Pacific Northwest
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PNNL-34876

Manufacturability Advancement of Low-Temperature Titanium Electroplating Methods

September 2023

Christina Arendt
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U.S. DEPARTMENT OF ENERGY

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

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Abstract

Three tasks were proposed for this work. All three were completed. The tasks were as follows:

Task 1: A larger plating system will be purchased for process scale-up. TiF_3 will be tested as the metal precursor in an effort to reduce water sensitivity of the process.

Task 2: Ti on steel samples will be created at PNNL and shipped to Atlas Technologies. Atlas Technologies will diffusion bond the samples to aluminum and test the bond strength. The results will be reported to PNNL.

Task 3: Investigation into DOE mission relevant Ti and Zr alloys and demonstration on larger scale work pieces.

Acknowledgments

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1.0 Introduction

Three tasks were proposed for this work. All three were completed (Hubbard et al., 2020). The tasks were as follows:

Task 1: A larger plating system will be purchased for process scale-up. TiF_3 will be tested as the metal precursor in an effort to reduce water sensitivity of the process.

Task 2: Ti on steel samples will be created at PNNL and shipped to Atlas Technologies. Atlas Technologies will diffusion bond the samples to aluminum and test the bond strength. The results will be reported to PNNL.

Task 3: Investigation into DOE mission relevant Ti and Zr alloys and demonstration on larger scale work pieces.

1.1 Task 1: Scale-Up

TiF_3 was tested as the metal precursor. Plating successfully occurred using the trifluoride salt. The behavior was nearly identical to the tetrafluoride (as seen in **Figure 1**).

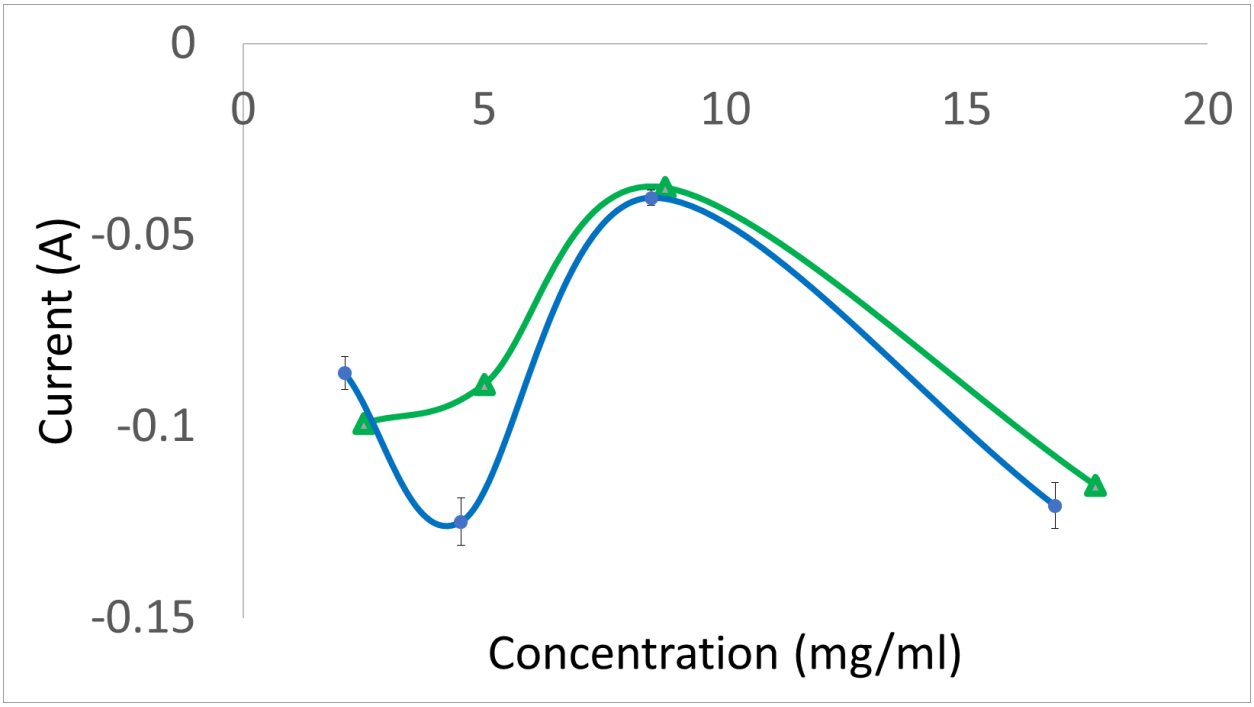


Figure 1. The behavior of TiF_4 (green) compared to TiF_3 (blue). The plating speed is largely the same between the two, though TiF_3 is slightly faster at lower concentrations.

