

Titanium substrate preparation for electroplating with hydrofluoric acid free methods

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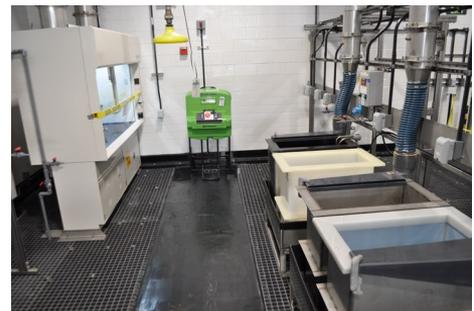


Sigma is a manufacturing research and development facility adjacent to our materials research facilities

All have been significantly modernized recently

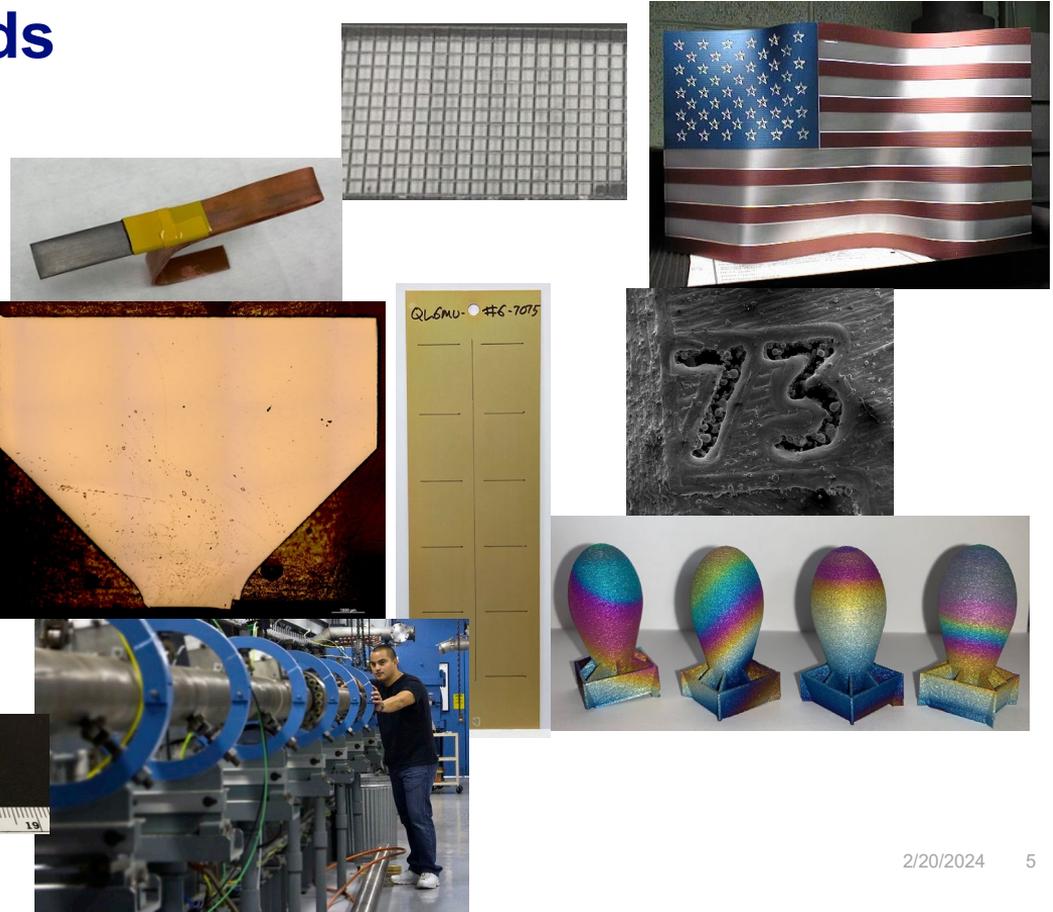


Our labs have all been renovated



The plating/finishing lab offers many capabilities, and serves diverse R&D needs

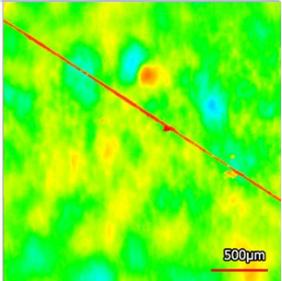
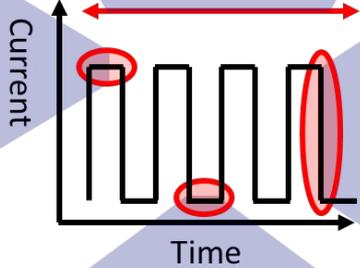
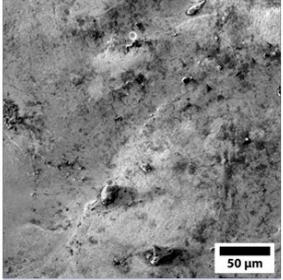
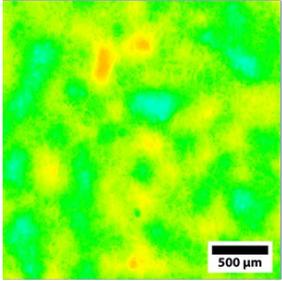
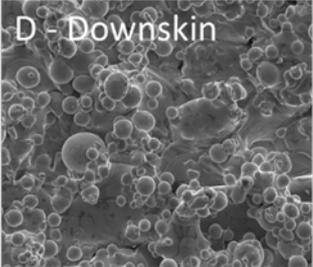
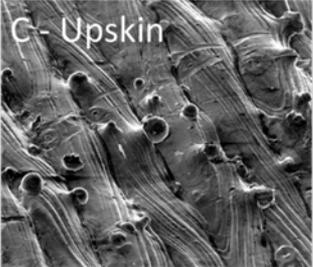
