Development of Corrosion- and Erosion-Resistant Coatings for Advanced Ultra-Supercritical Materials

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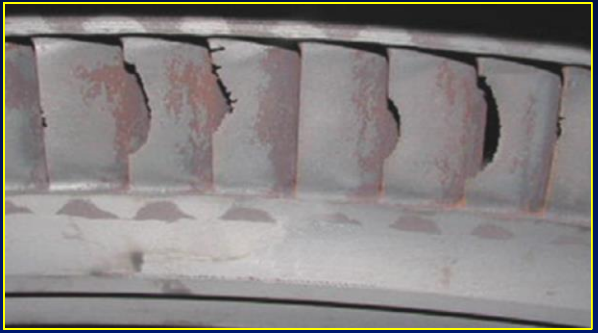
Materials Issues for Advanced Ultra-Supercritical (A-USC) Steam Turbine Blades

- **Under A-USC conditions, γ′-strengthened Ni-base alloys (e.g., Haynes 282) are being considered for various power plant components.**
  - **Internal oxides along alloy grain boundaries (due to Al & Ti additions)**
  - **Solid particle erosion (SPE) of high-pressure (HP) blades: impact of exfoliated solid particles from boiler tubes**



Swaminathan, et al., in *Advances in Materials Technology for Fossil Power Plants*, ASM International, 2014.

- **Of the four SPE-resistant coatings, only Tribaloy T-400C showed acceptable erosion rates at 760°C.**

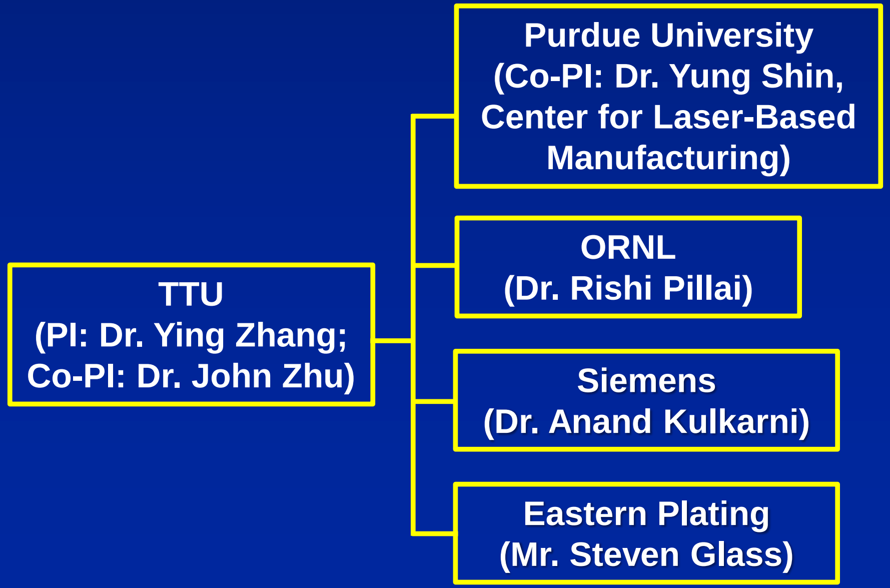
Coating	Nominal composition (wt.%)	Process	Substrate	Steam (1000h, 760°C)	Erosion (760°C)
Stellite 6B	Co-30Cr-4.5W-2Si-1.5Mo-1.1C	Wrought form	N/A	Good	Poor
Tribaloy T-400C	**Co-14Cr-27Mo-2.6Si**	**Alloy fusion**	**304 SS**	**Good**	**Good**
Metco 45	Co-10.5Ni-25.5Cr-7.5W-0.5C	HVOF	Hastelloy X	Fair	Poor
$NiCr-Cr_3C_2$	(Ni-20Cr)-75%Cr_3C_2 composite	HVOF	Hastelloy X	Fair	Poor

