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Electrochemical Surface Preparation of Passive Metallic Substrates for Electroplating

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The overall objective of this work is to prepare metallic substrates of passive materials electrolytically 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 pre-cleaning steps that often include toxic solutions 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 remove the surface oxide successfully and plate on passive substrates, from a benign electrolytic process.

Keywords: *Electrolytic surface preparation, pulsed waveforms, surface activation, passive metallic substrates*

Introduction

Titanium is a metal that has excellent chemical and mechanical properties. Two of its most popular properties are corrosion resistance and the highest strength-to-weight ratio of any metal. Furthermore, titanium has excellent flexibility, strong springback characteristics, high temperature performance and it is biocompatible. These excellent properties make titanium a suitable candidate not only for structural, but also for specialty applications.

However, sometimes titanium alone does not meet the property requirements of the application and needs to be enhanced by applying a thin film of a different material according to the application. This paper discusses the application of a thin nickel (Ni) layer on a titanium substrate to enable later electroless deposition of a nickel-boron coating. Other specialty applications include the use of titanium as a substrate for the deposition of an active catalyst such as Raney nickel alloys,[1] ruthenium oxide[2] and Mackinawite[3] for the production of hydrogen from water, for supercapacitor applications and for solar energy conversion, respectively.

The main drawback of titanium is that it forms a very thin, passive, low-conductivity oxide layer on its surface, which prevents good adhesion of the electroplated film. Therefore, before electroplating any metal, titanium substrates have to be activated in order to improve adhesion. Activation of the substrate is achieved by performing a pre-cleaning process that consists of removing oils, impurities, chemical films and oxides from the surface. Usually, in the industry pre-cleaning 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.[4] The overall objective of this study was to develop an environmentally-benign process that would remove the oxide layer so that a nickel strike could be plated electrolytically 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 pre-cleaning 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. Our work relied on the advanced application of pulsed electric fields to mitigate the need for aggressive chemicals.

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The *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 the forward, γ_{or}, and reverse, γ_{rev}, pulses. The average voltage, V_{avg}, is defined as:

$$V_{avg} = V_{for}\gamma_{for} - V_{rev}\gamma_{rev} \quad (1)$$

where,

$$\gamma_{for} + \gamma_{rev} \leq 1 \quad (2)$$

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

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 direct contact with the electrolyte, normal anodic dissolution cannot proceed without breakdown of the film. For DC-ECM, a high cell voltage is required to breakdown the passive oxide layer. Partial breakdown of the oxide film often occurs, which causes pits on the surface. The *Faradayic* process solves this problem by eliminating the passive oxide film rehealing. During the reverse period of the process, the workpiece becomes cathodic. By properly adjusting the process parameters, we can selectively consume the nascent oxygen gas or the oxide film on the work piece by the following reactions:

$$\tfrac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \quad (3)$$

$$M(Ox) + 2xH^+ + 2xe^- \rightarrow M + XH_2O \quad (4)$$

Therefore, the *Faradayic* process can reduce/eliminate the oxide film rehealing and eliminate the pits associated with partial oxide film breakdown.[5]

Experimental procedure

Baseline data was obtained by attempting to plate directly 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 was as follows:

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

The plating cycle delivered a constant current of 1.2 A, which delivered a current density of approximately 13 A/dm^2. The resulting voltage, which is dependent on the anode-to-cathode spacing, was approximately 2.6 V. For applications such as trivalent chromium plating, the plating cycle is set at 4 min. In this study however, it was desired to extend the plating cycle to 12 min such that a thicker coating could be observed. We believed that this increased coating thickness would present no unusual plating abnormalities. The coating thickness, as measured via contact profilometry, was between 2.54 and 3.81 μm (0.00010 and 0.00015 in.). This thickness was assumed to be constant for all coupons (See the profilometer trace in Fig. 2.).

