Advances in Selective Plating: Deposition on Titanium Alloys

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The surface of titanium 6Al-4V alloy was electrochemically treated to increase surface area, reduce the oxide film and apply immediately an adherent metallic coating by brush plating. The electrochemical pretreatments anodically etched and microroughened the surface, while the cathodic treatment reduced the oxide. A nickel strike electrolyte was flowed directly into the anode - cathode gap to displace the pretreatment solution while the titanium surface was maintained under cathodic potential control to prevent reformation of titanium oxide. The nickel strike layer plated on the treated surface had good adhesion and provided a substrate for subsequent deposits. The electrochemical treatments and nickel plating induced negligible hydrogen embrittlement in the titanium alloy substrate tested in accordance with General Motors Engineering Standards, GM3661P.

Keywords: *Selective plating, brush plating, plating on titanium, plating on titanium 6Al-4V*

Introduction

The high strength and low weight of titanium, along with the tenacious compact surface oxide film which readily forms, makes it beneficial for use in many applications in the aerospace, industrial and medical fields. The strength, hardness and working temperature of titanium is further improved by alloying. One of the alloys finding particular utility in these fields is the titanium 6% aluminum, 4% vanadium alloy, 6Al-4V.

The use of titanium and titanium alloys in mechanical engineering applications is limited, because of poor tribological properties such as poor adhesive wear resistance, resulting in galling and cold welding, poor fretting behavior and high coefficient of friction.[1] The tribological performance can be improved by applying surface treatments and coatings while retaining the desirable attributes of the underlying substrate. Coatings on titanium are also applied for the purposes of heat reflection, emissivity, corrosion resistance in hot acidic environments, conductivity, lubricity, brazing and resizing.

Electrodeposition is an effective method for applying a coating on a metal. In order for an electrodeposited coating to have optimal adhesion to titanium, the oxide layer should be removed. Titanium is intrinsically very reactive, so whenever the metallic surface is exposed to air or any environment containing available oxygen, the oxide film is formed.[2] The tenacity of the oxide layer makes its removal problematic. A common method to remove oxide from titanium is exposure to an acid fluoride-containing electrolyte.[3] The toxicity of fluoride and the rapidity with which the oxide reforms after removal are issues with this method.

A major factor determining adhesion between two materials is surface area. Surface roughening of titanium is carried out by abrasion, grit blasting and etching. However, quickly reformed oxide after these treatments reduces adhesion. Titanium surface preparation techniques are a key to achieving robust adhesion of the coating to titanium.[4]

Selective brush plating is a metallization technique which utilizes a small volume of solution contained in a fabric matrix between the anode and cathode in a plating cell. The small volume of solution and proximity of the anode and cathode enables procedures and techniques to be utilized which are impractical with other electroplating or coating methods.

Experimental

Titanium sheets 1.1 mm thick and tubes 0.83 mm thick were obtained from Tico Titanium and United Titanium. The titanium substrates tested were titanium 6Al-4V, titanium 6Al-6V-2Sn and commercially pure Grade 2 titanium. The sheets and tubes were used in the as-received condition. The surfaces were mechanically finished prior to deposition as part of the surface preparation techniques investigation. The mechanical treatments were dry or wet abrasion with red 3M Scotch-Brite®, wire brushing and abrasive blasting with aluminum oxide and silicon carbide.

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The chemicals used to formulate surface preparatory solutions and plating baths were reagent grade without further purification. Deionized water was used for solution makeup and rinsing. The nickel strike layer was applied using an acid nickel sulfate plating solution.[**] The rectifier was a SIFCO model SPL-75, capable of being switched rapidly between cathodic and anodic modes.

The anode was a noble metal-coated titanium mesh supported by a polypropylene block. Holes drilled through the block allowed solution to flow through the anode structure onto the workpiece. The anode-to-cathode gap was determined by the thickness of the fabric matrix between the anode and cathode. The gap was approximately 5 mm (~0.2 in.). The fabrics evaluated included red, brown and grey 3M Scotch-Brite®, cotton, polyethylene terephthalate and gauze.

