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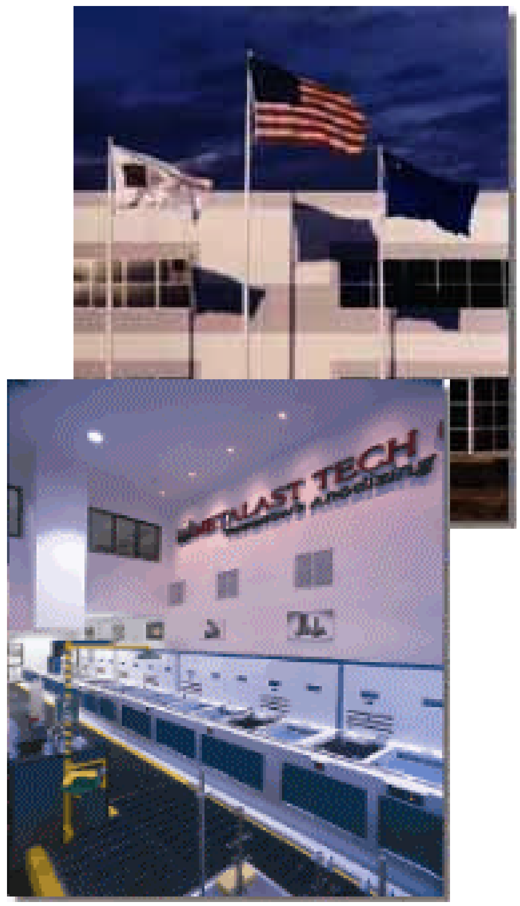
TECHNICAL BULLETIN

Titanium Anodizing

An in house evaluation by
METALAST International, Inc.



http://www.metalast.com

METALAST Tech Center
2241 Park Place
Minden, NV 89423
775-782-8324
fax: 775-782-1008

Abstract

Titanium is anodized for both decorative and functional purposes. When titanium is anodized in acidic, neutral, and mildly basic solutions a very thin (0 to 200nm) nonporous, transparent oxide is produced. The oxide is transparent, but the parts have vivid rainbow-like colors due to interference coloring. Anodizing in strongly alkaline solutions can produce coatings up to several microns which can be used to prevent galling and increase corrosion resistance. The oxide thickness is primarily voltage controlled. However, other factors such as material, pretreatment, anodizing solution chemistry and temperature, load size, anode:cathode ratio, anodizing time, and tank configuration affect the color of the part making it difficult to predict and control the resultant color.

Background

Titanium is anodized for various purposes: [1,2] 1) to provide a decorative finish 2) to protect metal from atmospheric corrosion 3) to reduce the friction on sliding surfaces (i.e. to prevent galling) and 4) to provide thermal control. Titanium is relatively easy to anodize and a variety of electrolytes can be used from strongly acidic to strongly basic.[3] Anodizing in acidic, neutral, and mildly basic solutions produces a very thin (0 to 200nm) decorative coating. Anodizing in strongly alkaline solutions can produce coatings up to several microns.[4]

The color of the anodized titanium is produced by interference colors.[5] A thin layer of titanium oxide is produced during the anodizing process. White light falling on the oxide is partially reflected and partially transmitted and refracted in the oxide film. The light that reaches the metal/oxide surface is mostly reflected back into the oxide. Several reflections may take place. A phase shift occurs during this process along with multiple reflections. The degree of absorption and number of reflections depends on the thickness of the film. The light that was initially reflected from the oxide surface interferes with the light that has traveled through the oxide and been reflected off the metal surface.

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Depending on the thickness of the oxide, certain wavelengths (colors) will be in-phase and enhanced while other wavelengths will be out of phase and dampened. Hence, the observed color is mainly determined by the oxide thickness.

Literature reports that the oxide thickness is determined by the applied voltage with a growth constant of 2-3 nm per volt.[6] At any given voltage the oxide film grows to a specific thickness and then stops when the resistance increases to a point where no current is being passed. The phenomenon of voltage-controlled oxide thickness indicates that the color is also voltage controlled.

