Anodizing of Ti and Ti Alloys for Different Applications: A Review

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Abstract— Titanium has low density, high strength to weight ratio and excellent corrosion and wear resistance. When titanium is suspended in an electrolytic bath as an anode and a current is passed through the bath, oxygen is produced at the anode surface. This oxygen combines with the titanium to form titanium oxide. The interference taking place between the oxide and light results in the appearance of colors on the metal surface and oxides with different thickness generate different colors. This passive oxide film formed on titanium surface is responsible for its high corrosion resistance. Thus it has wide range of applications in aerospace, automotive and biomedical industries. This paper presents a review of pure anodized titanium and its alloy, to evaluate optimum conditions of anodizing treatment for different application that is when various parameters of anodizing process are changed such as time of anodizing, bath composition and voltage are changed.

Keywords: Titanium, Passive Oxide Film, Anodizing Treatment, Aerospace, Biomedical Applications

I. INTRODUCTION

Titanium is a chemical element with the symbol Ti and atomic number 22. It is a lustrous transition metal with a silver color, low density, and high strength. The two most useful properties of the metal are corrosion resistance and strength-to-density ratio, the highest of any metallic element [1]. Pure titanium is ductile, about half as dense as iron and less than twice as dense as aluminium; it can be polished to a high lustre. The metal has a very low electrical and thermal conductivity and is paramagnetic (weakly attracted to a magnet). Two crystal structures exist: below 883 °C (1,621 °F), hexagonal close-packed (alpha); above 883 °C, body- centred cubic (beta). Titanium is important as an alloying agent with most metals and some nonmetals. Some of these alloys have much higher tensile strengths than does titanium itself. Titanium has excellent corrosion resistance in many environments because of the formation of a passive oxide surface film. No noticeable corrosion of the metal occurs despite exposure to seawater for more than three years. Its combination of high strength, low density (it is quite light in comparison to other metals of similar mechanical and thermal properties), and excellent corrosion-resistance make it useful for many parts of aircraft, spacecraft, missiles, and ships. It also is used in prosthetic devices, because it does not react with fleshy tissue and bone. Although at room temperatures titanium is resistant to tarnishing, at elevated temperatures it reacts with oxygen in the air [2].Though Titanium is well known as one of the most corrosion-resistant metals, it can suffer corrosion attacks in some specific aggressive conditions. To further increase its corrosion resistance, it is possible either to modify its surface, anodizing is the best treatment. [3]

Anodizing is one of the easiest techniques for modifying the thickness, composition and morphology of oxides appearing on valve metals, such as aluminium and titanium. The treatment involves anodically polarizing a metal to a fixed voltage in an electrochemical cell containing a counter electrode and an electrolyte providing conduction. Common electrolytes are acids, such as H2SO4 and H3PO4, and salts, such as (NH4)2SO4, Na2SO4 and NH4BF4 [3].

The main parameters affecting the characteristics of the resulting oxides are as follows:

– Current density of anodization
– Anodizing voltage
– Duration
– Electrolyte composition, pH, concentration and temperature
– Agitation of the solution
– Chemical composition and surface finishing of the electrode.[3]

Anodized film of Titanium offers different spectrum of colors from Grey-Brown Blue-YellowPink-Violet-Teal Green-in different baths such as NaOH, KOH, Chromic Acid, H2SO4, Coke, H3PO4, NaH2PO4, and Na2HPO4.[4,5]

II. LITERATURE REVIEW:

Anodizing is an electrolytic oxidation process for thickening the oxide layer on active titanium metals[6]. Anodic oxidation is a surface improvement technique for implants which is very cheap, and also enables the formation of uniform coatings on the surface[7]. Passive layers which are formed during anodic oxidation are more stable than oxide layers which are formed on the alloy surface in contact with air [8]. These metal surfaces are covered by a very thin oxide layer in contact with air. This very thin layer of high porosity and low mechanical strength cannot protect metal against corrosion [9].The oxide layer thickness is directly related to anodizing voltage so that by increasing the voltage the anodic film thickness increases [10]. Thecolors formed on titanium surface after anodizing are known as interference colors [17]. There is no pigment associated with the production of these colored surfaces. Accordingly, two theories were stated to explain for the self-color formation during anodizing of titanium on its surface as follows:

– Color formation can be due to stoichiometric defects in the oxide layer composition.
– Color formation can be due to the interference of waves in crystalline layers. [11]

Now it is specified that the main cause of formation of color is the interference of waves in transition oxide layer of titanium [12,13]. Colors formed on titanium parts after anodizing are known as interference colors [10].