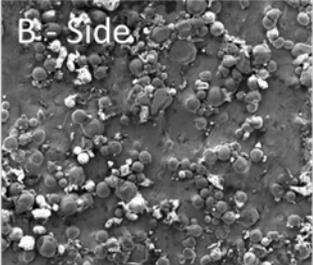
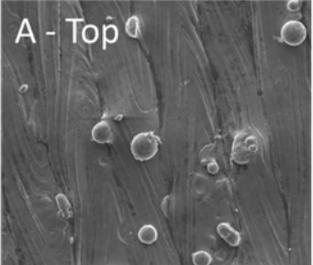
- One-off to production scale, routine to cutting edge
- Cleaning, Corrosion & Echem testing
- Anodizing, chromate conversion
- Plating (Ni, Cu, Au, Ag, Etc.)
- Unusual and difficult materials (Be, U, Ta, W, Re, Zr, Etc.)
- Process development (coatings, multilayers)
- Characterization
- Diagnostic development
- Experiment, theory, and model development



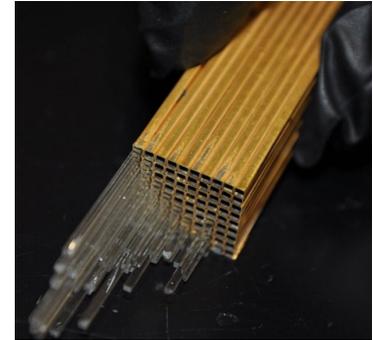
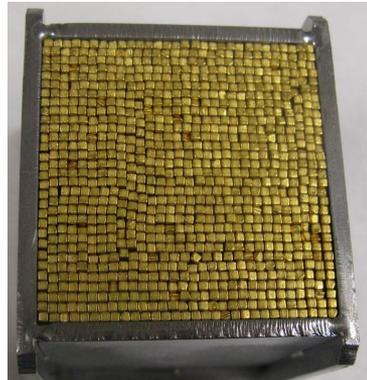
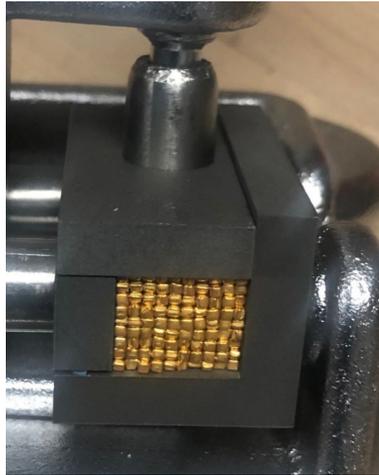
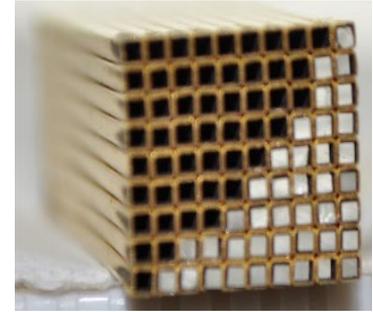
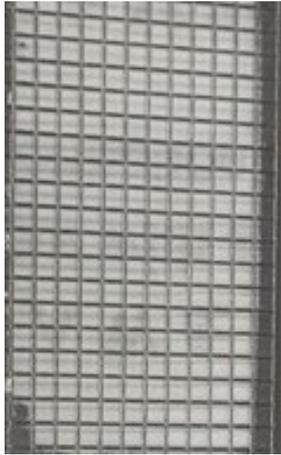
A few projects got us going down a path to evaluate the “difficult” metals to prepare and plate