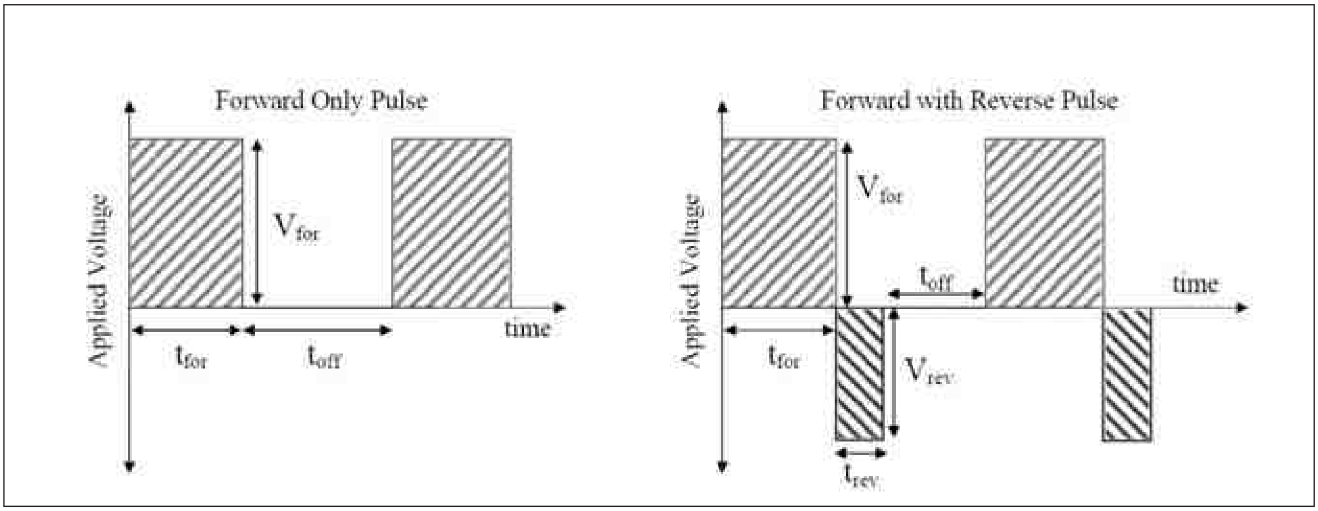

Figure 1—Simple examples of pulsed waveforms.

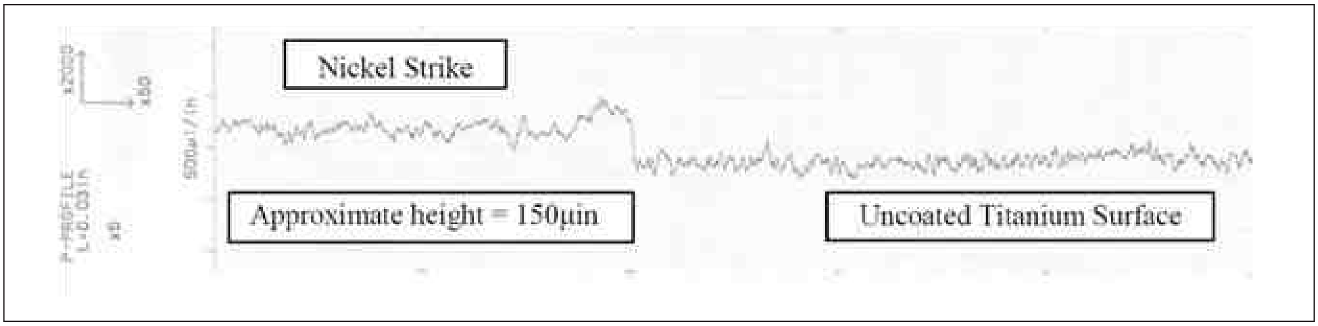

Figure 2—Profilometer trace of baseline coupon to determine nickel strike thickness.

Figure 3 is a photograph of the scribe mark put into the baseline coupon. The width of the scribe mark is approximately 17.8 μm (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 were 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.

Cleaning process and nickel plating

The cleaning process was immediately followed by the nickel-plating operation. The cleaning solution was deaerated by bubbling argon gas into the solution for a minimum of 30 min prior to the experiment, as well as during the process itself. The entire setup (cleaning, rinsing and plating) was located inside a glove bag filled with argon. The intent was to minimize any oxide film growth that may have occurred on the titanium surface after cleaning and prior to plating. Complete elimination was difficult since each bath is aqueous in nature. Therefore, they possessed all of the necessary requirements for oxide film growth. Furthermore, the nickel strike would 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 was 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 commonly used in the electrochemical machining of titanium and its alloys.[6] This particular bath was selected because of the presence of fluoride 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

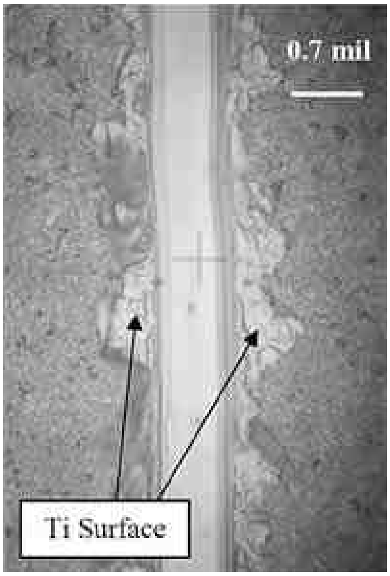

Figure 3—Photograph of scribe in baseline process.

Table 1
Summary of cleaning trials

Trial ID	Cleaning waveform	Duration, sec	Plating current density, A/dm^2
1	+2.5 V_{DC}	30	16
2	+2.5 V_{DC}	120	16
3	+2.5 V_{DC}	120	13
4	None		13
5	+4.0 V, 95 msec; -1.0 V, 5 msec	120	13
6	+4.0 V, 50 msec; -0.5 V, 50 msec	120	13
7	+4.0 V, 5 msec; -0.5 V, 5 msec	120	13
8	+4.0 V_{DC}	120	13
9	+2.5 V, 50 msec; -0.5 V, 50 msec	120	13

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

is quite low. The temperature of the cleaning bath was held at room temperature for all trials in this study. No agitation was used during the cleaning cycle.