At different voltages applied the thickness of titanium oxide film are varied. The higher the voltages applied, are the thicker film. The different thickness of titanium oxide film causes the variations of refractive index and reflective index which produces various colors of anodized titanium, as shown in fig.1 [21].

Fig. 1: Titanium Spectrum at different voltage ranges

Fig. 2. shows that the anodic current density increases with increasing applied voltage. A very high current density was noticed initially. The rate of reduction in current density with time is very fast at the beginning; it slows down gradually and becomes near to constant at the later stages. A voltage greater than 80 V frequently resulted in streaking and pitting of the coating [10].

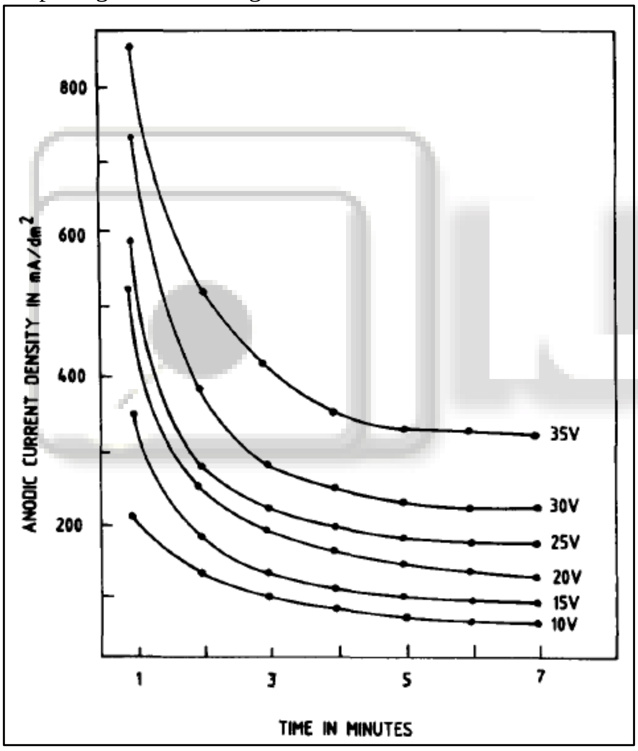

Fig. 2: Variation of anodic current density with time for various applied voltages, electrolyte, 165gl^{-1} H_2SO_4: Temperature 23°C.

The current density-time curves for titanium anodizing at constant Voltage at temperatures of 15, 23, 30, and 38 C are shown in fig 3. As expected, at higher temperatures the anodizing current density tends to be higher owing to the higher conductivity of electrolyte [18, 19]. At Temperatures greater than 50°C, the bath draws an unusually higher Current and the coating obtained is often patchy and discontinuous, probably because of the etching action of electrolyte [19]. The preferable temperature range for titanium anodizing is 15-38°C. [10]

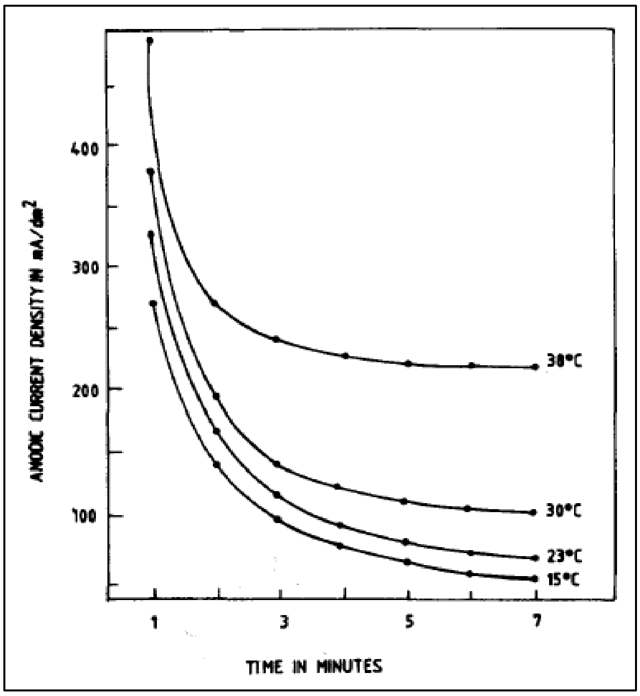

Fig. 3. Variation of anodic current density with time for various operating temperatures: electrolyte, 165gl^{-1} H_2SO_4: voltage 15V