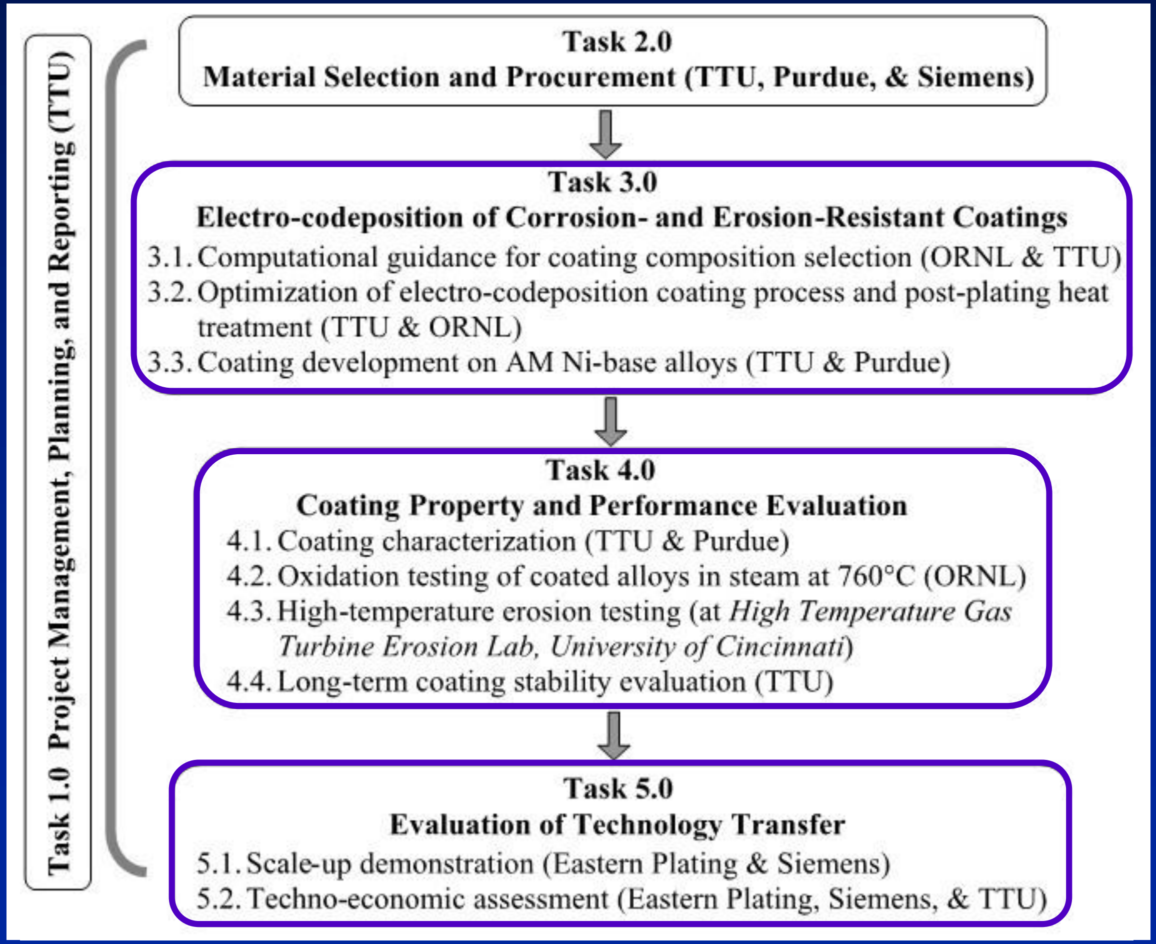
R. Viswanathan, et al., "Steam turbine materials for ultrasupercritical coal power plants," Final Technical Report, DOE Award Number DE-FC26-05NT42442, 2009.

J.P. Shingledecker, "The US DOE/OCDO A-USC materials technology R&D program," in *Materials for Ultra-Supercritical and Advanced Ultra-Supercritical Power Plants*, pp. 689-713, Woodhead Publishing, 2017.

