlO-, which precipitate when neutralized at the stage of displacement of wastewater:

$$AlO_2^- + H^+ + H_2O \rightarrow Al(OH)_3\downarrow$$

Acid-alkaline effluents come into the tank of the drive, where there is a partial neutralization, by the reaction:

$$H^+ + OH^- \rightarrow H_2O$$

From the tanks of drives, as noted earlier, water enters the tank-neutralizer, which feeds the alkaline agent (10% NaOH) to prove the pH to 5,0 ... 5,8. In the reactor, in the process of neutralization reaction, the formation of insoluble metal hydroxides occurs:

$$Me^{2+} + 2OH^- \rightarrow Me(OH)_2$$

Next, wastewater enters the tank, where the flocculant is added. From the settling tank, the moist sludge comes to the press filter, and the water is fed to the neutralizer.

In the neutralizer of purified sewage water, where water is mixed with acid-alkali drains and chromium-containing effluents, acid is supplied to obtain a pH close to neutral. The sludge after dehydration is removed in special containers and exported from the plant site. Thanks to the separate cleaning of chrome drains, a simpler removal of chromium from the sludge is possible.

After neutralization in sewage there are anions of strong acids SO_4^{2-}, NO_3^- and the anions of weak acids PO_4^{3-}, therefore, purification of water by the method of reverse osmosis Before installing a reverse osmosis, a mechanical filter with a throughput up to 1 μm is installed. The placement of the filter will last when the reverse osmosis installation is used. The water obtained after cleaning in the installation can be returned to production and reused.

Also, the required performance of the installation of reverse osmosis for the production program is calculated.

For the economical part the main technical and economic parameters f of anodic coating on aluminum alloy parts and the full cost of production were calculated.

- The cost is 217.52 uah / m^2 a year;
- the profit is 457 572 uah per year;
- the investments are 2 644 934 uah;
- the profitability is 17%;
- the period of return on investment is 5.7 years.

Such a result indicates the ability to satisfy the consumer's need and get profit out of it.

Onthebasisofthedevelopedproject, itwasfoundthattherearеharmfulsubstancesintheproduction, aswellasthefollowingtypesofenergyarepresent: electric, thermalandmechanical. Inaddition, duetothepresenceofequipmentontheworkofthenoiseandvibration, whichisalso a negativefactorintheworkingenvironment.

Afteranalyzingallthedangerousandharmfulfactors, measuresweretakentoensuresafeworkingconditionsandfiresafety.

To reduce the amount of harmful substances released into the working area and their impact on workers, the following safety measures are foreseen:

1. Baths in which gaseous substances are formed equipped with on-board suction cups.

2. Preparation of electrolytes is carried out only under the hood.

3. To reduce the penetration of electrolytes on the floor, spaces between the baths are equipped with special fluoroplast canopies.

4. To ensure the minimum removal of the electrolyte, the operator operates over the bath for a time enough to maximize the drainage of the electrolyte from the parts.

5. To reduce the removal of the electrolyte, a bathtub is also provided after anodizing and sealing (due to the presence of Cr^{6+}).

To ensure the protection of people from electric current, the following measures are taken:

1. Individual protection of personnel, which is represented by special dielectric gloves, also has rubber mats, and tools are used only with insulating handles.

2. There is a clear control over the integrity of the isolation, with the presence of a preventive examination.

3. There is a protective shutdown of electrical installations.

4. Regular safety instructions are provided.

In the event of a fire, a fire extinguishing system is provided, which includes sandboxes and foam fire extinguishers at workplaces, in addition there are internal fire cocks that are part of the fire water pipeline and automatic fire alarm. In the event of a fire, a safe evacuation of people through evacuation exits is provided, and doors in the rooms open towards the exit.

The equipment must be wiped off from dust and dirt, which can cause heating of parts of the equipment, and as a result of the flare of combustible substances and the occurrence of a fire.

The roof of the building is protected from lightning by using a lightning rod.

Keywords: anodizing, oxide film,aluminum, sulfate electrolyte, anode, cathode, galvanic bawastewater.