- Additively manufactured metal surface preparation
 - Pulsed electrochemistry
- Imaging scintillator grids
 - Selective etching or alternative techniques
- Graded density materials
 - Re (crowded solvents, complexing additives, pulsed electrochemistry)

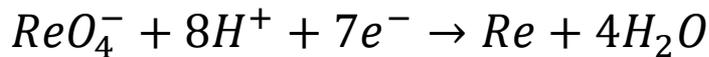
We are working to understand how pulse parameters control electropolishing of additively manufactured metals



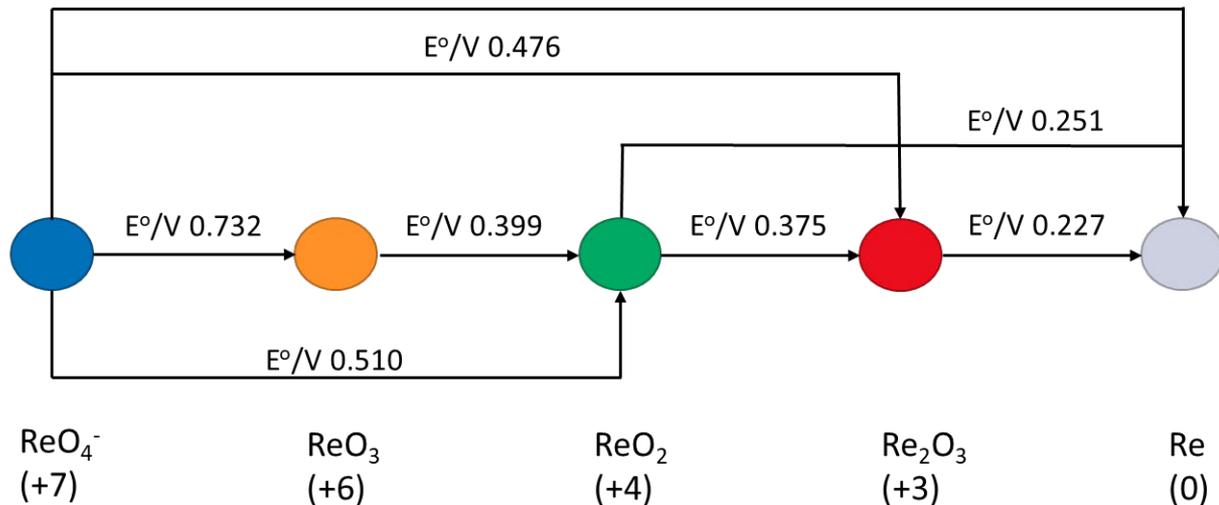
Etching tungsten septa for scintillator grids led to alternative approaches, and desire to reduce cost



For these scintillators and graded density materials, we pursued Re coatings



E°/V 0.369



List of potential oxides

- Re_2O

- ReO

- Re_2O_3

- ReO_2^*

- Re_2O_5

- ReO_3^*

- Re_2O_7^*

*isolated and observed in bulk phases

- We were unable to reproduce literature electrolytes with industrially relevant setups
- Required crowded solvents, complexing agents, pulsed electrochemistry
- See presentation by Mike McBride

We also pursued tungsten plating from literature aqueous method – this one works

A paper presented at the Fifty-ninth General Meeting of the Electrochemical Society, held at Birmingham, Ala., April 25, 1931, President Kahlenberg in the Chair.