The oxide coatings obtained in sulphuric acid electrolyte are highly stable. The humidity, repetitive heating, thermal cycling and thermovacuum performance tests do not affect the physical and optical properties of the coatings. These coatings are therefore extremely suitable as a thermal control surface for space applications. [10]

III. PROCEDURE OF ANODIZING

A. Cutting and polishing:

Pure Titanium and titanium-Tantalum Alloy plates were used. They were smoothed by abrading with fine emery paper. The specimen was washed with distilled water and polished in alumina suspensions [15]. They were then washed with distilled water and finally dried in a stream of hot air. Final etching of the substrates with HF solution and the washing and drying procedures were repeated just before use.

B. Degreasing:

Solvent degreasing is a process used to prepare a part for further operations such as electroplating or painting. Typically it uses petroleum, chlorine or alcohol-based solvents to dissolve the machining fluids and other contaminants that might be on the part. Solvent degreasing is a process in which a cleaning agent is applied directly to the surface by spraying, brushing or wiping. This process removes oil, grease, dirt, loose particles and any other contaminants that may exist on the surface of the material [15].

C. Electrolytic cleaning:

Electrolytic cleaning is a method of removing soil, scale or corrosion products from a metal surface by subjecting it as an electrode to an electric current in an electrolytic bath. It is a form of electroplating that can be applied to all electric conductive materials. The electrolytic method is cheap and effective, causing minimal alteration to the metal surface [15].

D. Acid Pickling:

Pickling is a metal surface treatment used to remove impurities, such as stains, inorganic contaminants, rust or scale from ferrous metals, copper, precious metals, Titanium alloys and aluminum alloys.

E. Water Rinsing:

Water rinsing results in removal of loose dust, stains, scales present on the surface of the metal after various other pretreatments are performed on it.

F. Anodizing:

Anodizing is an electrolytic passivation process used to increase the thickness of the natural oxide layer on the surface of metal parts.

The process is called anodizing because the part to be treated forms the anode electrode of an electrolytic cell. Anodizing increases resistance to corrosion and wear, and provides better adhesion for paint primers and glues than bare metal does. Anodic films can also be used for several cosmetic effects, either with thick porous coatings that can absorb dyes or with thin transparent coatings that add interference effects to reflected light.

Anodizing is also used to prevent galling of threaded components and to make dielectric films for electrolytic capacitors. Anodic films are most commonly applied to protect aluminum alloys, although processes also exist
\for titanium, zinc, magnesium, niobium, zirconium, hafniu m and tantalum. (14)

The treatment involves manipulation of the natural oxide layers on the metals to produce thicker and more durable films. When applied thinly, anodized films also tend to cause light interference resulting in attractive surface patterns and multicolor effects.

Oxide formation on the surfaces of metals is a naturally occurring phenomenon that results from exposure to oxygen and moisture in the air. Although oxidation on ferrous metals, also known as rust, can cause the eventual destruction of the material, metals such as aluminum alloys, zinc, titanium, magnesium and tantalum can benefit from an oxide layer. If manipulated to be thick enough, these oxidative layers can offer corrosion and wear resistant properties to these metals. This is the principle that underpins the anodizing process used to impart protective and attractive finishes on many non-ferrous metal items.
Figure 4 shows the anodizing process setup.