Adhesion of the plated metal to the titanium substrate was tested following the procedures given in Aerospace Material Specification AMS 2451A and ASTM B571. Adhesion was evaluated using the chisel-knife, tape, quench and bend tests. The titanium sheets were bent 180° around a diameter equal to the thickness of the sheet in the bend test. The part was quenched from 250°C (482°F) into RT water. The tape was pulled with a quick motion at a 180° angle to the surface. A sharp cold chisel used to penetrate the coating. A good result in each of these tests shows no separation of plating from the basis metal. The tensile adhesion of a 50-μm thick nickel coating on titanium 6Al-4V was measured following ASTM C633 using adhesive EC2086. The interface between titanium and plating was examined in cross-section with a Nikon Epiphot microscope. A Mahr PS1 stylus profilometer was used to measure roughness.

Results and discussion

The titanium alloy, the acid type and concentration, and the pretreatment conditions impact the adhesion of an electrodeposited coating to pure titanium and its alloys. One objective of the research work was to develop a fluoride-free electrolyte which could effectively treat titanium. Sulfuric, nitric, sulfuric/nitric mixtures, sulfamic, ammonium bifluoride and phosphoric acid at various concentrations were evaluated. Visible oxide films formed during the anodic treatment in some of the acid solutions which could not be cathodically reduced. The presence of the film coincided with poor deposit adhesion.

Figure 1 shows a nickel deposit plated on titanium Grade 2. Figure 1 is representative of the issues involved with obtaining adherent coatings on a titanium surface. The Grade 2 titanium surface was blasted with 180 grit silicon carbide and activated. This coupon survived tape and bend tests. The separation between the nickel deposit and the substrate, considered to involve the titanium oxide film, makes the adhesion suspect. Nickel was brush plated over the oxide film; however, adhesion was poor in localized areas.

Mechanical methods to improve adhesion by increasing the surface area and exposing a fresh, clean titanium surface were tested. Mechanical working of the surface by abrasion with grinding media, wire brushes, or by blasting with silicon carbide or wet or dry alumina increased the surface area. The deposit adhesion was improved versus an unworked surface. The adhesion was not high enough to routinely survive the 180° bend test.

Titanium undergoes active dissolution in strong acids. Acid etching to increase the surface area and remove the oxide film was tested in hydrochloric and sulfuric acids. The surface was matte in appearance after the acid etches. Hydrogen evolution during active dissolution in the acids indicated that the titanium surface was free of oxide. Low deposit adhesion was observed on the chemically-etched titanium surfaces.

Research was undertaken to identify an electrochemical treatment method for use with titanium which had the capability to increase the surface area in a controlled manner and provide an oxide-free surface that enabled good deposit adhesion. The electrochemical treatment included both an electrolyte and an anodic/cathodic etch/activate methodology to promote microetching of the titanium surface to increase surface area and reduce the surface oxide.

The electrochemical treatments anodized the titanium surface to microetch / roughen it. This was immediately followed by a cathodic treatment in the same solution to reduce oxide and then immediately followed by replacing the pretreatment solution with a nickel strike plating solution. The electrochemical treatments were carried out under potential control. Mixtures of sodium chloride, nickel salts, and hydrochloric and citric acids were identified which met the objectives of an etch/activate electrolyte. The nickel strike and buildup were plated using the acid nickel sulfate brush plating solution.