Project Objectives and Proposed Tasks

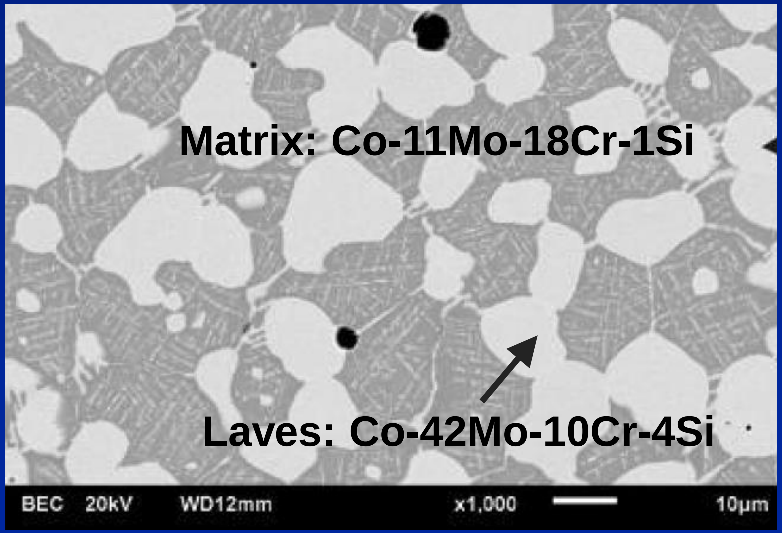
- **Develop and evaluate the corrosion- and erosion-resistant coatings for A-USC HP blade materials using a cost-effective electrolytic codeposition process**
- **Enhance and balance the corrosion and erosion resistance without compromising mechanical integrity of coated alloys**
- **Based on the study by *A-USC Materials Consortium*, a composition similar to Tribaloy T400-C was selected as the baseline coating composition.**





Tribaloy-Based Alloys and Coatings

- Tribaloy alloys were originally developed for applications of extreme wear in combination with high temperatures and corrosive media.
- Tribaloy alloys can be Ni-based (e.g., Ni-32.2Mo-13.9Cr-2.5Si), Co-based (e.g., T-400C: Co-27Mo-14Cr-2.6Si), or Co/Ni-based (e.g., T-900: Co-16Ni-23Mo-18Cr-2.7Si).
- T-400C consists of a large volume of hard intermetallic Laves phases (1000-1200 HV) dispersed in a relatively soft solid solution matrix.
- Current Tribaloy coating processes such as high-velocity oxy fuel (HVOF) spray are line-of-sight and not ideal for coating complex-shaped HP steam turbine blades.
- **Compositional optimization and new coating process development are needed.**



Cr: corrosion/oxidation resistance (partitioning in both matrix & Laves phase)

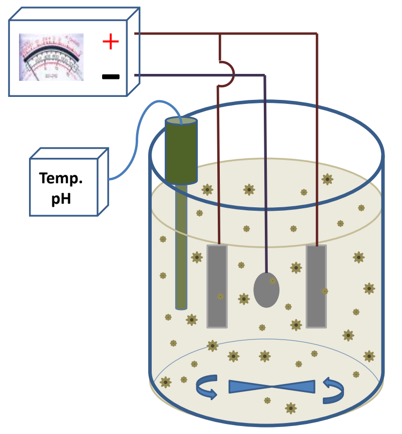
Mo: high temperature strength

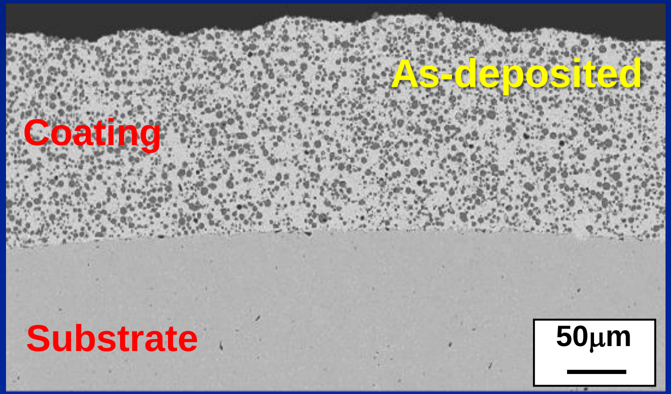
Si: essential for the Laves phase formation

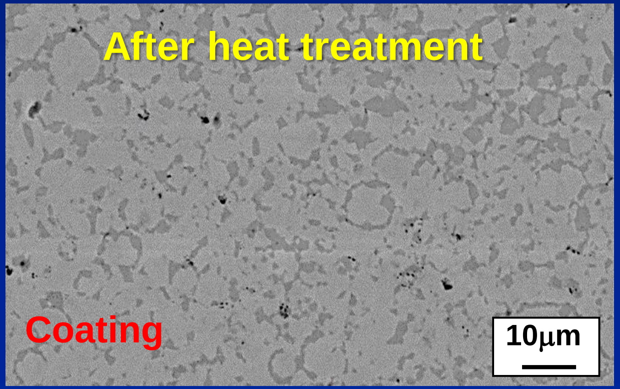
R. Viswanathan, et al., Final Report, DOE Award DE-FC26-05NT42442, 2009.

Why Electrolytic Codeposition?

