Electrochemical Surface Preparation of Passive Metallic Substrates for Electroplating

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Abstract

The overall objective of this work is to electrolytically prepare metallic substrates of passive materials for subsequent electrodeposition. The challenge in plating on passive materials such as titanium, stainless steel and nickel–based alloys, is the tenacious oxide film that readily forms on the surface almost instantaneously when exposed to the atmosphere. This is overcome in current practice, through aggressive precleaning steps that often include toxic electrolytes such as nitric, sulfuric and hydrofluoric acids. An alternative surface preparation technique to mitigate the need for aggressive chemicals is presented in this work. The focus of this engineering study was to develop the preliminary understanding required to successfully remove the surface oxide and plate on passive substrates, from an electrolytic benign process.

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Introduction

Titanium has become very popular in recent years as a substrate for electrodeposition due to its strong mechanical properties.[1,2] The high strength to weight ratio of titanium, as well as its excellent flexibility and strong springback characteristics, high temperature performance, corrosion resistance, and biocompability are highly beneficial in a broad array of structural and specialty applications. In addition, its high electrical conductivity makes it a suitable material for the fabrication of current collectors used in fuel cells. However, these applications are limited by the formation of unstable, low conductive oxides on the surface of titanium and its alloys. This problem can be solved with a thin layer of a noble metal on the titanium surface.

The titanium substrate has to be activated before attempting to plate a thin film of any metal on its surface to improve adhesion. The activation of the substrate is achieved with a precleaning process, removing oils, impurities, chemical films and oxides from the surface. Usually, in the industry this precleaning process is achieved using a series of steps which involve the use of toxic and aggressive chemicals detrimental to the environment, such as nitric, sulfuric and hydrofluoric acids.[3,4,5] Therefore, the overall objective of this study was to develop an environmentally benign process to electrolytically plate a nickel strike on a titanium substrate to prepare it for a subsequent electroless nickel boron coating. It is believed that a nickel strike is necessary to ensure adequate adhesion of the nickel boron coating.

Nevertheless, the challenge in plating on titanium is the tenacious oxide film that readily forms on the surface. This is overcome in current practice through aggressive precleaning steps that often include hydrofluoric acid as mentioned above. The focus of this engineering study was to develop the preliminary understanding required to successfully remove the surface oxide and plate a thin nickel strike on a titanium coupon, from a relatively benign process, without reforming the surface oxide. Faraday will rely on the advanced application of pulsed electric fields to mitigate the need for aggressive chemicals.

Faradayic Process

The Faradayic Process is an advanced, non-steady state electrochemical technique that relies on pulsed electric fields (PC/PRC) instead of a constant electric field (DC) to provide enhanced process control without the need for complex chemistries.

A typical waveform consists of a forward voltage pulse held for some duration of time (V_{for} and t_{for}) followed by an off period (t_{off}) where no voltage is applied. For enhanced process control, a reverse voltage pulse held for a set period of time (V_{rev} and t_{rev}) may be necessary. The period of the waveform is the summation of the on times and off time. The frequency is the inverse of the period. The duty cycle is defined as the ratio of the on time to the period. Duty cycles are defined for both the forward, γ_{for}, and reverse, γ_{rev}, pulses. The average voltage, V_{avg}, is defined as:

$$V_{avg} = V_{for}\gamma_{for} - V_{rev}\gamma_{rev} \qquad \text{(Eq 1)}$$

where,

$$\gamma_{for} + \gamma_{rev} \leq 1 \qquad \text{(Eq 2)}$$

The average voltage influences the material removal rate, the dimensional accuracy, and the surface quality. Simple examples of pulsed waveforms are shown in Figure 1.

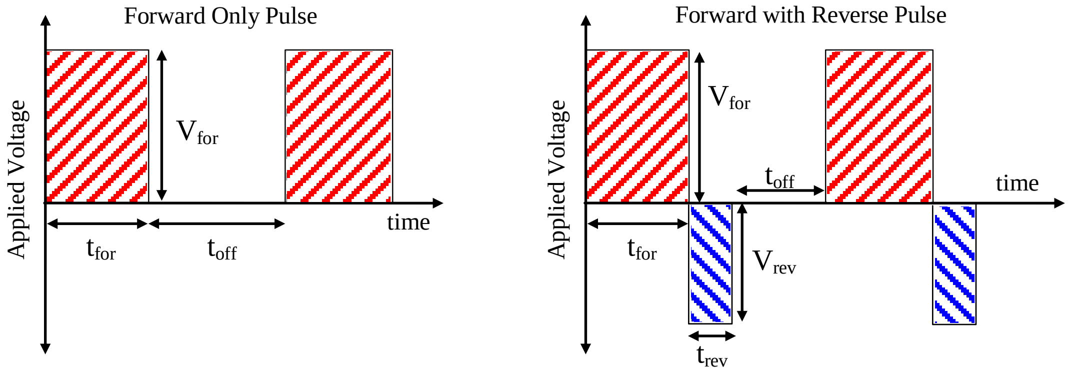

Figure 1. Simple Examples of Pulsed Waveforms

For a given average voltage, traditional DC processes are limited to only one process variable (the steady-state voltage or current). In an electrically mediated process, however, there are nearly an infinite number of process parameter combinations that can provide the desired average voltage. By selecting the appropriate combination of parameters, the mass transport rate, current distribution, and hydrodynamic condition can be strongly influenced during the metal dissolution process.