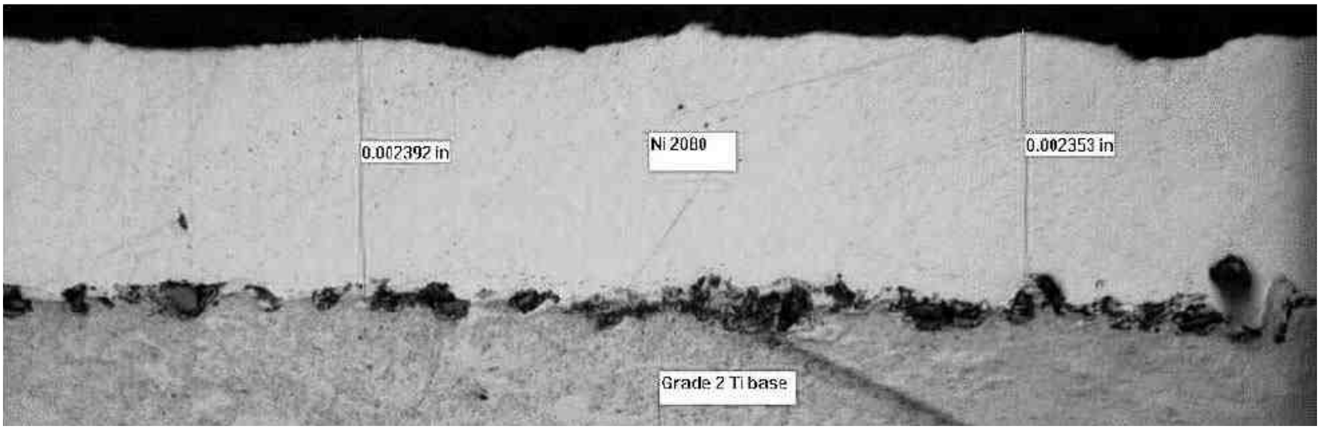

Figure 1—*Cross-sectional photomicrograph of a nickel deposit plated on a nickel strike layer which shows separation at the interface between titanium Grade 2 and nickel strike.*

[**] *SIFCO 2080/5600, SIFCO Applied Surface Concepts, Independence, OH.*

Table 1
Brush plating process for producing the nickel coatings on titanium 6Al-4V shown in Fig. 2

Step	Operation	Material	Conditions
1	Abrade	Scotch-Brite®	Wet with Etch/Activate Solution
2	Etch	Etch/Activate Solution	14V anodic, 10 sec
3	Activate		4 - 8V cathodic, 1 min
4	Strike Plate	Acid Nickel	8 - 18V cathodic, 0.078 A-hr/cm^2

Figure 2 shows a cross-section of a brush plated nickel coating on a Ti 6Al-4V coupon. The interface between the titanium and nickel is free of the bulk oxide. Figure 2 shows that the smooth surface of the original titanium was microetched during pretreatment. Nickel plated readily into the microroughness features. The adhesion was checked by tape and bend tests. The nickel deposit did not separate from the titanium 6Al-4V substrate during tape or bend tests. Thin panels of 6Al-4V and 6Al-6V-2Sn titanium alloys broke in one 180° bend without separation or peeling of the deposit. Grade 2 titanium can be bent a full 180° without breaking. The bend test was more rigorous in revealing low adhesion than the tape test.

Several factors contribute to the excellent adhesion exhibited by the structure in Fig. 2, including mechanical interlocking, increased surface area and lack of an oxide film. These three attributes were generated during the brush plating process. Brush plating is particularly suited for generating these three attributes due to the small volume of electrolyte, to close contact between the anode and the cathode, and to the rapidity with which electrolytes can be switched from activation to strike plating.

The plating procedure used to make the deposit in Fig. 2 is given in Table 1. Important considerations for this process are to keep the titanium under potential control at all times, keep the plated area 100% covered by the wrapped anode, use rapid switching from anodic to cathodic, allow no rinsing between steps, and do not reuse the solution.

Tests produced further understanding of the chemistry and process to activate the titanium surface. The scale on the rolled panels had to be removed mechanically. Abrasion of the panel was a must for good adhesion in the absence of blasting. Grit blasting, wire wheel abrading, grinding and abrasive pad rubbing were effective in preparing the surface for the etch/activate process. A machined surface requires little in the way of mechanical work prior to etch/activate. Deep scratches are to be avoided during abrasion as these can develop pits in the anodic etch.

A rinse is not included between the process steps in Table 1. When the titanium surface is removed from the electrolyte the oxide film readily forms in either air or water which interferes with the adhesion between the deposit and the substrate.[4] The solutions in this work are compatible and a water rinse between the process steps is not required. A final rinse is carried out to remove electrolyte components after the plating process is complete.