- **Electrolytic codeposition ("composite electroplating"):**
  Fine particles dispersed in an electroplating solution are codeposited with the metal onto the cathode (substrate) to form a multiphase coating.
  - **Non-line-of-sight**
  - **Low cost (capital investment, energy consumption, powder waste)**
  - **Dense and homogeneous composite coatings**
  - **A unique multi-phase coating achievable upon diffusion treatment**







NiCoCrAlY coating made via electro-codeposition

(Y. Zhang, "Electrodeposited MCrAlY Coatings for Gas-Turbine Engine Applications," JOM, 2015)

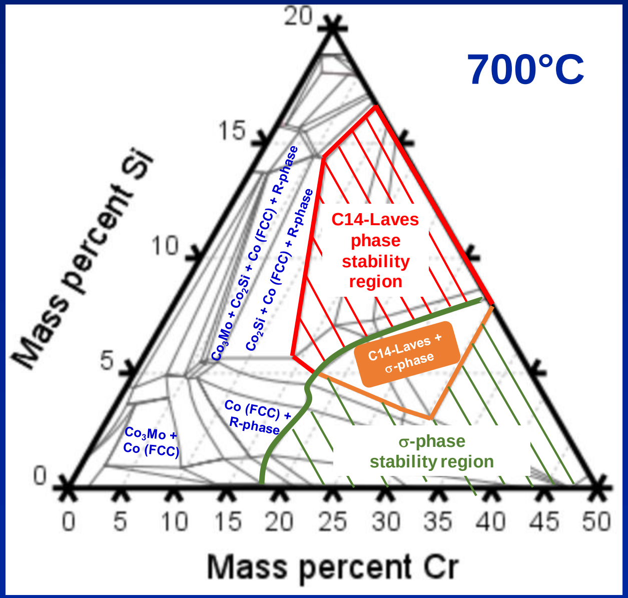
Project Milestones

Milestone	Planned Completion Date	Actual Completion Date	Verification Method	Status/ Comments
1. Submission of revised PMP	11/30/2019	8/29/2019	PMP file	Completed
2. Kickoff meeting	12/31/2019	12/20/2019	Presentation file	Completed
3. Material selection and procurement	01/31/2020	01/27/2020	All supplies & materials for alloying, plating and AM experiments are acquired.	Completed
4. Optimization of electro-codeposited coatings	8/25/2020	08/20/2020	γ+Laves phase based coatings with the desired microstructures are synthesized.	Completed
5. Completion of 760 °C steam oxidation testing on coated samples	10/30/2020	12/8/2020	Mass change data for the coated samples are obtained for ≥ 1,000 h exposure in steam.	Completed
6. Completion of solid particle erosion testing for the coated samples	1/30/2021	5/3/2021	Erosion rate data for coated samples are obtained under a simulated turbine operating condition at 760°C.	Completed
7. Techno-economic analysis	3/31/2021	3/30/2021	Scale-up design and cost analysis of the coating process are completed.	Completed

- All seven milestones have been completed.

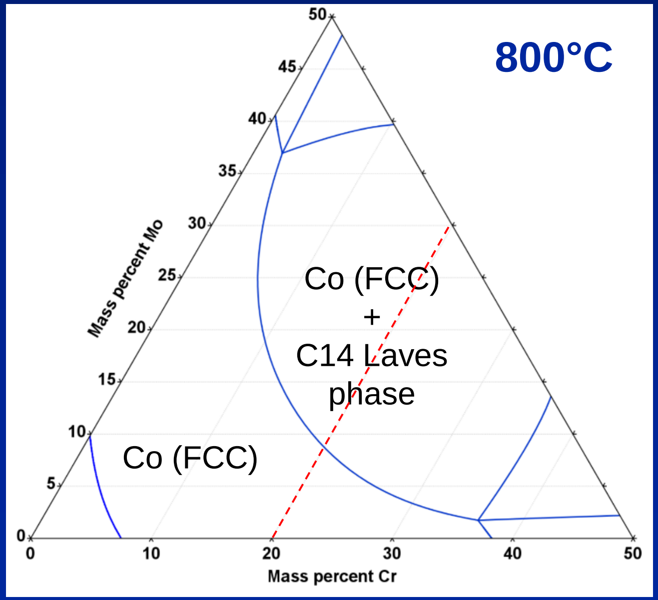
Task 3.0 – Electro-codeposition of Corrosion- and Erosion-Resistant Coatings

- **Subtask 3.1 Computational guidance for coating composition selection (ORNL & TTU)**
  - Dr. Pillai (ORNL) used Thermo-Calc to explore the γ + Laves space.
  - The two-phase region of Co (FCC) + C14 Laves phase lied within a large composition range.
  - Increases in Cr and Mo contents could stabilize Laves phase.
  - For 20% Cr, increasing Mo from 10 to 30% would not change the phase constitution, i.e., γ (Co) + C14 Lave phase.