Two new plating systems were purchased for scale-up efforts: a Gamry paint test cell and a Gamry multiport corrosion cell. The paint test cell was largely used while custom inserts for the multiport corrosion cell were being designed and fabricated.

Electroplating in the Paint Test Cell

We were able to scale up workpiece size from previous efforts using the paint test cell, but the setup has several limitations. Chiefly, the plating bath cannot be stirred using a simple magnetic stir plate, as the cell is set up vertically atop the workpiece. This leads to reduced plating speed, which we believe is because our system is diffusion limited. However, we did use this setup for several demonstration pieces, and it is available for future development efforts. The fully assembled setup is shown in **Figure 2**.

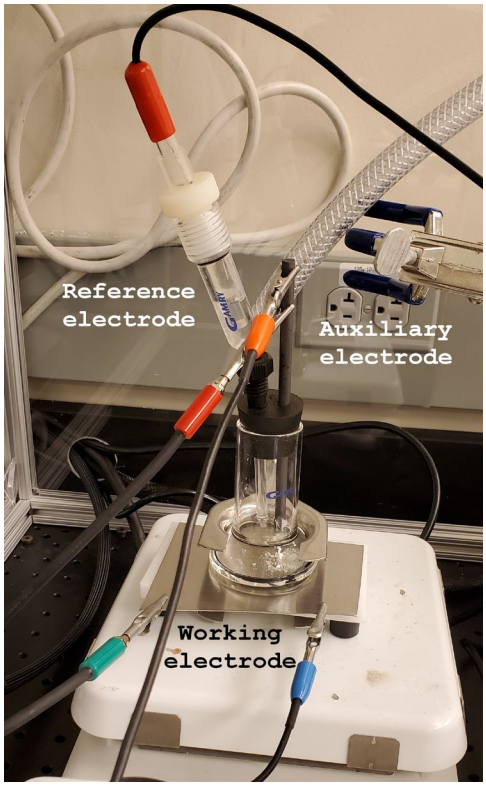


Figure 2. Fully assembled paint test cell.

Electroplating in the Multiport Corrosion Cell

In order to maximize workpiece size while minimizing the amount of DES used for the plating bath, a custom PTFE insert was designed and fabricated for the multiport corrosion cell. This insert, shown in **Figure 3**, holds the workpiece and the electrode vertically in the cell and has a small slot to allow for a stir bar at the bottom of the cell. **Figure 4** shows the assembled corrosion cell. Additional modification of part of the cell was necessitated by the poor contact between the graphite and metal leads (shown in **Figure 5**).

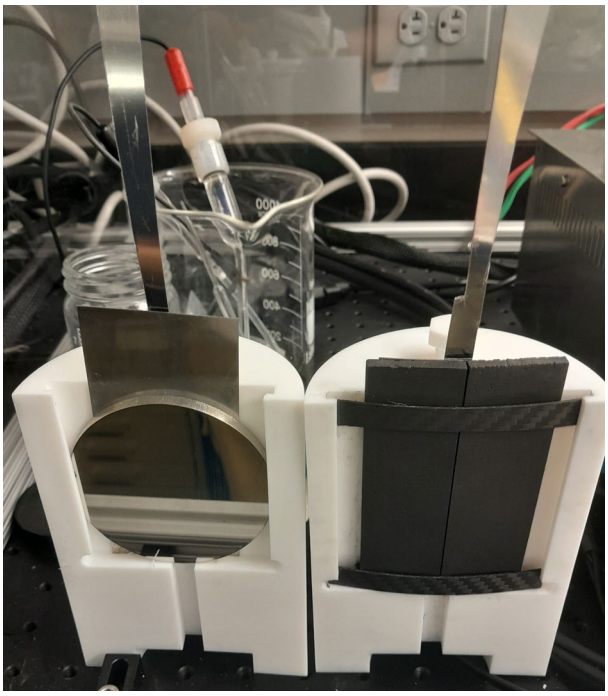


Figure 3. The two halves of the custom PTFE insert for the corrosion cell. The workpiece is on the left and the electrode is on the right.