Oxide Film Control for Passive Materials

In the case of passive materials, the oxide film on the superalloy is self-healing and reforms in the presence of oxygen or even water. Since this passive film has low electrical conductivity and prevents the work piece from a direct contact with the electrolyte, normal anodic dissolution cannot proceed without breakdown of the film. For DC-ECM, high cell voltage is required to breakdown the oxide passive layer. Partial breakdown of the oxide film often occurs which causes pits on the surface. The *Faradayic* Process solves this problem by eliminating the oxide (passive) film rehealing. During the reverse period of the *Faradayic* Process, the work piece becomes a cathode. By properly adjusting the *Faradayic* Process parameters, we can selectively consume the nascent oxygen gas or the oxide film on the work piece by the following reactions:

$$1/2O_2 + 2H^+ + 2e^- \longrightarrow H_2O \qquad (5)$$

$$M(O_x) + 2xH^+ + 2xe^- \longrightarrow M + XH_2O \qquad (6)$$

Therefore, the *Faradayic* Process can reduce/eliminate the oxide film rehealing and eliminate the pits associated with partial oxide film breakdown.[6]

Experimental Procedure

Baseline data was obtained by attempting to directly plate on the as received surface, which would be representative of an aged part. The coupon was plated using a Woods nickel strike bath. The composition of the bath is as follows:

HCl	10%
$NiCl_2$	25%
DI H_2O	65%

The plating cycle delivered a constant current of 1.2 amps, which delivered a current density of approximately 13 A/dm^2. The resulting voltage, which is dependent upon the anode-to-cathode spacing, was approximately 2.6V. For applications such as the trivalent chromium plating efforts at Faraday, the plating cycle is set at 4 minutes. In this study, however, there was a desire to extend the plating cycle to 12 minutes such that a thicker coating is observed. It is believed that this increased coating thickness would not present any unusual plating abnormalities. The coating thickness, as measured via contact profilometry, is between 0.000100 - 0.000150 inch. This thickness is assumed to be constant for all coupons. (See profilometer trace in Figure 1.)

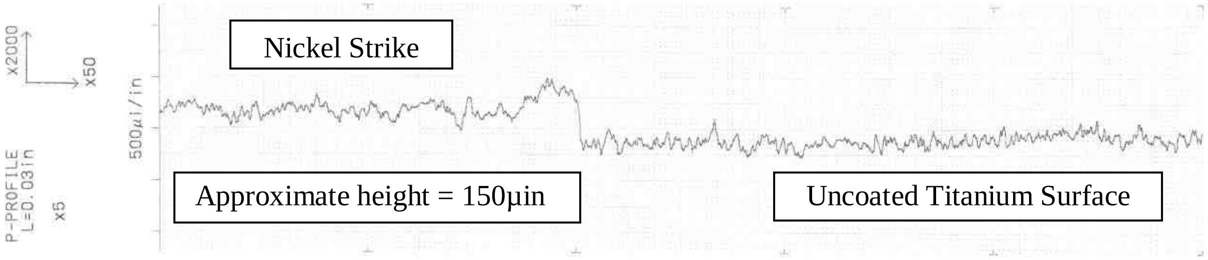

Figure 1: Profilometer trace of baseline coupon to determine nickel strike thickness

Figure 2 is a photograph of the scribe mark put into the baseline coupon. The width of the scribe mark is approximately 0.0007 in. As can be observed in the photo, there is a large amount of delamination of the coating, indicating poor adhesion between the coating and substrate. This result is exactly as one would expect for titanium due to the tenacious oxide film that is present on the surface. The remaining coupons will be characterized in the same manner and compared to these results. Once again, a coating with good adhesive properties would show no delamination along the scribe.