THE ELECTRODEPOSITION OF TUNGSTEN FROM AQUEOUS SOLUTIONS.¹

By COLIN G. FINK² and FRANK L. JONES.³



The national laboratories have historically contributed to the finishing industry

ELECTRODEPOSITION

The Materials Science
of Coatings and Substrates

by

Jack W. Dini

Lawrence Livermore National Laboratory
Livermore, California



Figure 1: Plating magician with his vats of "magic" additives. From Metal Progress, 107, 71 (Jan 1975). Reprinted with permission of ASM International.

LANL has several approaches to formal partnerships...

Partnership agreements **facilitate moving a technology to an application that has market value.** They enable LANL staff to **work directly with a partner to help with their product development** and **further development of the LANL technology.** All partnership agreement must **benefit both the Lab and industry** and align with Program Office, Line Management and Funding Sponsor requirements.

CRADA

A CRADA allows LANL and its partners to work together to optimize their resources, leverage technical expertise and capabilities, and generate intellectual property emerging from the collaboration.

SPP-NFE

Strategic Partnership Project–Non-Federal Entities (SPP-NFE) enables access to the Laboratory’s scientific capabilities, specialized instrumentation, and facilities for defined scopes of work.

SBIR/STTR

The SBIR and STTR programs provide an avenue for U.S. small businesses to engage in Federal Research/ Research & Development that has the potential for commercialization.

NDA

A Non-Disclosure Agreement (NDA) protects proprietary information provided by one party to another from further disclosure. This agreement is often used to cover initial interactions.

The New Mexico Small Business Assistance Program (NMSBA) provides New Mexico small businesses addressing technical challenges access to unique expertise & capabilities of Los Alamos & Sandia national labs as well as NMSU, NMT, UNM, NMMEP to:

- ▶ Seek no cost assistance from lab staff to solve specific technical challenges;
- ▶ Receive support in the form of lab hours up to \$40K in assistance for businesses in rural counties & \$20K in urban counties.

Benefits to NM Business



Experts solving your technical challenges



Testing and evaluation from a national laboratory makes a company more appealing to investors and grant makers



Builds relationships with technical experts for future collaboration



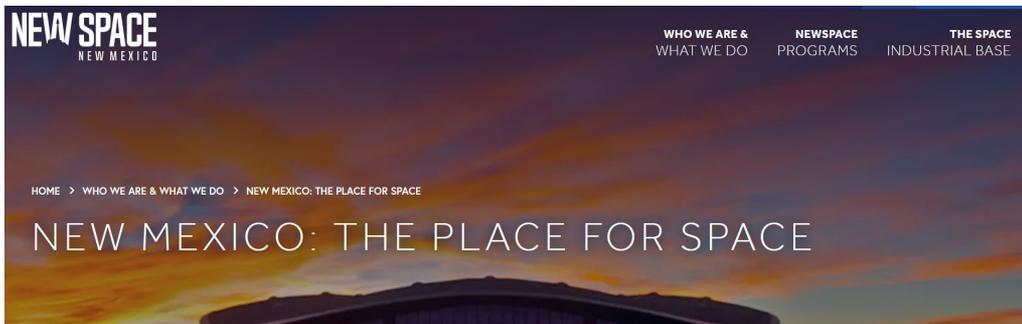
Increased understanding of product, market, & technology



Demand for space components in New Mexico is having an impact on finishing companies



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SPACE COMPANIES

There are a variety of New Mexico space companies that range in size from large prime contractors to innovative high-tech startups some of which have started via government contracts. New companies are starting in New Mexico with private investment. New Mexico has over 80 companies working in the space industry. Virgin Galactic, the anchor tenant of Spaceport America, is gearing up to take tourists to space. Virgin Galactic's SpaceShipTwo has successfully reached an altitude of over 50 miles and is expecting that its first commercial suborbital flights will begin in 2020. Virgin Galactic has over 600 space enthusiasts signed up for its flights, at a cost of \$250,000 per person.