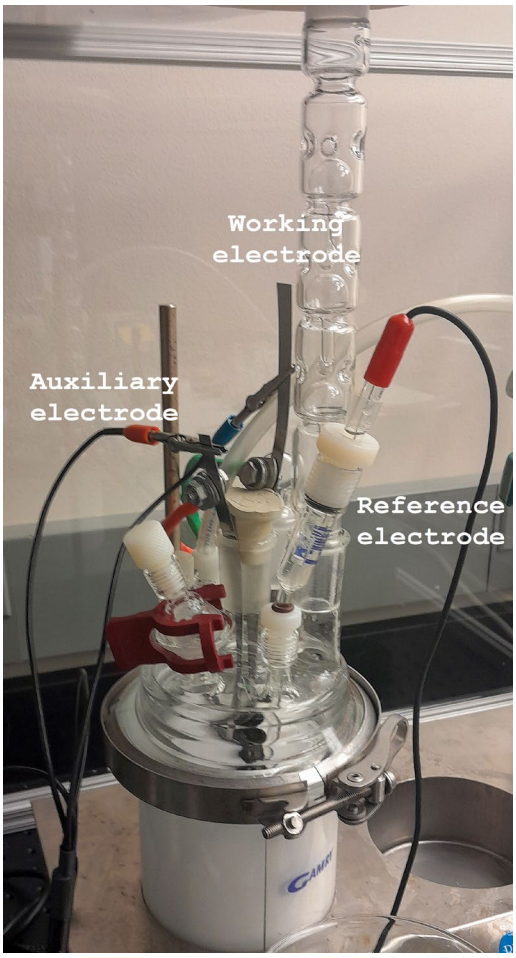


Figure 4. Fully assembled corrosion cell, equipped with condenser and Argon inlet (line in the back).

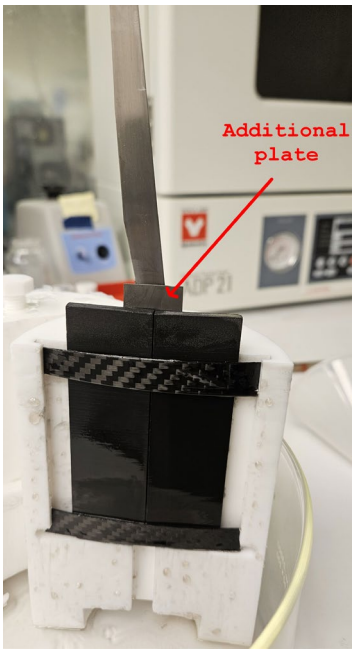
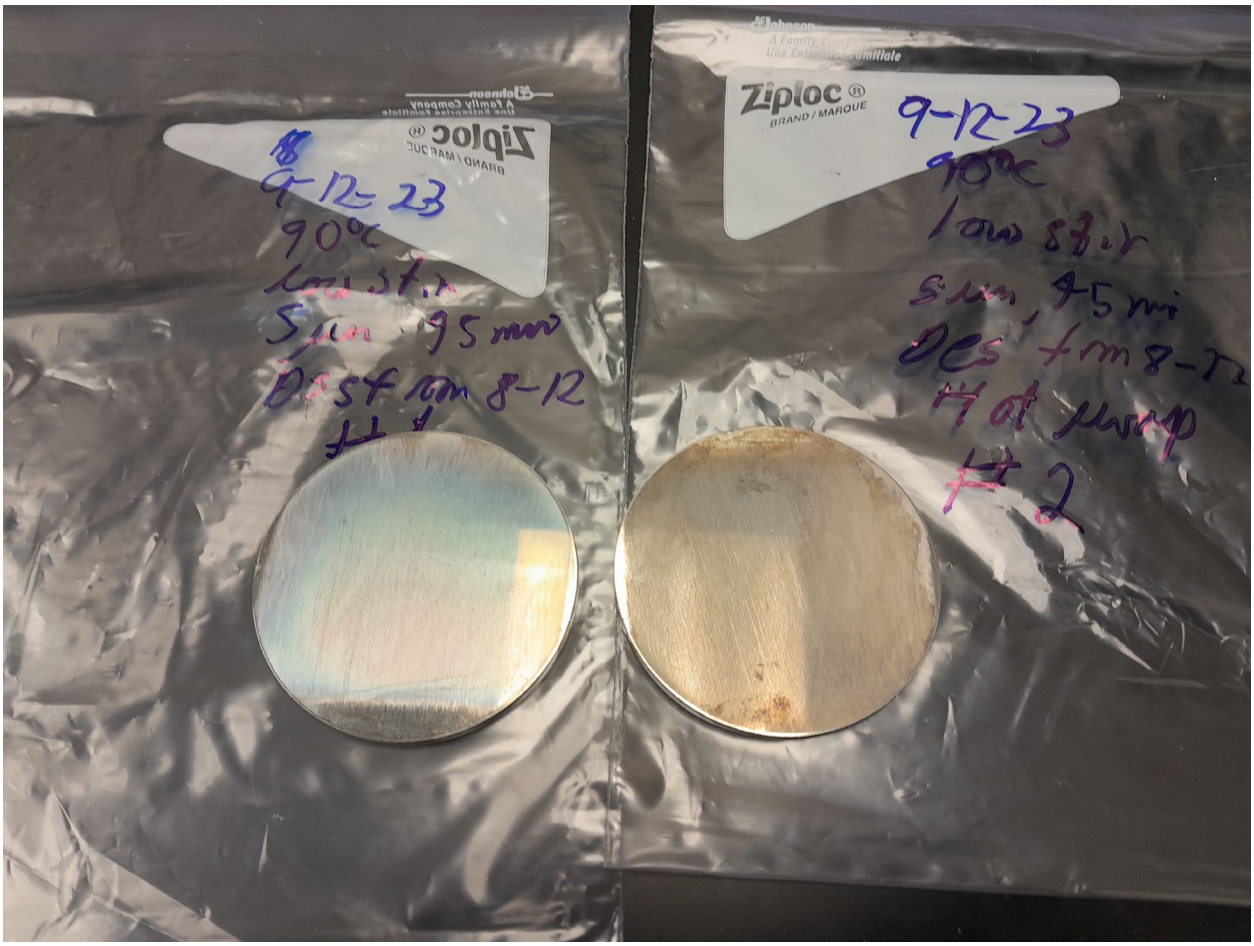