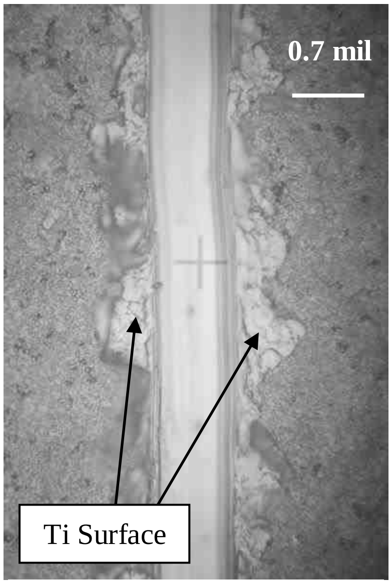

Figure 2: Photograph of Scribe in Baseline Process

Cleaning Process and Nickel Plating

The cleaning process is immediately followed by the nickel-plating operation. The cleaning solution is deaerated by bubbling argon gas into the solution for a minimum of 30 minutes prior to the experiment, as well as during the process itself. The entire setup (cleaning, rinsing, and plating) is located inside a glove bag that is filled with argon. The intent is to minimize any oxide film growth that may occur on the titanium surface after cleaning and prior to plating. Complete elimination is difficult since each bath is aqueous in nature; therefore, they contain all of the necessary requirements for oxide film growth. Furthermore, the nickel strike will tarnish when allowed to dry. This is shown on the samples in this study; however, this can be addressed in a production environment by keeping the nickel coating wetted with DI water between the steps of the coating process.

The cleaning solution is an aqueous, neutral salt solution with the following composition:

NaCl	180 g/L
NaBr	60 g/L
NaF	2.4 g/L

This bath is a published electrolyte to be used in the electrochemical machining of titanium and its alloys.[7] This particular bath was selected because of the presence of F^- ions, which are known to attack titanium and its oxide layer. The remaining constituents are intended to provide adequate conductivity of the solution, since the NaF solubility is quite low. The temperature of the cleaning bath was held at room temperature for all trials in this study. There was no agitation during the cleaning cycle.

The nickel strike will be obtained using a Woods bath (10% HCl, 25% $NiCl_2$, & 65% H_2O), which is a relatively inefficient bath but results in a highly adhesive nickel layer on various steels. This composition may very well not be the optimal plating bath; however, due to the limited scope of this study, it is a bath that Faraday is familiar with since it is used in on-going research in plating functional chrome from a trivalent bath. Prior to plating, the sample and anodes are thoroughly rinsed to prevent contamination of the plating bath. The electric field that was applied is a simple current controlled DC waveform. Pulsed electrolysis may very well improve the coating characteristics; however, the focus of this limited study was to increase coating adhesion through an improved surface preparation technique. The programmed current density was 13 A/dm^2. The temperature of the plating bath was held at room temperature for all trials in this study. There was no forced agitation during the plating cycle.

Results and Discussions

The following table identifies each trial that was conducted for this set of tasks. Note that Trial #4 was the baseline process.

The results of this set of experiments are as follows:

1. The results of Trials 1-3 show delamination during the scribe test in a manner that is similar to the baseline process. This is shown in Figure 3a, which is a photograph of the scribed surface of sample #3. This indicates that a DC voltage of 2.5V (in combination with the duration used in this

study) does not adequately clean the surface prior to plating. In comparison, a combination of 4V and 120 seconds does appear to be enough based on Trial 8 (Figure 3b).

2. The result of Trial 5, shown in Figure 3c, shows delamination consistent with the baseline process. This may indicate that an anodic pulse of 1V is too high and it is detrimental to the plating process. Further investigation, however, would be necessary to validate this claim.

Table 1: Summary of Cleaning Trials

Trial ID	Cleaning Waveform	Duration [sec]	Plating Current Density [A/dm^2]
1	+2.5 VDC	30	16
2	“	120	“
3	“	“	13
4	None		“
5	+4.0V, 95 msec -1V, 5 msec	“	“
6	+4.0V, 50 msec -0.5V, 50 msec	“	“
7	+4.0V, 5 msec -0.5V, 5 msec	“	“
8	+4.0 VDC	“	“
9	+2.5V, 50 msec -0.5V, 50 msec	“	“

Note: In this table, a positive voltage indicates a cathodic charge.

3. In comparison, Trial 6 appears to be slightly better than 7 (shown in Figures 3d and 3e). This indicates that the frequency of the waveform (10 Hz and 100 Hz) may have an influence on the plating results.
4. One of the best results is Trial 9 (see photo in Figure 3f), which is similar to Trial 6 with the only deviation being a smaller cathodic peak voltage.