INTELLECTUAL CAPITAL

- Livability, an online magazine, ranked Albuquerque, New Mexico's largest city, fourth of 2018's 10 Best Cities for STEM Workers
- New Mexico has one of the highest percentages of the total workforce performing STEM jobs
- The combined number of employees for Air Force Research Laboratory, Los Alamos National Laboratory and Sandia National Laboratories is over 21,000
- New Mexico's workforce is also diverse with over 45% Hispanic and 5% Native American populations

Theta Plate, Inc is a small business in Albuquerque, NM that specializes in precision coatings

- Varieties of Au, Ag, Pt, Rh
- Specialty and common Ni, Cu
- Increasing space component business



Preparing and plating on titanium was identified as a challenge of common interest

Preparing and plating titanium has been a subject of interest for many years

- Some methods were described in the literature

A. K. Sharma, "Electroless nickel and gold plating on titanium alloys for space applications," *Metal Finishing*, 23, July 1992

BY JOHN W. BIBBER, SANCHEM, INC., CHICAGO, ILL

Zincate- or Stannate-free Plating of Magnesium, Aluminum, and Titanium

28 | *metal finishing* | July/August 2009



Figure 3: Titanium bolts before (left) and after (right) plating with electroless nickel.

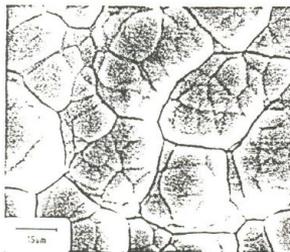


Fig. 1. Scanning electron micrograph of electroless nickel: 1500x.

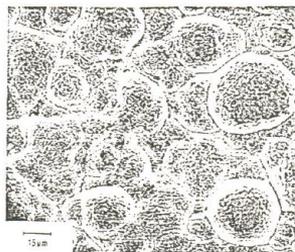


Fig. 2. Scanning electron micrograph of gold coating: 1000x.

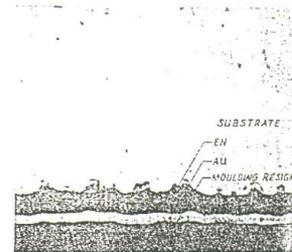


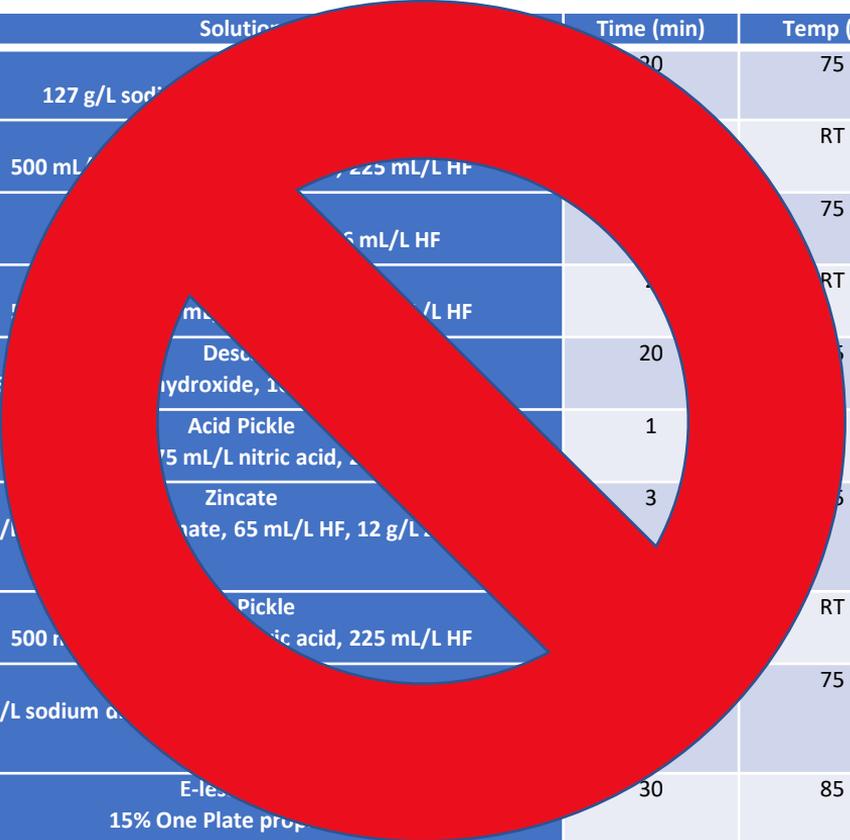
Fig. 3. Photomicrograph of a cross section of a gold-plated test coupon (480x).