Figure 3 shows scanning electron microscope images of the titanium 6Al-4V surface after each of the process steps. Rolling lines are evident on the as-received panels, Fig. 3a. Abrasion replaced the rolling marks with a new mechanical finish, Fig. 3b. The effectiveness of the anodic etch is shown in Fig. 3c. At the high magnification, micron and sub-micron size etch features are observed in the surface. These represent good anchoring points for subsequent deposits. Figure 3d shows the cathodically-activated surface on which the oxides are reduced and a flash of nickel is plated. The subsequent nickel strike layer shown in Fig. 3e is dense with a slightly nodular morphology.

The change in surface roughness by each of the surface treatments was measured with a mechanical profilometer. Data in Table 2 shows that although the panels had a rolling direction, the average roughness was similar in both directions. The Scotch-Brite® abrasion decreases the roughness slightly. The roughness is increased by the anodic etch step. The anodic etch induced microroughness is a key component in attaining good deposit adhesion to the titanium 6Al-4V panel.

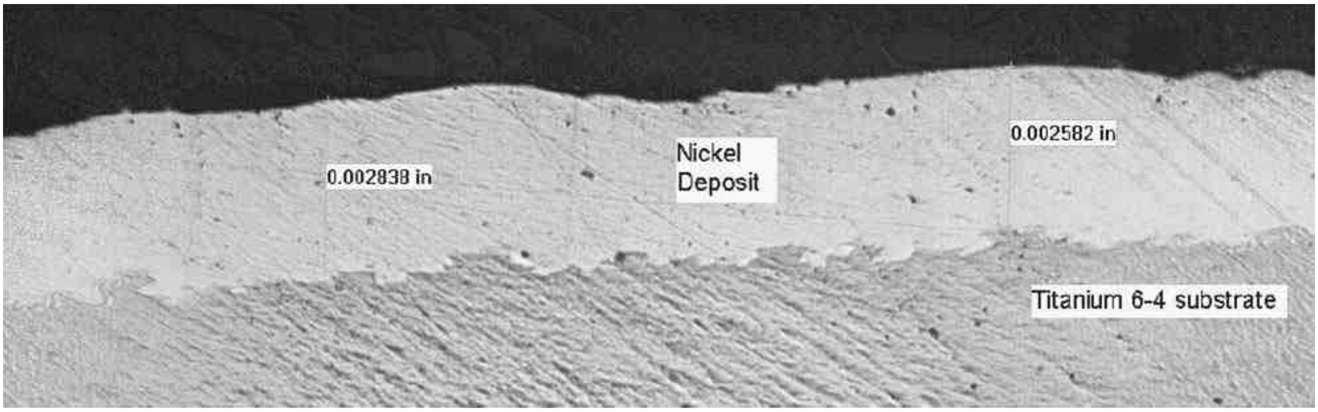

Figure 2—*Cross-section photomicrograph of nickel deposit on titanium 6Al-4V. Titanium surface etch/activated by procedure in Table 1.*

Table 2

Surface roughness of titanium 6Al-4V panels after each of the surface treatments measured with a stylus profilometer

	Average Roughness, R_a (μm)	
	Machine Direction	Cross-machine Direction
As received	0.7	0.8
Abraded	0.5	0.4
Etched	5.8	5.0
Activated	6.6	3.7
Strike Plated	1.4	2.1

The activation step designed to reduce the oxide formed during the anodic etch reduces the surface roughness. The average R_a of the machine and cross-machine directions after activation is somewhat lower than the average R_a after etching. A slight smoothening of the surface morphology is seen in Fig. 3d. The roughness of the plated layer seen in Fig. 3e is more a function of the nickel brush plating parameters when the surface is microroughened to the morphology shown in Fig. 3c.

The interface between the deposit and titanium alloy substrate was examined using a scanning electron microscope. The microroughness is evident in Fig. 4. The anodic etch creates reentrant structures in the titanium alloy surface into which the nickel strike plate is deposited. The lack of a bulk oxide film on the titanium is also evident. Any sign of separation between the two metals is also lacking.

The tensile adhesion of nickel to titanium 6Al-4V was measured following ASTM C633. The average values measured on multiple stubs is reported in Table 3. The surfaces of the titanium 6Al-4V stubs were pretreated by machining or SiC grit-blasting, then abrading, etching and activating, using the process in Table 1. A 50-μm thick nickel deposit was plated from two acid electrolytes. The failure mode in all specimens was adhesive, at the nickel coating - titanium interface. Of note, the grit-blasted surface did not increase the tensile adhesion versus the machined surface. The bond strength did not depend on the type of acid nickel plating solution used for the strike plate and buildup.