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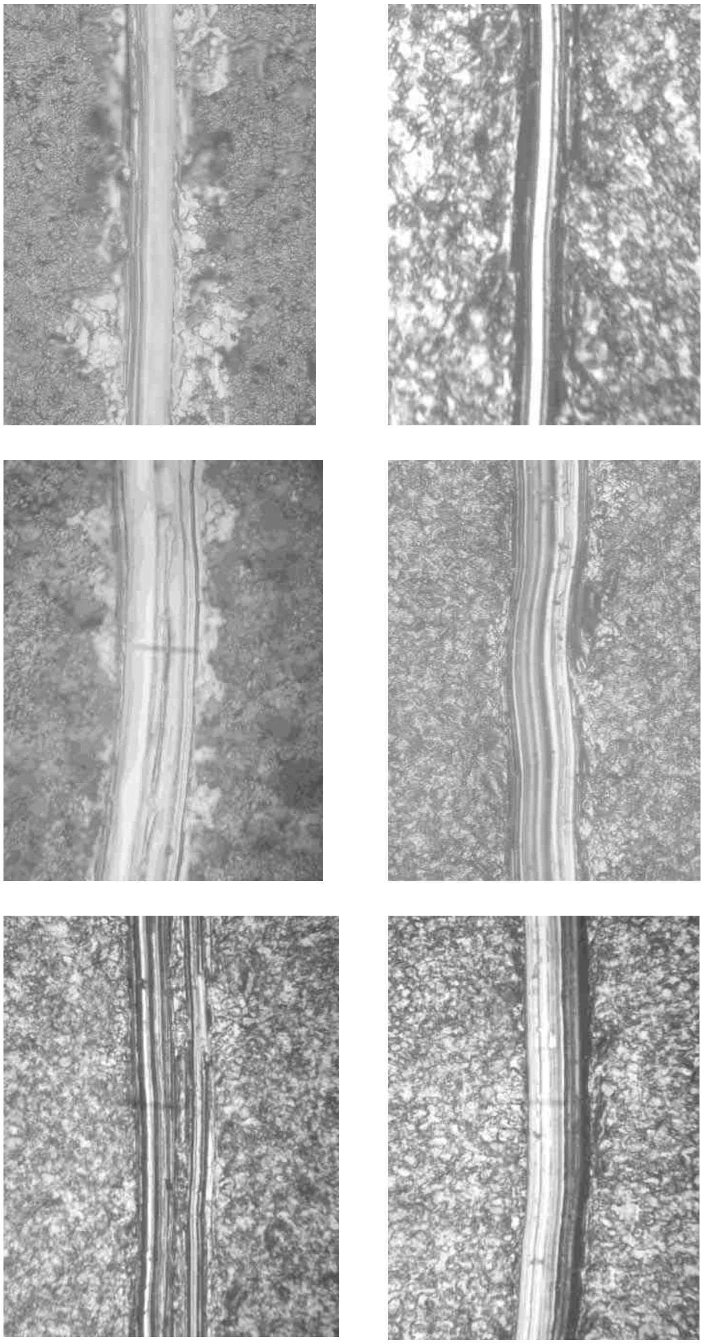

Figure 3. Micrographs of scribes in trials #: a) 3, b) 8, c) 5, d) 6, e) 7 and f) 9. Note micrographs taken at same magnification. Width of scribe mark is approximately 0.7 mils.

Conclusions

The purpose of this engineering study was to demonstrate that a titanium surface could be treated using a relatively benign precleaning process to facilitate the electrolytic plating of an adherent nickel strike. The cleaning process investigated was to apply a predominantly cathodic electric field to the sample while immersed in a water based, salt electrolyte. The shape of the electric field ranged in this study from a simple DC waveform to a square pulse waveform that included both a cathodic and anodic pulse. The samples plated in this study were subjected to a scratch test where the amount of coating delamination at the scribe edge is directly related to the adhesion of the coating. Preliminary results indicate that the cleaning process does indeed improve the adhesive properties of the coating. Furthermore, the application of a pulsed electric field appears to achieve this improvement with a lower peak cathodic voltage when compared to a similar DC waveform.

The challenge associated with applying a cathodic charge to titanium in an aqueous environment is hydrogen pickup, which can cause embrittlement of the substrate. Faraday believes that this effect can be minimized by the periodic application of an anodic pulse, which will consume the nascent hydrogen gas created during the preceding cathodic pulse. By balancing the cathodic to anodic pulse ratio, one should be able to minimize the amount of hydrogen available at the surface of the substrate. In addition, Faraday intends to operate at or near room temperature, which will also reduce the hydrogen pickup rate. Of course, this assumption needs to be validated and is at the heart of further work in this area.

Future Work

As this study was very limited in its scope, there remains a significant amount of work in the fundamental area of this process. The following is a list of short-term goals in the continuation of this work:

1. Define the optimal cleaning bath composition.
2. Conduct an extended matrix of key experimental parameters to better define the operating window of this process.
3. Compare different nickel strike plating bath compositions.
4. Identify the quantitative measure of merit such that the nickel strike characteristics can be compared to those achieved using conventional, aggressive cleaning processes.
5. Measure amount of hydrogen pickup as a function of the applied electric field.

The following is a list of long-term goals in the continuation of this work:

1. Define the optimal nickel strike bath composition.
2. Identify the optimal cleaning process parameters.
3. Develop thermal treatments to eliminate all absorbed hydrogen in the substrate.

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