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Electroplating on Titanium

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Electroplating is one of the desirable surface treatments of titanium and its alloys. Concerning good quality and adherence of further electrochemical coatings a method for removal and displacement of the protective titanium oxide layer of Ti-6A1-4V had to be adopted. Benefit was obtained by a combination of the substrates sufficient pre-treatment and the electrodeposition of a thin Au/Pd layer. After annealing, this can serve as adhesion promoter of further electrodeposition on Ti-6A1-4V.

Keywords: *titanium-aluminium-vanadium alloy (Ti-6Al-4V), electrodeposition, pre-treatment, activation, gold-palladium alloy deposition (Au/Pd)*

1. Introduction

As the result of excellent material properties such as light weight, high mechanical strength, corrosion stability and good biocompatibility titanium and its alloys have found their way into multiple fields of applications. The latter two properties are the result of a thin oxide layer on the titanium surface. Normally in surface engineering of titanium, this non-conductive oxide layer is strengthened e.g. by anodization, in order to improve corrosion resistance or biocompatibility.

In some cases, however, it is necessary to coat titanium and its alloys with metal layers e.g. by electroplating.[1-5) Here, the oxide layer has to be removed before the electrodeposition of a metal layer can be carried out. Otherwise the quality and adherence of the coating will be inferior. The removal is commonly achieved by pickling of the substrate in a fluoride-containing mineral acid.[6) The major problem in this procedure lies in the quick re-passivation of the titanium surface as soon as it is pulled out of the pickling bath. It is thus necessary to protect the surface from re-oxidation before the desired metal can be electrodeposited.

We have studied the electrodeposition of a thin layer of Au/Pd alloy as a means of protecting the titanium surface from oxidation before the electro-deposition of the actual metallic coating.

2. Experimental

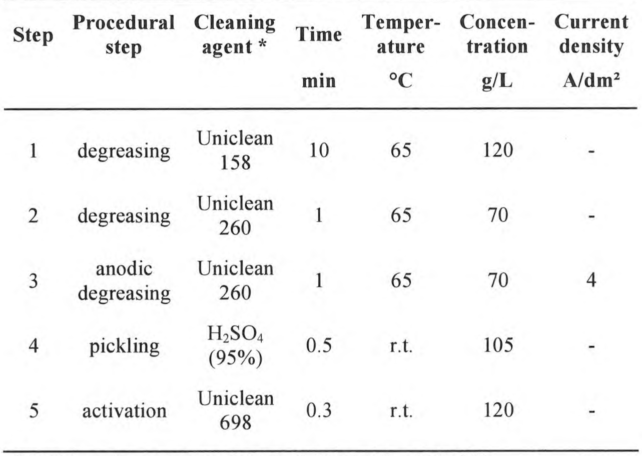
2.1 Material

From a sheet of industrial quality Ti-6A1-4V (ASTM B 265, Grade 5) and 1mm thickness, pieces with 3 .5*3.5 cm edge length were sliced with a metal shear. The surface shows thin scratches and residues from mechanical machining.

2.2 Pre-treatment and Activation

Contaminations, grease, dirt and residues of the substrates fabrication have been abraded mechanically With pulp. The applied sequence for pre-treatment is specified in Table 1.

Table 1. Applied sequence of Ti-6Al-4V pre-treatment



Step	Procedural step	Cleaning agent *	Time min	Temper-ature °C	Concen-tration g/L	Current density A/dm²
1	degreasing	Uniclean 158	10	65	120	-
2	degreasing	Uniclean 260	1	65	70	-
3	anodic degreasing	Uniclean 260	1	65	70	4
4	pickling	H_2SO_4 (95%)	0.5	r.t.	105	-
5	activation	Uniclean 698	0.3	r.t.	120	-

* Uniclean is a product of Atotech Deutschland GmbH:
Uniclean 158: weak alkaline, hydrophobic cleaning agent
Uniclean 260: weak alkaline, electrolytic degreasing agent
Uniclean 698: fluoride containing pickling agent

The cleaning steps implied multi-step degreasing and pickling. Every step was followed by rinsing in deionised water.

2.3 Electroplating

The pH was kept constant between 6.8 and 7.2. The Au concentration in the bath was 4-5 g/L. For optimization of electrodeposition the temperature, current density and deposition time have been varied.

The alloy deposition bath Titech DP (Atotech Deutschland GmbH) consisted of $(NH_4)_3Au(SO_3)_2$, $PdSO_4$, NH_4SO_3, $NaSO_3C_6H_4NO_2$ and $C_{14}H_{23}N_3O_{10}$ (DTPA).

As the pH is declining rapidly during the proceeding and also during dwell time NH_3 (1M) is added for correction. The anode consisted of a platinised titanium mesh.

A high-precision power source by Knick was used. For good adhesion of the alloy as well as subsequently deposited metal layers, it was necessary to anneal the Au/Pd-coated samples. Therefore the high temperature furnace VMK 135 by Linn Elektronik was used.