Hydrogen embrittlement was tested by performing General Motors Engineering Standard GM3661P, "Determination of Hydrogen Embrittlement by Static Loading." A sustained test load in bending of 85% of the yield is applied to the part for 24 hr. Titanium 6Al-4V coupons predrilled with a 0.25-in. diameter hole for a stress riser were plated on one side with 15 μm (0.0006 in.) of nickel using the process in Table 1. The coupon under load is shown in Fig. 5. Six coupons were plated, three were tested as-plated and three were heat treated at 190°C (375°F) for 24 hr prior to test.

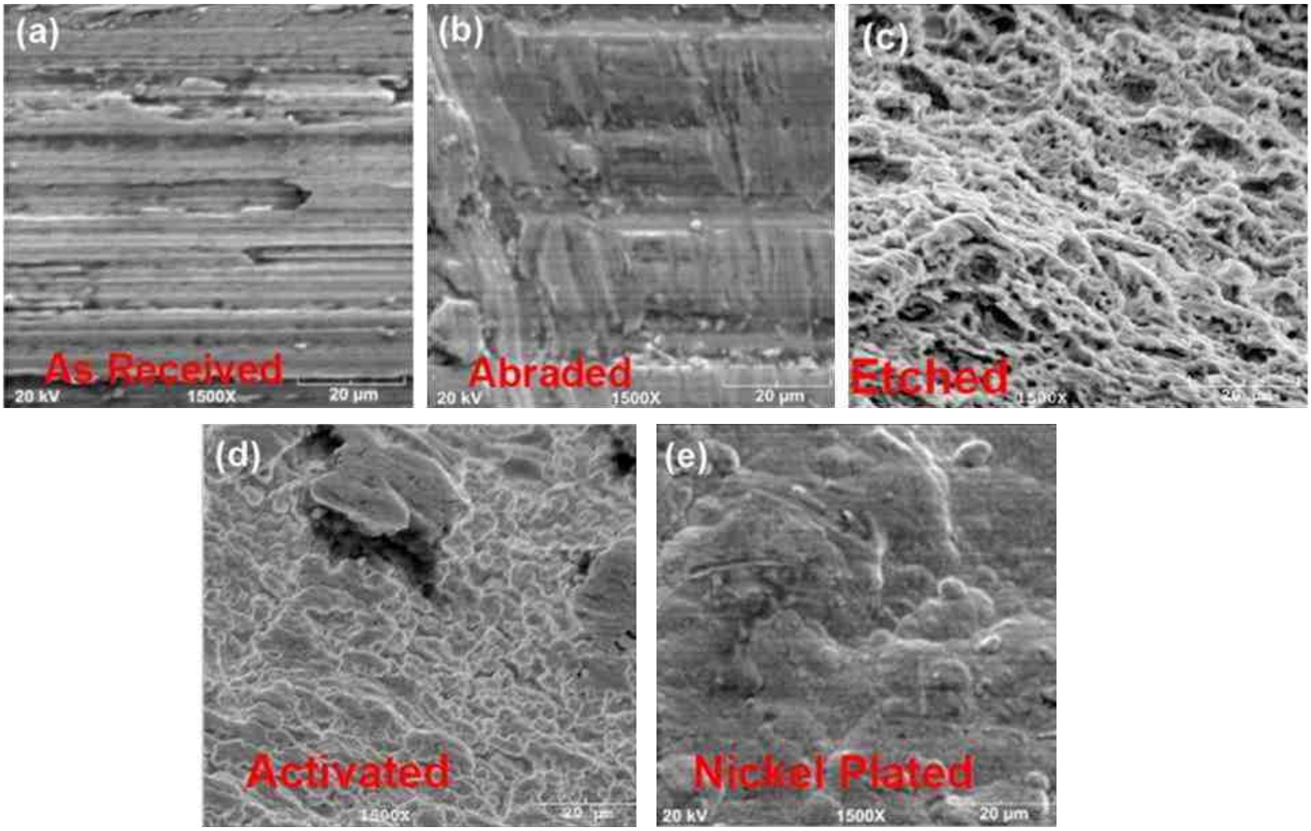

Figure 3—*Scanning electron microscope images of the titanium 6Al-4V panel surface at 60° tilt after individual process steps, (a) as received, (b) Scotch-Brite™ abrasion, (c) anodic etch, (d) cathodic activate and (e) nickel plating.*

