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Electroplating Titanium from Ionic Mixtures

September 2021

Lance Hubbard Christina Arendt Bethany Lawler



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Abstract

Titanium & Zirconium metal films have been electroplated by a near-ambient scalable process for high value-add/lower volume applications. The films have been commercially tested as bonding layers

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1.0 Introduction

We have developed a novel method of electroplating thin metal films from deep eutectic solvents (DES). The film quality is high & contamination is low. The plating solvent constituents are not carcinogenic. refractory metals are used for their corrosion & erosion resistance, high melting temperature, and excellent mechanical properties. Titanium and zirconium have been demonstrated (Figure 1) in our system, but other metals are possible.



Figure 1. Overview photographs and scanning electron micrograph of the plated refractory films.

Titanium is a refractory metal. useful for corrosion resistance and diffusion barriers. Titanium application areas include medical, aerospace, electronics, and thermal systems. The current methods of plating Ti:

- Applied coatings (plasma spray, etc.)
 - Mostly limited to near two-dimensional surfaces (Briant 2001; Gonsalves, Rangarajan, and Wang 2002)
- Molten salt electroplating (Simka, Puszczyk, and Nawrat 2009; Tsuda et al. 2004; Kuznetsov 2009; Uda et al. 2006; Lee et al. 2012)
 - Major reliability problems
 - Contamination issues

Electroplating Ti "would be, by all means, a technological breakthrough" (Aurbach et al. 2007).

2.0 Materials and Methods

The process occurred in a Gamry's Dr. Bob's Cell with non-aqueous silver references, a glassy carbon counter electrode, and was completed on steel (316) foils & rods. Deep eutectic solvent (Ar cleaned Ethaline) with 0.125 M TiF4 and 0.25 M LiF, was used as the plating bath. Electroplating with DC and AC pulses was both trialed. Pulse platin was most successful with a 100 ms plate and 10 ms rest. The bath was stirred under an Ar bubble and blanket. The plating was performed in a glove bag flushed with Ar (Figure 2). See (Hubbard, Arendt, and Webster 2020) for more details on the plating bath methods and setup.



Figure 2. Photograph of the electrochemical cell under Ar environment.

3.0 Plating Challenges

<u>Any</u> amount of water in the system will cause the plating to fail (believed to be below part-perbillon levels). Steps taken to remove water from the system:

- Ethaline solvent must be dried and degassed
- Ar gas cover must be dried
- Plating must be done at >110°C
- Water adsorbs onto the glass of the Dr. Bob's Cell
 - ✓ Causes oxidation to both substrate and film
 - ✓ Cell must be vacuum dried and stored under vacuum

While conventional wisdom suggests that Ti metal cannot be made from Ti⁴⁺ in the presence of chlorine (Endres et al. 2008), the current results suggest that this is not true as long as measures are taken to remove all water from the system (Figure 3).



Figure 3. Photograph plated oxide due to water contamination and a successful titanium on steel coating.

4.0 Results and Discussion

Titanium films up to 6 microns thick have been deposited on steel. Bright Ti metal films were deposited at temperatures from 110-120 °C. below that surface oxides over metal from 80-100 °C. Pits and cancerous rust evolved at near ambient conditions, Figure 4A.

A bright-metal film was chemically oxidized to explore the visual confirmation of coating coverage and conformity. After 60 days a uniform oxide was established on the surface of the Ti. The color was as expected and the oxide thickness did not visually change indicating a conformal and uniform oxide layer was present, hence it evolved from a conformal and uniform metal coating on the coupon, Figure 4B.



Figure 4. A) Photographs of the Ti on steel coupons after plating vs the bath plating temperature with an arrow indicating the evolution from oxides to metallic coatings. B) The controlled oxidation of the Ti layer to investigate the macroscopic uniformity of the coating. With an arrow from the bright metal to uniform oxide layer over the course of 60 days.

The surface coverage is high with few ~500 nm diameter pinholes. The pinhole density on the order of single digits/100 μ^2 . Titanium thickness increases with plate time at a rate of ~1.2 μ /hr. The coating is microscopically conformal with few pinholes. The surface roughness is increased 16% over 5 hrs of plating. For coatings over 3 microns thick the electron micrograph thickness was conformed optically, Figure 5A-C.

The elemental signal of titanium increased with plating time based on X-Ray fluorescence analysis, Figure 5D. For contaminations measurements:

- Sulphur's signal was less than background
- Chlorine's signal was less than background
- Calcium contamination increased from background to 2.3 times background over 5 plating hrs. (ppm levels)

Also, a simple bend test showed now mechanical delamination. UV-microscopy showed little to no salt contamination past the plating meniscus. A tape test showed no film delamination. Aluminum-Titanium-steel diffusion bonding gave a strength of 120 ± 12 MPa which was approximately the same a sputtered titanium films of similar thickness. The titanium film is well adhered and has relatively low contamination.



Figure 5. A) Helium scanning microscope image of the Ti layer on steel showing a small 500 nm diameter pinhole found in a 1-micron thick coating. B) Cross section scanning electron image of a 3-um thick to coating on steel. C) Ti layer thickness vs plate time from microscopy analysis. D) Ti signal intensity from X-ray florescence elemental analysis.

5.0 Conclusions

Titanium electroplating up to 6 microns thick on steel at lower temperatures have been demonstrated from a system nearly devoid of water. This film has the potential to influence medical implants, aerospace components, furnaces, and high-vacuum systems with an economical process for three dimensional parts in low-throughput high value-added runs. This process is revolutionary and has the potential to benefit many lives.

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Pacific Northwest National Laboratory

902 Battelle Boulevard P.O. Box 999 Richland, WA 99354

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