- LANL and Theta set out to evaluate some approaches
 - Focus was decreased hazard – eliminating use of HF was desired
 - Quality coating, adhesion, and repeatability required

As a baseline, some traditional double HF-zincate techniques were evaluated

Solution	Time (min)	Temp (°C)
Etch 127 g/L sodium dichromate, 46 mL/L HF	20	75
Acid Pickle 500 mL/L DI, 275 mL/L nitric acid, 225 mL/L HF	2	RT
Etch 127 g/L sodium dichromate, 46 mL/L HF	20	75
Acid Pickle 500 mL/L DI, 275 mL/L nitric acid, 225 mL/L HF	2	RT
Descale 500 g/L sodium hydroxide, 100 g/L copper sulfate	20	95
Acid Pickle 500 mL/L DI, 275 mL/L nitric acid, 225 mL/L HF	1	RT
Zincate 100 g/L sodium dichromate, 65 mL/L HF, 12 g/L zinc sulfate	3	75
Acid Pickle 500 mL/L DI, 275 mL/L nitric acid, 225 mL/L HF	1	RT
Zincate 100 g/L sodium dichromate, 65 mL/L HF, 12 g/L zinc sulfate	6	75
E-less Nickel 15% One Plate proprietary	30	85

This traditional technique did not produce uniform or adherent coatings reliably



Solution	Time (min)	Temp (°C)
127 g/L sodi	20	75
500 mL / 225 mL/L HF		RT
5 mL/L HF		75
mL/L HF		RT
Dest	20	75
hydroxide, 1		
Acid Pickle	1	
5 mL/L nitric acid, 2		
Zincate	3	75
100 g/L / 65 mL/L HF, 12 g/L		
Pickle		RT
500 mL / nitric acid, 225 mL/L HF		75
100 g/L sodium a		75
E-le	30	85
15% One Plate prop		

We also tried similar HF-zincate approaches with alternative nickel layers

Solution	Temperature	Time (min)	Voltage
Blue Gold Degreaser	60°C	6 min	
Descale (if applicable) 500 g/L Sodium hydroxide, 100 g/L Copper sulfate	90°C	20 min	
Nitric/HF pickle 275 mL/L Nitric acid, 225 mL/L HF	RT	3 min	
Chromic/HF etch 127 g/L Sodium dichromate, 46 mL/L HF	75°C	30 min	
Woods Nickel Strike	RT	3 min	3V

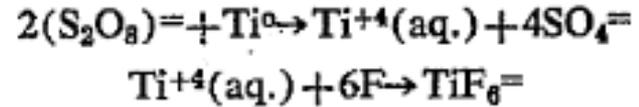
This also did not work...



Solution	Time (min)	Voltage
Bl... 500 g/L Sodi... Copper sulfate	6 min 20 min	
2... ic acid, 2...	RT min	
127... mic/HF etch lichromate, 46...	75°C min	
Nickel Strike	RT min	3V

Based on some discussions at SUR/FIN last year, we investigated the persulfate approach of Multi-Etch

A. B. Thomas, "Non-hazardous etching solutions" US Patent 2,942,954, 1960



2,942,954

NON-HAZARDOUS ETCHING SOLUTIONS

Alvin B. Thomas, Indianapolis, Ind., assignor to General Motors Corporation, Detroit, Mich., a corporation of Delaware

No Drawing. Filed Oct. 20, 1955, Ser. No. 541,858

4 Claims. (Cl. 41—42)

Commercial formulation & instructions for several metals available from Multi-Etch

A process was developed using Multi-Etch and a similar homebrew recipe

Solution	Temperature	Time	Current
Blue Gold Degreaser	RT	6 min	
MultiEtch at manufacturer recommended concentration OR generic equivalent: 7.5wt% ammonium persulfate 3.5wt% sodium fluoride	60C	3 min	0.1 ASI
Ni Sulfamate	40C	10 min (change for desired thickness)	0.1 ASI

It works!