The nickel strike was produced from a Woods bath (10% HCl, 25% $NiCl_2$ and 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 optimal. However, due to the limited scope of this study, it is a bath familiar to us as it has been used in other areas of our on-going research.

Prior to plating, the sample and anodes were thoroughly rinsed to prevent contamination of the plating bath. The applied electric field was a simple current-controlled DC waveform. Although pulsed electrolysis may very well improve the coating characteristics, 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 discussion

Table 1 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 were as follows:

1. The results of Trials 1 - 3 show delamination during the scribe test in a manner similar to the baseline process. This is shown in Fig. 4a, which is a photograph of the scribed surface of Sample 3. This indicates that a DC voltage of 2.5 V (with the duration used in this study) did not adequately clean the surface prior to plating. In comparison, a combination of 4.0 V and 120 sec does appear to be enough, based on Trial 8 (Fig. 4b).

2. The result of Trial 5, shown in Fig. 4c, shows delamination consistent with the baseline process. This may indicate that an anodic pulse of 1.0 V is too high and is detrimental to the plating process. Further investigation, however, would be necessary to validate this claim.

3. In comparison, Trial 6 appears to be slightly better than Trial 7 (shown in Figs. 4d and 4e, respectively). This indicates that the frequency of the waveform (10 and 100 Hz, respectively) may have an influence on the plating results.

4. One of the best results was Trial 9 (Fig. 4f), which is similar to Trial 6 with the only deviation being a smaller cathodic peak voltage.

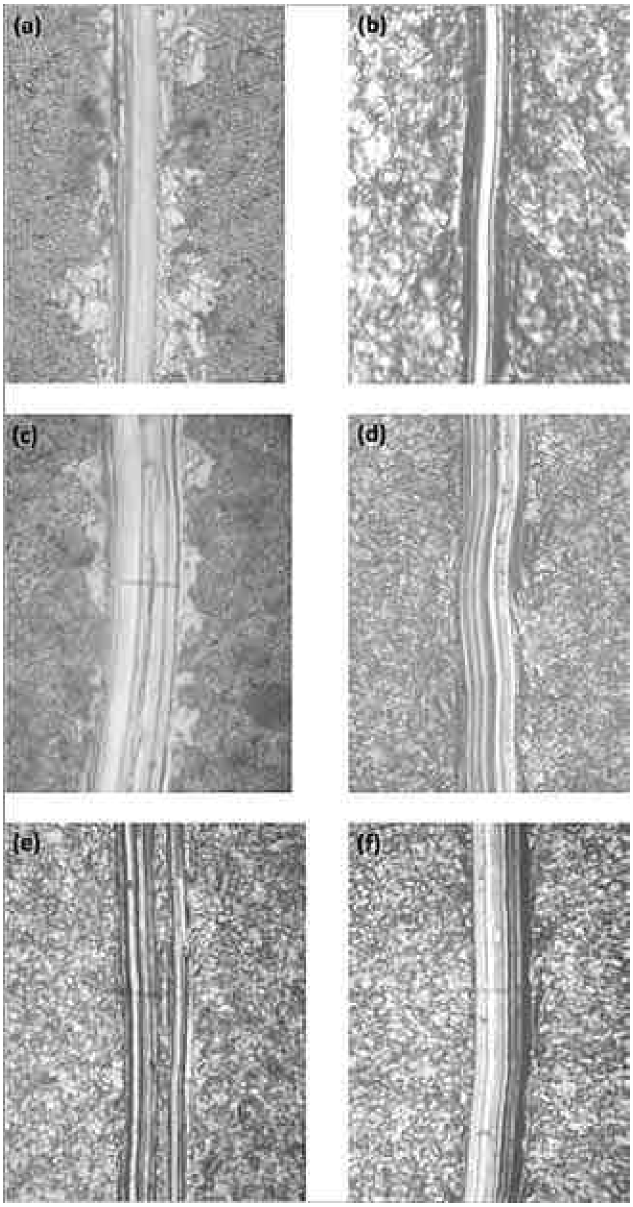

Figure 4—Micrographs of scribes in Trials #: (a) 3, (b) 8, (c) 5, (d) 6, (e) 7 and (f) 9. Note that the micrographs were taken at same magnification. The width of the scribe mark is approximately 17.8 µm (0.7 mil).

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 from a simple DC waveform to a square pulse waveform that included both a cathodic and an anodic pulse. The samples plated in this study were subjected to a scratch test where the amount of coating delamination at the scribe edge was 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. We believe 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, operating at or near room temperature 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. 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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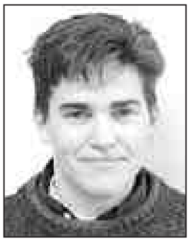

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