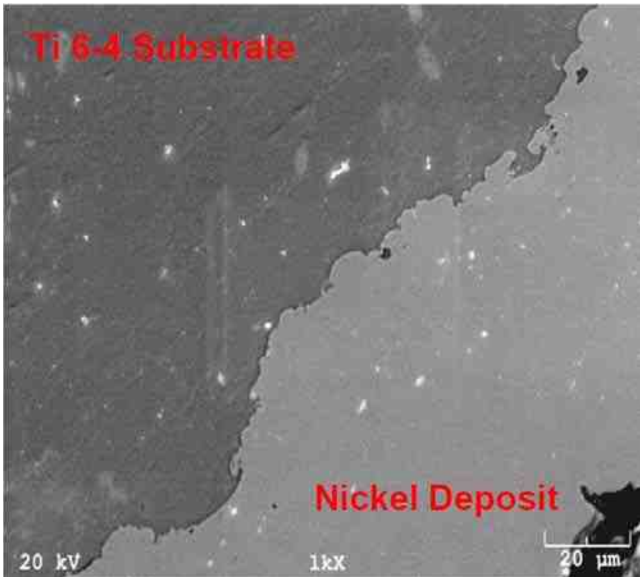

Figure 4—*Scanning electron microscope image of the interface between Ti 6Al-4V and nickel strike plate.*

No failure or cracking was observed on the three tested as-plated coupons or the three coupons tested after heat treatment. All samples were satisfactory for hydrogen embrittlement to specification GM3661P. If the test samples withstand the applied load for 24 hr, for the particular part and process conditions evaluated, the embrittlement effect of hydrogen is considered negligible.

This technology was tested with the Ti-6Al-6V-2Sn titanium alloy. Deposit adhesion to the tin-containing alloy was satisfactory, passing bend and tape tests. This technology was found to be ineffective with commercially pure Grade 2 titanium. It does not provide adequate adhesion. Deposit adhesion on Grade 2 generally passes tape but fails bend tests. A wide range of parameters and chemistries evaluated did not microroughen and activate Grade 2 titanium.

The titanium alloys appear to perform differently than Grade 2 during the anodic etch. The alloys microroughen while a thin visible oxide film forms on Grade 2. The film persists through the cathodic activation. Commercially pure titanium appears to passivate more quickly than the alloys, compromising adhesion. It is speculated that the alloying constituents are more prone to dissolution during the anodic etch than titanium, leading to the microroughened surface morphology.

A principle benefit from researching plating on titanium is to improve surface properties. A duplex coating electroplated on Ti-6Al-4V is shown in Fig. 6. The Ti-6Al-4V substrate was prepared by the process in Table 1, applying a 35-μm thick (0.0014 in.) nickel layer. The nickel plated Ti-6Al-4V was then brush plated using an acid copper electrolyte to a thickness of 350 μm (0.014 in.). This structure was then machined to reduce the copper roughness. No delamination of copper from nickel or nickel from Ti-6Al-4V was observed due to the stresses imposed during the machining operation. The exposed copper was then brush plated with a 60-μm thick (0.0024-in.) nickel cap. This duplex coating structure is often used to repair surface defects.