Co-Cr-Si-10Mo (wt.%)

Calculated Phase Diagrams



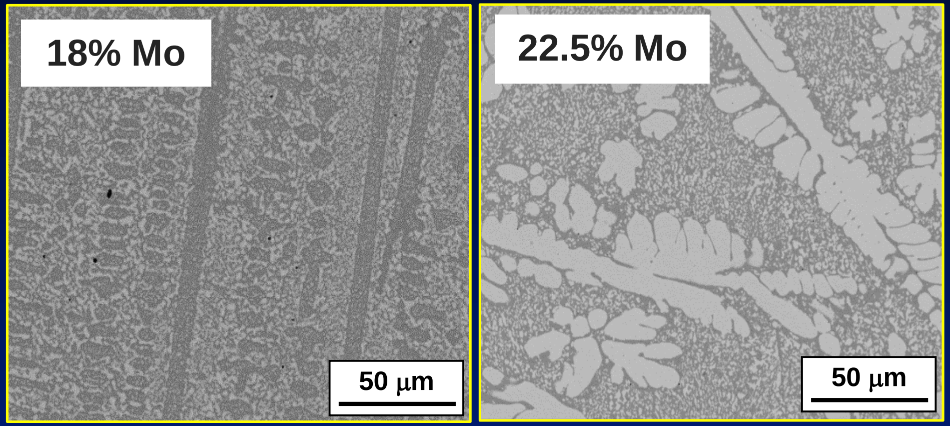
Co-Cr-Mo-2.6Si (wt.%)

Selected Model Alloys & Electrodeposited Coatings

ID	Composition (wt.%)	Notes/Justification	Oxidation			Erosion
			Air, 800°C	Steam, 760°C		760°C
			200h	500h	1000h	
H282	Ni-10Co-20Cr-8.5Mo-2.1Ti-1.5Al	Commercial Ni-base alloy	✓	✓	✓	✓
T-400C	Co-14Cr-27Mo-2.6Si	T-400C composition	✓	✓		
T-900	Co-16Ni-18Cr-23Mo-2.7Si	T-900 composition	✓	✓	✓	
#1	Co-20Cr-12.5Mo-2.6Si	Baseline low Mo	✓			
#2	Co-20Cr-18Mo-2.6Si	Increased Mo to 18% in #1	✓		✓	
#3	Co-20Cr-22.5Mo-2.6Si	Increased Mo to 22.5% in #1	✓			
#4	Co-20Cr-18Mo-2.6Si-0.4Y	Similar to #2, added 0.4Y	✓		✓	✓
#5	Co-20Cr-18Mo-2.6Si-0.7Y	Similar to #2, added 0.7Y	✓		✓	
#6	Ni-20Cr-18Mo-2.6Si- 0.4Y	Similar to #4, replaced Co with Ni	✓		✓	
#7	Ni-41.3Co-20Cr-18Mo-2.6Si-0.4Y	Similar to #4, Ni/Co = 0.4	✓		✓	
#8	Ni-18Co-20Cr-18Mo-2.6Si-0.4Y	Similar to #4, Ni/Co = 2.3	✓		✓	
#9	Ni-16.5Co-20Cr-18Mo-2.6Si-0.6Y	Similar to #8, with 0.6 Y	✓			✓
#10	Ni-16.5Co-20Cr-14Mo-4X-2.6Si-0.6Y	Similar to #9, replaced some of Mo with X	✓			
Gen-1 Coating	Mo similar to and Cr slightly higher than that in T-400C/T-800	Close to traditional Tribaloy alloy compositions	✓	✓		
Gen-2 Coating	Higher Cr and lower Mo over Gen-1	Higher Cr for improved oxidation resistance	✓		✓	✓
Gen-3-1	Lower Mo over Gen-1, but with 0.4Y	Y addition for improved oxidation resistance	✓		✓	✓
Gen-3-2	Lower Mo over Gen-1, but with 0.7Y	Higher Y addition for better oxidation resistance	✓		✓	✓
Gen-3-3	Similar Mo & Cr to Gen-2, but with 0.7Y	Y addition for improved oxidation resistance	✓		✓	✓

