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Поступила 16.08.2000

Summary

The experimental results of examination of the optical emission of microwave plasma discharge in oxygen, performed in order to determine the spectral lines, peculiar to the process of the plasma chemical removal of the photoresist masks, are submitted. It is determined, that due to the specific manifestation of the "loading" effect when processing the silicon substrates in the microwave plasma discharge, the control of the process of removing photoresist from small batches of substrates should be performed by controlling the intensity fluctuations of the strip CO ($\lambda=519,82$ nm), and in case of processing the large quantity of substrates – as per the line OI ($\lambda=777,7$ nm; $\lambda=844,6$ nm).

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Introduction

The practice of anodizing, or controlled oxidation, of aluminum and aluminum alloys is more than seven decades old. The primary intent of anodizing aluminum and alloy parts is to protect the highly reactive surface against corrosion in aqueous environments, such as humid air and sea water. Because the anodic coating can be produced in a variety of colors, painted anodized parts are used in architectural applications. Furthermore, because the anodization process produces a hard ceramic coating, many times harder than that of the substrate from which it is formed, anodic coatings are also used to protect aluminum parts from abrasion, especially sand abrasion.

Traditional Anodizing

Traditional anodizing is an electrochemical oxidation process. The part to be anodized is connected to the positive terminal of a Direct Current (DC) power source and a nonreactive metal, such as stainless steel, is connected to the negative terminal. The aluminum part, or the anode, and the stainless steel cathode are immersed in an electrolytic bath and a DC voltage is applied across them. The potential difference is of the order of 20–100 V and the current densities are 1–10 A/dm².

The electrolytic baths comprise aqueous solutions of chromic acid, orthophosphoric acid, sulfuric acid, oxalic acid, or combinations thereof. Because the electrolytic baths have appreciable resistivity and because the anodization process itself is exothermic the temperature of the electrolytic bath increases greatly during anodizing.

Since the anodizing process is quite sensitive to temperature, the bath temperature is controlled rather closely by heat exchanger or refrigeration equipment. Today's advanced anodizing technologies include several proprietary hard anodizing processes that employ a wide range of electrolyte compositions, operating conditions and a limited aluminum alloy compositions.

The type and thickness of coating obtained greatly depends on the composition of the electrolytic bath, operating conditions and alloy compositions. The military specification MIL-A-8625F, for example, alloys for non architectural applications.

Despite the many decades of experience and the expensive equipment employed by the traditional anodizing plants, the acid bath based DC anodizing process has severe limitations.

- By the very nature of the low voltage DC power employed, the anodic coating is quite porous. Often the volume percent of pores is as much as 50%.

- Because of the low current densities employed, it takes many hours to produce a coating of a few tens of micrometers thick.

- The electrolytic baths comprise extremely low pH acidic electrolytes and thus the process does not meet many of today's environmental regulations. The expensive equipment, such as the electric power supplies and heat exchanger, makes the process capital intensive.

- The traditional process, for reasons not quite apparent, cannot be used for anodizing aluminum alloys containing high concentrations of Cu and Si.

- Thus, many aerospace and automotive parts cannot be satisfactorily anodized, if at all.

- The present process, while appropriate for a limited range of the wrought aluminum alloys, cannot be used for anodizing other reactive metals, such as Ti, Zr, Mg, etc., and intermetallic compounds and metal matrix composites. Thus, most of the promising aluminum based advanced alloys and composites cannot be protected by the traditional anodizing process.

- Above all, the hardness of even the so called hard anodic coatings is far below the hardness of alpha alumina, the principal component of the anodic coating. Accordingly, the full strength potential of the anodic layer cannot be realized by the traditional process.

- Indeed, the other potentially beneficial properties of aluminum oxide, such as the high thermal and electrical resistivities and the high dielectric breakdown strength are not even addressed.

This state of affairs is primarily due to the porosity of the coating produced by the traditional acid based electrolytic processes at low power levels, and to certain extent the poor bonding between the aluminum alloy substrate and the anodic layer.

The Microplasmic Process

In recent years, the Microplasmic Corporation, a start up R&D company of Peabody, MA, USA has developed a unique anodizing technology, called the Microplasmic Process for all types of aluminum alloys. It is an electrochemical micro arc oxidation process for which a US patent is pending. A controlled high voltage AC power is applied to the aluminum part submerged in an electrolytic bath of proprietary composition. Due to the high voltage and high current, intense plasma is created by micro arcing at the specimen surface and this plasma in turn oxidizes the surface of the aluminum specimen. Thus the process is called Microplasmic Process. The oxide film is produced by subsurface oxidation and considerably thicker coatings can be produced.