The following table, taken from reference 7, lists the color spectrum of anodized titanium along with the applied voltage and calculated oxide thickness. Samples were anodized in 165 g/L sulfuric acid at 23 ˚C for 4-5 minutes.

Applied voltage (V)	Color	Calculated film thickness (Å)
2	Silver	
6	Light brown	241
10	Golden brown	362
15	Purple blue	491
20	Dark blue	586
25	Sky blue	702
30	Pale blue	815
35	Steel blue	926
40	Light olive	1036
45	Greenish yellow	1147
50	Lemon yellow	1246
55	Golden	1319
60	Pink	1410
65	Light purple	1573
75	blue	1769

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Process Parameters and Facility Requirements

The titanium metal needs to be cleaned and deoxidized prior to anodizing. An inhibited alkaline cleaner can be used to clean the parts. The deoxidizing step requires a mixed acid solution with either ammonium bifluoride or HF. The deoxidizing step is critical since the color and uniformity of the final finish are dependent on the concentration of fluoride and the immersion time in the deoxidizing solution.

Titanium can be anodized in any solution that is capable of carrying current. Common solutions used include: 200 g/L sulfuric acid, 5% trisodium phosphate, and 5% sodium bicarbonate (baking soda). A solution of 200 g/L sulfuric acid and 10 g/L oxalic acid produces parts with uniform color.

Cathode material should be titanium with twice as much cathode to anode.

Anodizing can be performed at room temperature, but the temperature of the anodizing solution should be controlled to ± 2˚C to obtain reproducible colors.

A DC rectifier is required with an output of 100 V and amperage based on the load size. Current densities of 20 A/ft^2 may be required. Parts are run by ramping up to a determined voltage and leaving the part at that voltage for a few minutes.

The maximum voltage primarily determines the color of the part. However, process control is difficult because other factors affect the color such as: material and finish, deoxidizing, temperature, anode:cathode ratio, load size, anodizing time, and tank configuration.

Advantages/Disadvantages

The color of anodized titanium is brilliant with an iridescent quality. The color will not fade or wear off since it is produced by the physical phenomenon of light scattering off the oxide and metal surface. However, any coating placed on top of the oxide, such as finger prints, will affect the color.

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Titanium metal is highly corrosion resistant, but tends to gall. Proper anodizing of titanium increases its corrosion resistance and prevents galling.

The biggest limitation of anodizing titanium is the difficulty of obtaining process control. The deoxidizing step is critical for the final appearance of the part, so the fluoride concentration and immersion time need to be constantly monitored. The anodizing process is voltage controlled, but the final color also depends on the quantity of current passed through the part and how quickly the current passes through the part. Thus, part size, load size, and tank configuration greatly determines the color of the part. Any variation in operating parameters (tank chemistry, solution temperature, ramp times, etc.) can produce an oxide that differs slightly in thickness, however, a difference in thickness of only 10 nm produces parts that can be drastically different in color.

Anodic Film Properties

Anodizing in acidic, neutral, and mildly basic solutions produces a very thin (0 to 200nm) decorative coating. Anodizing in strongly alkaline solutions can produce coatings up to several microns.

Applications

Due to its lightweight, high strength-to-weight ratio, and ability to withstand high temperatures (up to 900 ˚C)[7] titanium and its alloys have many applications in the aerospace industry. However, full utilization of titanium is limited due to its tendency to gall and seize and its reactivity to atmospheric oxygen. Anodizing titanium decreases galling, improves corrosion resistance, and provides stable optical properties to its components. These characteristics make anodized titanium an ideal material for space applications.

Excellent corrosion resistance makes this metal desirable for chemical and food processing, medical applications such as implants and surgical hardware, and marine environments.

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Decorative anodizing can be used to color code tools and hardware according to size and type and for jewelry and hobby items (bicycles, golf clubs, paint guns, etc.).

References

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