(54) Title: SURFACE MODIFICATION OF ALUMINUM ALLOY PRODUCTS FOR MICRO-ARC OXIDATION PROCESSES

(57) Abrégé/Abstract:
This invention relates to an effective method of accelerating micro-arc oxidation processes to form a thick, smooth and modified oxide layer on aluminum alloy products. Said method involves the modification of aluminum alloy products by forming a thin, dense and nonporous alumina barrier layer (or dielectric layer) and a modification substance layer. These two layers coexist and together serve as promoting layers which accelerate the subsequent micro-arc oxidation process.
Abstract

This invention relates to an effective method of accelerating micro-arc oxidation processes to form a thick, smooth and modified oxide layer on aluminum alloy products. Said method involves the modification of aluminum alloy products by forming a thin, dense and nonporous alumina barrier layer (or dielectric layer) and a modification substance layer. These two layers coexist and together serve as promoting layers which accelerate the subsequent micro-arc oxidation process.
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Description of the Invention

This invention relates to a surface modification process of aluminum alloy products using surface treatment techniques to produce a thin, dense and nonporous alumina barrier layer and a modification substance layer which together accelerate the micro-arc oxidation process.

Background of the Invention

Aluminum and its alloys are extremely desirable metals for cookwares, automotive components and machinery parts because they are relatively inexpensive, lightweight (low density) and have good conductivity. However, aluminum is very soft, and consequently has poor wear resistance. As well, it is chemically active, and thus corrodes easily.

Using various surface treatments, the disadvantageous properties of aluminum and its alloys can be improved. For example, a conventional anodizing process to form an oxide layer, followed by a sealing treatment, can be used to improve the corrosion resistance of aluminum. A hard anodizing process can be used to form an oxide film with hardness values up to a maximum of HV 600, drastically improving the wear resistance of aluminum. For this reason, hard anodizing processes are being applied to the production of machinery parts, auto brakes, auto pistons and textile machinery parts. For applications that require higher wear resistance, such as aluminum cylinders and bearings, the hard anodizing process is not sufficient. Therefore, other surface treatments, such as ceramic powder coating, hard chromium electroplating and chemical nickel plating, must be used. However, because these films are different from the aluminum substrate, many difficulties are encountered in the different stages of the manufacturing process, including ineffective bonding between the aluminum substrate and its film.

The recent development of the micro-arc oxidation process has provided a potential solution to these problems. Using micro-arc oxidation processes, a thick oxide film with HV 2000 can be obtained. Until now, an effective, technical and economical micro-arc oxidation process has not been developed and commercially used. This is due to the high consumption of energy through long treatments which use high voltage and high current density. In addition, low energy efficiency and a low coating growth rate have made this process less commercially viable. Furthermore, the oxide layer formed through this conventional method produces a high percentage of a soft, rough and
porous layer which must be removed before using the aluminum alloy product. This further increases the cost of micro-arc oxidation processes.

In this invention, the surface of the aluminum product will be modified prior to the micro-arc oxidation process. As a result, a hard and thick film can be obtained using the micro-arc oxidation process in a very short time. This film is also smoother than that produced through conventional micro-arc oxidation processes, potentially removing the need for any additional machining prior to commercial usage. This will effectively reduce the costs of the process, creating a feasible and economical process. In addition, using this invention, the aluminum oxide film can be modified to contain solid lubricants including graphite, molybdenum disulfide and tungsten disulfide and/or other hardening materials including metal oxides, carbides, borides, nitrides and silicides.

Currently, the only preparation step completed prior to using micro-arc oxidation processing is surface cleaning of the aluminum product. The diluted alkaline electrolyte used contains 1 – 10 g/L metal hydroxides, such as sodium, potassium, calcium or magnesium, in addition to 1 – 10 g/L metal silicates and aluminates. The pH of the bath is maintained in the range of 8 to 13. Various types of power sources, including DC, pulsed DC, symmetrical AC and unbalanced AC sources are used, resulting in growth rates in the range of 0.5 – 3.0 μm/min.

**Summary of the Invention**

The first step of this invention involves the formation of a thin (50 – 250 Å), dense and nonporous alumina barrier layer (or dielectric layer) through anodizing, electrolytic oxidation, chemical oxidation, physical vapour deposition and/or chemical vapour deposition.

In addition, a modification substance layer, consisting of 5 – 30 μm of metal oxide, carbide, boride, nitride, silicide and/or solid lubricant or composites, is formed on top of the alumina barrier layer using one or more of the following techniques: anodizing, electrolytic and/or chemical process, physical vapour deposition, chemical vapour deposition, and powder spray techniques. The modified product then undergoes micro-arc oxidation, reaching an appropriate voltage (450 – 600 V) in the micro-arcing region within the preset short time (usually the first minute) and maintaining this voltage range for the duration of the process. Using this process, a thick, smooth and modified oxide layer is formed within a short period of time.
The alumina barrier layer and modification substance layer coexist and both serve as promoting layers to accelerate the micro-arc oxidation process. Therefore, the micro-arcing region can be reached and maintained within a short time without damaging the aluminum substrate through high energy arcing due to high voltage and high current density. This process is different from conventional micro-arc oxidation processes which use low current density; high voltage and low duty cycle; or apply a high current density within the first minute then drop it to reasonable levels. Applying a low current density requires a longer period of time to reach the effective micro-arcing region during the micro-arc oxidation process. Applying a high voltage with a low duty cycle will prevent plasma damage; however, the low duty cycle will reduce the oxide film growth. Applying a high current density within the first minute followed by a drop to the low preset current density will also prevent plasma damage but the growth rate is still low because a high current density is not maintained.