- Both Multi-Etch and homebrew method allow for Ni and Ni/Au
- This method eliminates the need for HF, and is reproducible at scale



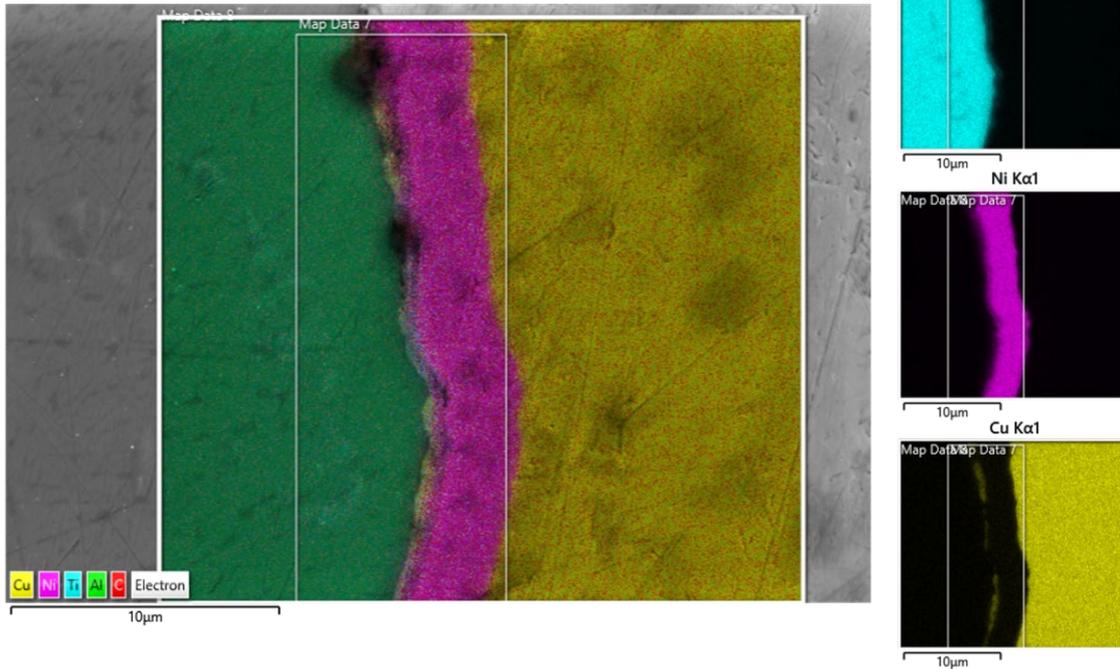
We tried to skip the Ni, and we tried other Ni baths

- Prep included Multi-Etch, then Au
- Instead of sulfamate, we tried strike and bright Ni chemistry
 - NONE of these worked reliably (or at all!)
 - Why?



We also tried one other pre-treatment, which shows great results, but we leave that to the imagination and maybe a future talk!

The Ni baselayer supports other coatings, and cross sections confirmed uniform, intimate interfaces



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– an Office of Science national user facility –

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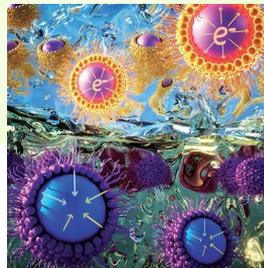
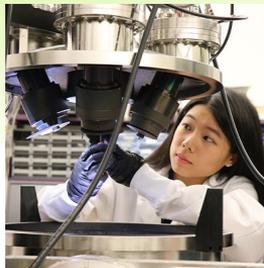
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Postdoc Programs

The Postdoctoral (Postdoc) Research program offers the opportunity for you to perform research in a robust scientific R&D environment, present and publish research, advance knowledge in basic and applied science, and strengthen

Acknowledgements

Ti Surface preparation

Theta Plate Inc.

Chris & Sandy Booth, Multi-Etch

Funding: New Mexico Small Business Assistance Program

Graded Density coatings

Michael McBride, Jamie Stull, Tariq Aslam, Brian Jensen

Funding: NNSA Science Programs

Rhenium coatings

Michael McBride, Jamie Stull, Nathan Brown

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