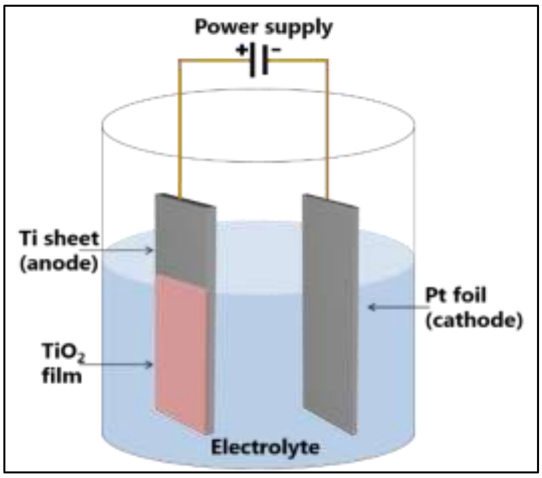

Fig. 4: setup for anodizing process

Anodizing is divided in 3 major types:

1) Sulphuric Acid Anodizing

It Embraces anything from heavy duty black dyed coatings for high-tech instruments to cheap colored ashtrays, expected to last in a pub for a few weeks. It also includes architectural anodizing primarily for protecting aluminum window frames etc from the elements. The natural color of these films is light gray; other colors are achieved by dyeing the film. [15]

2) Hard Anodizing

It is a branch of sulphuric acid anodizing where process conditions have been pushed in a certain direction to achieve significantly harder, thicker, denser films. Applications involve resistance to wear, corrosion, temperature effects etc. [15]

3) Chromic Acid Anodizing

It produces coatings of exceptional corrosion and chemicalresistance for its film thickness in an electrolyte, which is non-corrosivetowards aluminum. These coatings are thin, and relatively soft andgenerally only used in specialized applications [15].

G. Hot water sealing:

Anodizing changes the microscopic texture of the surface and the crystal structure of the metal near the surface. Thick coatings are normally porous, so a sealing process is often needed to achieve corrosion resistance. [14]
In hot water sealing, sample after anodizing process directly dip into hot distilled water at around 80-85^{0}C for 2-3 minutes [10].

IV. APPLICATION OF ANODIZED TITANIUM

Anodizing has a long history in the aerospace industry, where it was first used in 1923 to protect British seaplane parts from salt-water corrosion. Aerospace companies continue to use anodizing processes today to protect metals from effects of aging, wear and corrosion.

There are two commonly used types of titanium anodizing: Type 2 and Type 3. Type 1 is far less common, and is used in specialized high-temperature treatments.

Type 2 is mainly for wear purposes: It protects the metal surface against the effects of wear. When untreated titanium parts rub against each other, they produce titanium dust – a result that is not desirable with orthopedic implants, for example. Type 2 anodizing provides a wear-resistant surface and helps prevent seizing or friction between sliding titanium surfaces.

For aerospace applications, Type 2 anodized parts are compatible with aircraft fluids and can withstand extreme temperatures within a range of -70 °F to 260 °F. Type 2 anodized titanium resists corrosion from exposure to salt water and humidity.

Fig. 5: Anodized Ti engine part of aircraft

Fig. 6: Anodized Ti engine parts of aircraft

Type 2 anodized titanium parts are a distinctive gray color. This makes them easily distinguished from stainless steel, or from color anodized titanium.

Fig. 7: The middle screw is made of Type 2 anodized titanium.

Type 3 titanium anodizing is also called color anodizing. Color coding of components and devices greatly reduces errors in assembly or use. In medical and dental applications, color coding for size allows instant recognition of needed parts when time and accuracyare critical. Orthopedic implants, dental implants, medical instruments and device components can be coded with standardized or specialty colors to increase efficiency during surgery.

Fig. 8: Color anodized Ti implants and medical devices

In aerospace or other highly technical applications, color coding provides unambiguous identification of parts for ease, speed and accuracy of assembly.

Outside the medical device and aerospace industries, Type 3 colored titanium is also used in jewelry manufacturing.

Fig. 9: Anodized Ti jewelry

V. SUMMARY

In this paper, a summary of anodizing process for pure Titanium and its alloys is reviewed for its applications in different fields, for example aerospace, military and Biomedical industries. Optimum process parameters are reviewed and it has been found that anodic current density is increasing with increasing applied voltage for a constant value of the electrolyte temperature and to decrease with decreasing electrolytic temperature for constant value of the applied voltage. Colors of anodized titanium are voltage controlled or voltage dependent. Many vivid colors of titanium can be obtained by means of anodizing through changing voltage applied. With growing potential, the chromatic scale that can be achieved consists of the following order of colors: brown/ yellow – blue/light blue – gold -fuchsia/purple. This paper also discuss different steps in anodizing titanium and finally its applications.

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