In addition to more effective micro-arc oxidation, the existence of the modification substance layer mentioned in the invention provides many useful functions. First, it provides a micro-arc fusing substance which will absorb the localized energy during the process, thus protecting the aluminum substrate from plasma damage. Second, in the local micro-arcing area, this modification substance layer will locally fuse and solidify and thus incorporate constituents of the electrolyte and promote oxide growth. Third, any modifying substances within the modification substance layer can be permanently incorporated within the aluminum oxide layer during micro-arc oxidation processing. This can be used to provide permanent lubricating or hardening effects, for example. Fourth, using this method, the surface of the oxide layer after micro-arc oxidation processing will be smoother, denser and harder, potentially removing the need for any additional machining.

In practical applications of this invention, the barrier layer and modification layer formation can be done in a single treatment or multiple treatments. For example, in one treatment of conventional anodizing, an alumina barrier layer of approximately 100 – 150 Å and a porous modification aluminum oxide layer of 5 – 30 µm can be formed for the succeeding micro-arc oxidation process.

The following three examples illustrate the versatility of the modification process. The first example describes a method of forming an alumina barrier layer and porous modification layer in a single conventional anodizing process for Al 319 cast alloys. Example 2 describes a two-step process: first, conventional anodizing is used to form a barrier layer and porous Al₂O₃ layer
followed by electrolytic tin deposition. This porous Al₂O₃ layer, together with the tin deposits, forms a composite as the modification substance layer. Example 3 describes a three-step process: first, electropolishing is used to form an alumina barrier layer. Next, a M.B.V. conversion coating process is used to form a boehmite + solution anion (e.g. CrO₄, PO₄). In the third step, a graphite powder is applied to the top of the boehmite + solution anion surface to form the composite as the modification substance layer. These three examples describe modification processes which are followed by micro-arc oxidation processes using a pulsed DC power source, 100% duty cycle and 1 – 2 kHz frequency.

Example 1:
An Al 319 cast cylindrical specimen, 5 cm in diameter and 8 cm long, was cleaned. The specimen went through a conventional anodizing process for 25 minutes using an 18 wt% sulfuric acid solution at 15V. The specimen was rinsed with water before undergoing a micro-arc oxidation process in a solution containing 2 – 3 g/L KOH and 2 – 5 g/L Na₂SiO₃. The power was switched on and raised to 550V within the first minute and maintained this constant voltage for 5 minutes. At the end of the process, the electric power was switched off; the specimen was disconnected from the anode, removed from the electrolyte tank, cleaned with warm water and dried with warm air. A smooth oxide coating with average thickness of 110 μm was measured along the curved edge of the specimen.

Example 2:
An Al 6061 cylindrical bar sample, 5 cm in diameter and 8 cm long, was cleaned and put through a conventional anodizing process at room temperature using an 18 wt% sulfuric acid electrolyte for 30 minutes, resulting in a total oxide film (barrier and porous) of 20 μm. The specimen was rinsed thoroughly with water before undergoing a tin deposition process for 1-3 minutes in a room temperature solution containing 2 – 15 g/L stannous sulfate, 10 – 20 g/L sulfuric acid and 8 – 12 g/L tartaric acid. The specimen was rinsed again before undergoing the micro-arc oxidation process. The voltage was raised to 560 – 570 V within the first minute and maintained for 5 minutes in the electrolyte described in Example 1. A smooth oxide coating with average thickness of 120 μm was measured along the curved edge of the specimen.
Example 3:
An Al 6061 cylindrical bar sample, 5 cm in diameter and 8 cm long, was cleaned and put in a solution of 80% phosphoric acid and 10% n-butyl alcohol at 50 – 60°C for electropolishing. Depending on the applied voltage, a barrier layer of 50 – 100 Å can be formed. The specimen was rinsed with water before undergoing a 1 – 5 minute chemical conversion coating process using a M.B.V. solution of 3% sodium carbonate and 1% sodium chromate. Afterwards, graphite powder, a solid lubricant, was applied to the top of the surface before undergoing the micro-arc oxidation process. The voltage was raised to the micro-arc region at 500V within the first minute and maintained for 5 minutes. A smooth oxide layer with average thickness of 125 µm was found. Under microscope examination, graphite was found to be imbedded within the oxide layer, providing a permanent self-lubricating effect.
Claims

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method for producing a coating on aluminum and aluminum alloy products comprising the following order of operations:
   (a) forming a thin, dense and nonporous alumina barrier layer having thickness of 50 – 250 Å on the surface of aluminum and aluminum alloy products;
   (b) forming an additional modification substance layer of metal oxides, carbides, borides, nitrides and/or silicides, and/or graphite, molybdenum disulfide, tungsten disulfide, boron nitride and tin metal, having thickness of 5 – 30 μm on top of the said alumina barrier layer;
   (c) processing the modified aluminum and aluminum alloy products using micro-arc oxidation in the micro-arching region of 450 – 600 V.

2. The method as recited in claim 1 wherein the alumina barrier layer is formed by using anodizing, electrolytic oxidation, chemical oxidation, physical vapour deposition and/or chemical vapour deposition.

3. The method as recited in claim 1 wherein the modification substance layer is formed by using anodizing, electrolytic and/or chemical process, physical vapour deposition, chemical vapour deposition and/or powder spray techniques.

4. The method as recited in claim 1 wherein the alumina barrier layer and modification substance layer are formed by using a single or multiple treatments.

5. The method as recited in claim 4 wherein conventional anodizing is used to simultaneously form an alumina barrier layer and modification substance layer in one treatment.