2.4 Characterization

Following methods of surface characterisation have been applied:

Table 2. Equipment of characterization

Method		Equipment
Environmental scanning electron microscopy	ESEM	REM/EDX XL 30 ESEM FEG
X-ray fluorescence	XRF	Fisherscope X-Ray XAN-FD

3. Results

3.1 Pre-treatment and Activation

Once the titanium oxide layer had partially dissolved the pickling bath began to attack the metal itself Control of the acid concentrations was essential to keep the etching rate constant and was to avoid hydrogen uptake and thereby embrittlement of the substrate.

For this purpose the pickling process was terminated prior to H_2 evolution which could easily be observable by gas evolution at the metal surface. In practice the Ti-6Al-4V specimen had to be taken out of the pickling bath a few seconds before H_2 was generated. Unfortunately this did not result in good reproducibility of the etching step. Time between pickling and immersion of the titanium samples into the alloy deposition bath had to be kept to a minimum, in order to avoid extensive re-passivation of the substrate surface. After pickling the samples were briefly rinsed in deionised water and immediately transferred into the Au/Pd bath, where the electro-deposition started not more than 10 seconds after the samples had been removed from the pickling bath.

3.2 Alloy Composition

Tenuous layers of Au/Pd alloy could be electro-deposited on the pre-treated Ti-6Al-4V substrates. Correct pre-treatment of Ti-6Al-4V and electrodeposition parameters had great influence on the quality of the layer. Sub-optimal pre-treatment and/or wrong electro-deposition parameters resulted in Au/Pd films with holes and cracks, which are not suitable for further electroplating (Figure la). Under optimized conditions (Table 1, electrodeposition at 0.2 A/dm^2 and 55°C for 2 min) defect-free homogenous layers of Au/Pd could be obtained. (Figure lb).

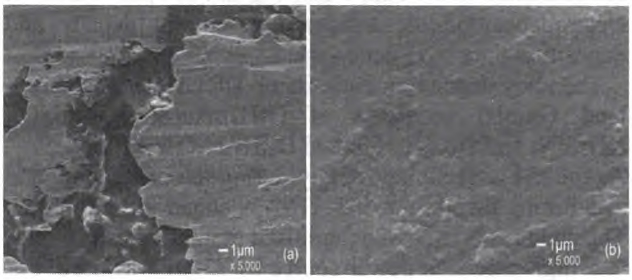


Figure 1. Scanning electron micrographs of the surface morphologies of Au/Pd alloy deposition on Ti-6Al-4V with different plating parameters: (a) holes and (b) perfect adherent coating.

It was unknown, however, how the electrodeposition parameters influenced the alloy composition. Therefore, a series of samples was Au/Pd plated with a range of current densities. The compositions of the alloy layers have been determined by X-ray fluorescence. Figure 2 shows an increase of palladium contents in the alloy with increasing current density. More than 5 wt.% of palladium could not be deposited, because the deposit burned at current densities above 0.4 A/dm^2. The increase in palladium contents of the alloy layer correlated with a change from gold to silver colour.

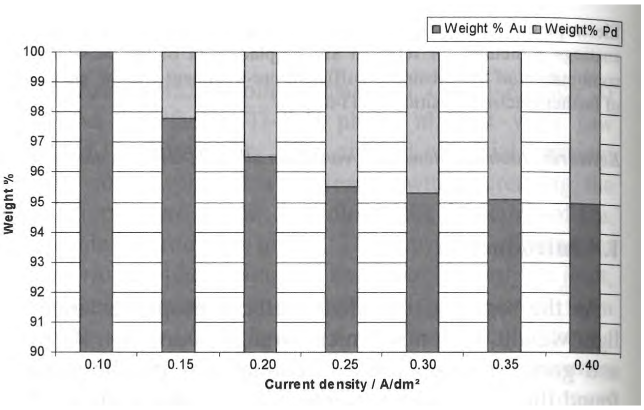


Figure 2. Compositions of 5 min electroplated Au/Pd alloy layers on Ti-6Al-4V at differing current densities.

In order to enhance the adhesion of the protective Au/Pd layer, the samples were annealed in a high-temperature furnace in air at 320°C and 400°C for 1 and 5 hours. While the Au/Pd layer could be peeled of the substrate before annealing with scotch tape, this was not possible after annealing. Moreover, the Au/Pd alloy layers even remained intact in bending tests. This might be due to formation of an intermetallic phase between the substrate and the alloy constituents.

4. Conclusions

Under optimized conditiones for pre-treatment of the substrate and the specified electroplating parameters defect-free and homogenous Au/Pd alloy layers can be electrodeposited on titanium. The Pd content of the alloy varies with the current density between 0 and 5 wt.%. Adhesion of the alloy layer can be enhanced by annealing at 320°C for 1 hour. This protective layer could serve as an adhesion promoter for further electroplated layers.

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