Table 3

Average tensile adhesion of nickel deposits on titanium 6Al-4V

Surface	Acid Nickel Strike Plate Solution	Adhesion	
		N/mm^2	lb/in^2
Machined	Sulfate	51	7,400
Blasted	Sulfate	45	6,500
Blasted	Sulfamate	46	6,600
EC2086 Epoxy		>90	>13,000

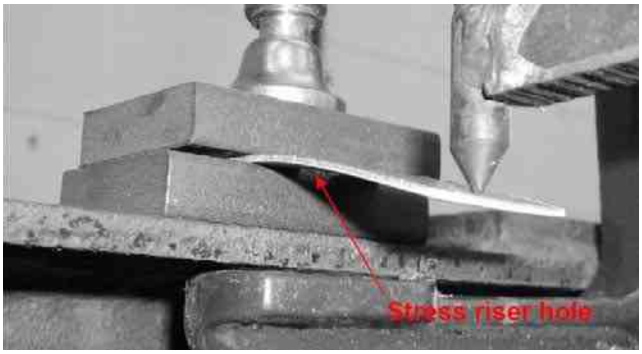

Figure 5—*Ti 6Al-4V coupon under cantilever load at 85% of yield for 24 hr.*

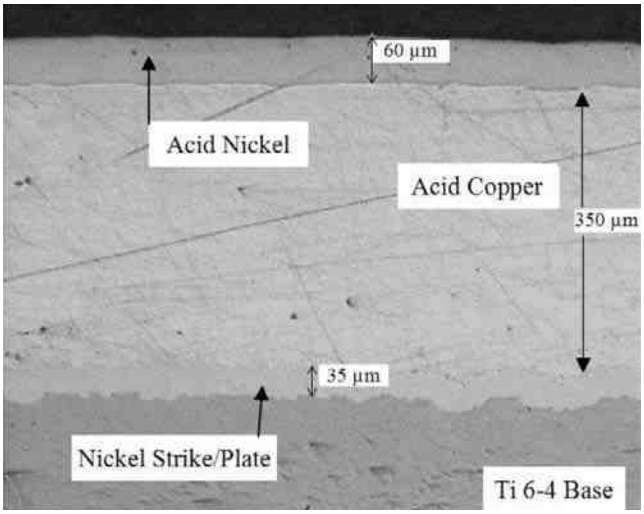

Figure 6—*Duplex coating Ni/Cu/Ni on Ti 6Al-4V.*

Conclusions

The application of adherent brush plated coatings onto titanium alloys Ti-6Al-4V and Ti-6Al-6V-2Sn was demonstrated using a special brush plating technique. The surface pretreatments of mechanical finishing, followed by anodic etching, cathodic activation, and plating a thin layer of nickel effectively prepared the surface. The surface was kept under potential control at all times during the electrochemical pretreatments. The anodic etch microroughened the surface which increased surface area. Cathodic activation reduced oxides formed during the anodic cycle. The etch and activation were performed in the same acid chloride electrolyte.

Future work

Future research work should look for the underlying principles for the good adhesion to the titanium alloys and improve it. The work should use this knowledge to identify a process to deposit coatings with improved adhesion on Grade 2 titanium. Deposition of other materials which have improved tribological performance onto the nickel-coated titanium 6Al-4V should also be investigated.

References

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About the authors

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Finishers' Think Tank

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Analysis

Most commercial zincate baths can be analyzed by the titration method. Usually the alkalinity is determined in one titration and metals (based on zinc) in a second titration. Replenishment is based on the analysis results. In standard operations, drag-out losses, coupled with vendor advice on bath depletion per surface area zincated, can fine-tune replenishment additions.

Testing for quality adhesion

Post-plate baking at 450°F (232°C) for one hour is followed by a cold water quench. Edge grind and peel back. Saw grind. Standard aluminum Q panels are processed in the cycle as a control.

Problems and corrections

Problem	Cause	Correction
Streaked, uneven zincate	A. Additives out of balance	Analyze, make adds
With poor adhesion	B. Bath temp. out of range	Adjust
A & B not effective	C. Surface preparation	Evaluate each step
Parts gas in zincate	Insufficient desmutting	Adjust or replace desmut
Spongy, poor adhesion	Excess zincate dip time	Adjust

The structure of the zincate film is detrimentally affected by drag-in of excessive aluminum, chromium, lead and fluoride.

Some tips for good operation and preventive maintenance

- Make chemical adds to each process bath, as established, on a regular basis.
- Do not exceed the optimum service life of the surface preparation baths.
- Where possible, know the alloy designations of aluminum processed.