Much as the traditional process, the Microplasmic process is an electrochemical process, but there ends the similarity. The Microplasmic process is radically different from the traditional anodizing processes in many respects. The distinguishing features of the process may be summarized as follows.

- The process employs alkaline electrolytes whose composition is extremely critical to the coating rate and the properties of the anodic film that is formed. The pH of the electrolyte is in the range 8–12 and is thus environmentally sound.

- The process employs Alternating Currents at high voltage and high current. Because of the high voltage, a microplasma surrounds the electrodes and the oxygen ions produced in the plasma diffuse through the anodic film into the aluminum substrate to react and form more anodic film.

- The high voltage and high current allow the production of anodic films of the same thickness as that of the traditional process in a fraction of the time.

- Because the voltages are higher than the breakdown voltage of the film formed, open channels are not necessary for sustaining the process and hence dense thick layers of nonporous film can be readily formed.

- Because the process employs AC power, the productivity is increased.

- The power from an electrical utility supply can be used with proper controls to the electrochemical tank thus making the process less capital intensive. There is no need for power rectification and waveform smoothing.

- The temperature of the electrolytic bath need not be precisely maintained. Indeed, successful coatings can be obtained even if the temperature excursions are as much as 10–20°C, further simplifying the process.

- The electrolytic composition itself is quite variable for different types of coatings.

- Because of the high density of the coating, practically there is no change in the dimension of the anodized part, and a completely finished part can be coated without major post processing finishing operations. The Microplasmic Process, however, produces an outer soft coating of about 15% that may be buffed off; the remaining inner layer, is an extremely hard ceramic layer.

- Above all, unlike with the traditional anodization process, aluminum alloy parts of any composition can be successfully anodized by the Microplasmic Process. Even more importantly, a variety of ceramic "alloy" coatings, such as Al_2O_3 , SiO_2 , Al_2O_3 , MgO , Al_2O_3 , CaO etc. can only be produced by the Microplasmic Process.

- The Microplasmic Process is also suited for a hard coating inside surface of a part i.e. cylindrical, conical or spherical hollow parts. Many coating processes in the market, like CVD, PVD, IVD, PEPVD, Sputtering, Thermal Spraying etc. are unable to coat inside surface of a long part.

Applications

Because the microplasmic process produces a thick, well bonded ceramic coating on a variety of reactive light metal alloys, it can be used for a broad range of applications. The primary application could be the replacement of heavier metallic alloys or the more expensive composite materials required by the aerospace and automotive industries by light metals (e.g., Al, Ti, Mg, and their alloys) coated by the Microplasmic Process. Other applications can be divided into the following categories: Chemical, Mechanical, Thermal, Electrical and Electronics, and combinations of these.

- Chemical: The ceramic coating can resist both aqueous and moderately high temperature and is resistant to strong acids and bases. Thus it can be used in chemical, and food processing industries.

- Mechanical: The hardness of the film is over 1300 kg/mm^2 and thus the film can be used to resist sliding, abrasive and erosive wear. In addition the friction coefficient is low and thus can be used in marginally lubricated systems.

- Thermal: The thermal conductivity of the anodic film is much less than of metals. Thus anodized parts can be used to maintain uniform distribution of temperature and resist thermal shock.

- Electrical and Electronic: The dielectric breakdown strength of the Microplasmic film is comparable to that of alpha Al_2O_3 and hence can be used as an insulating film on electrical and electronic components.

Additionally, the Microplasmic Process is also well suited for hard coating interior surfaces (such as those of hollow cylindrical and conical parts), recesses, blind holes, threaded sections, and so on.

Many coating processes in the market, such as Chemical Vapor Deposition (CVD), Physical Vapor Deposition (PVD), Plasma Enhanced Physical Vapor Deposition (PEPVD), Sputtering, Thermal Spraying, etc. are unable to coat the inside surface of a long part. Thus, where appropriate these expensive coating processes can be readily replaced by the Microplasmic Process.

Received 07.09.2000

Summary

It is an electrochemical micro arc oxidation process is described. A controlled high voltage ac power is applied to the aluminum part submerged in an electrolytic bath in a proprietary arrangement. The oxide film is produced by subsurface oxidation and considerably thicker coatings can be produced.