Figure 5. Auxiliary electrode part of the cell equipped with additional metal contact sheet.

1.2 Task 2: Demonstration Pieces

Twenty demonstration pieces were plated with varying thicknesses of titanium metal (5-35 um). The workpieces were provided by Atlas Technologies with a 0.6 RMA roughness or mirror polish finish. All workpieces were made of 316 stainless steel. The workpieces have been returned to Atlas for diffusion bonding and bond strength testing. That work is ongoing and Atlas will provide the results of their tests once completed.



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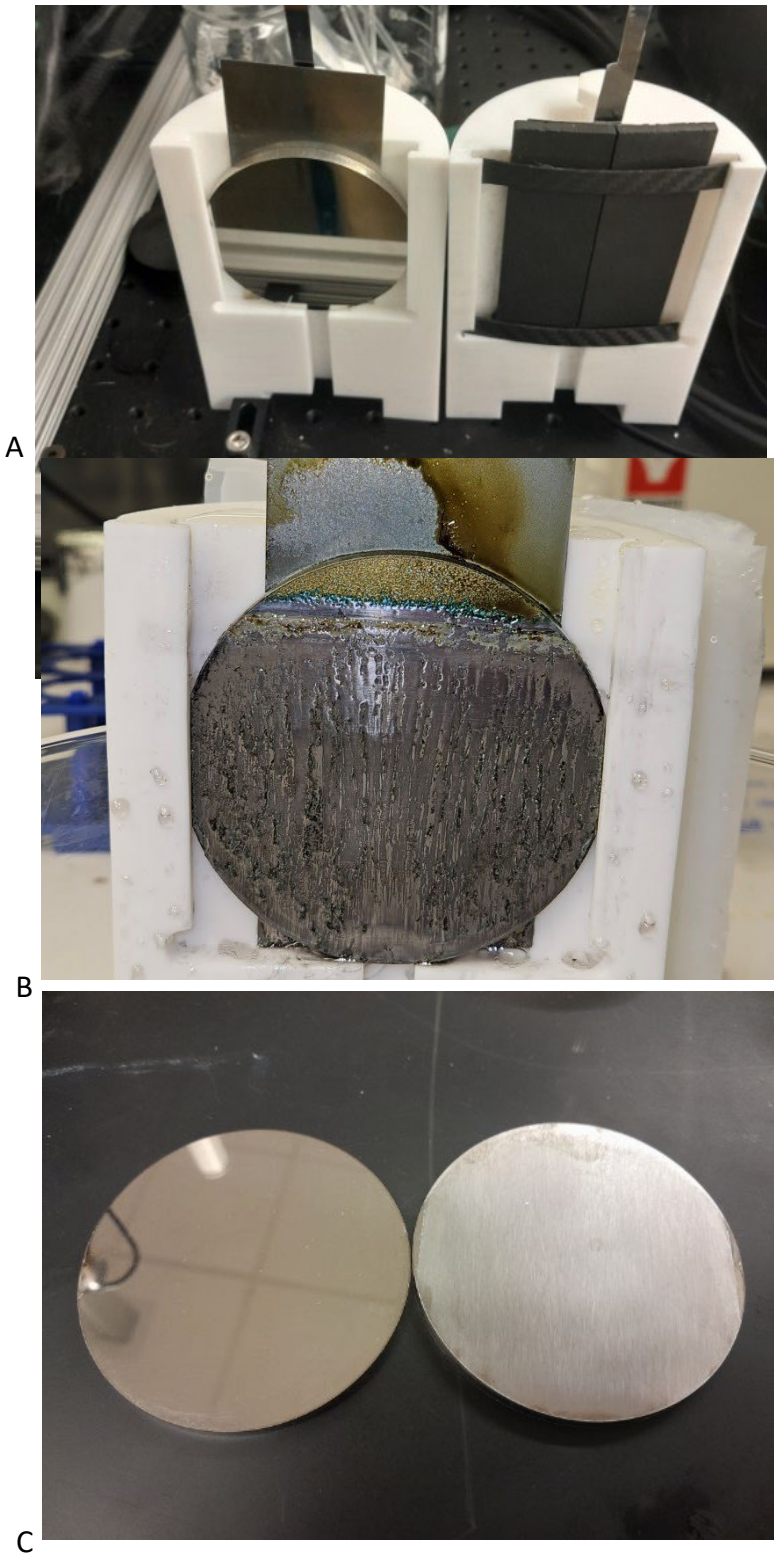

Figure 7. A) The demonstration piece and counter electrode. B) The plated workpiece prior to cleaning in ethanol and sonication. C) The original finish (left) and a coating of 35 um of titanium (right).

1.3 Task 3: Mission-Relevant Alloys

The results of this collaboration can be found in Sandia report SAND2023-10789.

2.0 Conclusions and Future Work

The work contained herein demonstrates that with current advancements, the active metal electroplating of titanium and zirconium has been moved to commercially relevant speed and has been confirmed on workpieces of interest. Specific achievements include:

1. The increase of plating speed to microns per minute.
2. The establishment of air-tolerant plating parameters.
3. Demonstration of plating uniformity over wide plating areas (10s of cm^2 and larger).
4. Demonstration of plating equipment with volume-limiting apparatuses.
5. Successful titanium plating from previously used solvent (up to 4x tested).

The combination of the above results yields a process that is now ready for commercial deployment and economics on a more industrial scale.

What remains to be established is the science and chemical kinetics behind the plating process. Previous work has led the field to believe that such a plating process was impossible (Castellana et al., 2006; Endres et al., 2008; Pereira et al., 2018; Uda et al., 2006). Initial chemical investigations suggest a role is being played by the polyol reduction process which influences the salt reduction occurring at ~-0.9V. The role of this process remains to be seen but provides a possible hypothesis as to why this unlikely plating process is so robust. Future work will enable qualification of the current platings in use-case scenarios and the kinetic description of the plating process.

3.0 References & Bibliography

Castellana, E. T., Kataoka, S., Albertorio, F., & Cremer, P. S. (2006). Direct writing of metal nanoparticle films inside sealed microfluidic channels. *Analytical Chemistry*, *78*(1), 107–112. https://doi.org/10.1021/ac051288j

Endres, F., Zein El Abedin, S., Saad, A. Y., Moustafa, E. M., Borissenko, N., Price, W. E., Wallace, G. G., MacFarlane, D. R., Newman, P. J., & Bund, A. (2008). On the electrodeposition of titanium in ionic liquids. *Physical Chemistry Chemical Physics*, *10*(16), 2189–2199. https://doi.org/10.1039/b800353j

Hubbard, L., Arendt, C., & Webster, R. (2020). *COMPOSITION AND METHOD EMBODIMENTS FOR PLATING METAL COATINGS*. https://patents.google.com/patent/US20200378027A1/en

Pereira, N. M., Pereira, C. M., Araújo, J. P., & Fernando Silva, A. (2018). Electrodeposition of an ultrathin TiO_2 coating using a deep eutectic solvent based on choline chloride. *Thin Solid Films*, *645*(October 2017), 391–398. https://doi.org/10.1016/j.tsf.2017.11.005

Uda, T., Okabe, T. H., Waseda, Y., & Awakura, Y. (2006). Electroplating of titanium on iron by galvanic contact deposition in NaCl-$TiCl_2$ molten salt. *Science and Technology of Advanced Materials*, *7*(6), 490–495. https://doi.org/10.1016/j.stam.2006.02.016

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