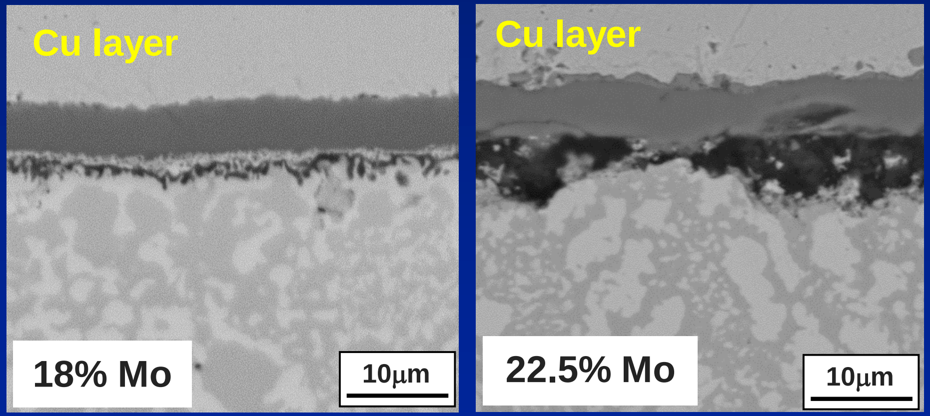
- **35 alloy compositions and 3 generations of coatings were evaluated.**

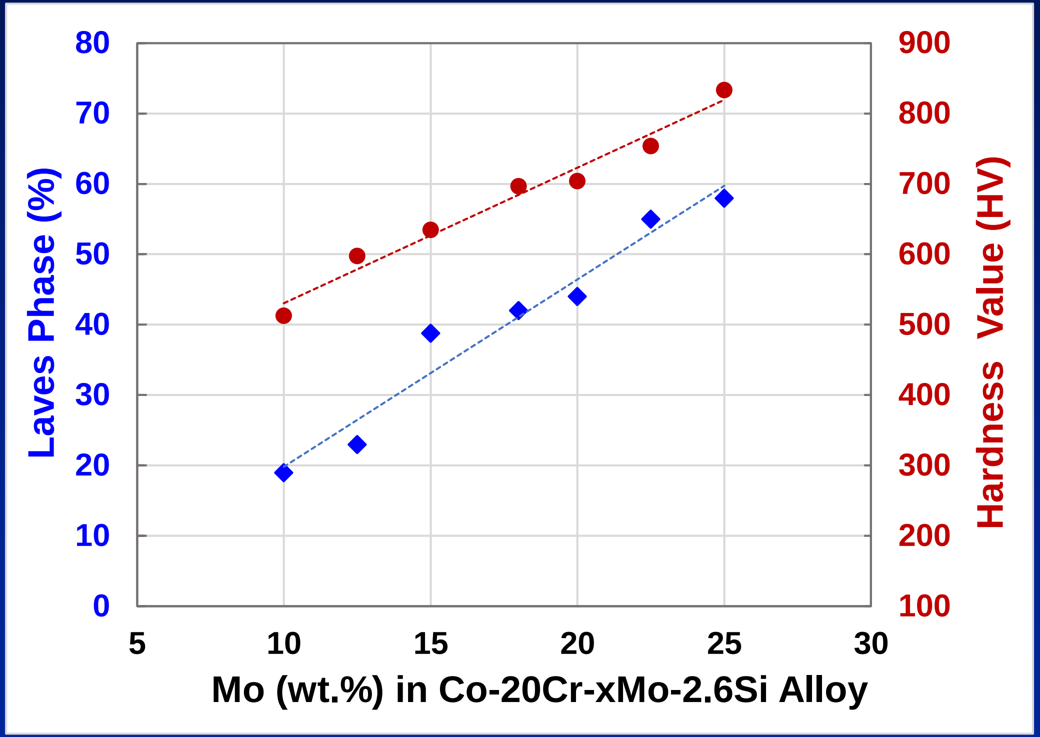
Tribaloy-based Model Alloys: Co-20Cr-xMo-2.6Si



- As the Mo content was increased, Laves volume fraction and alloy hardness increased almost linearly.

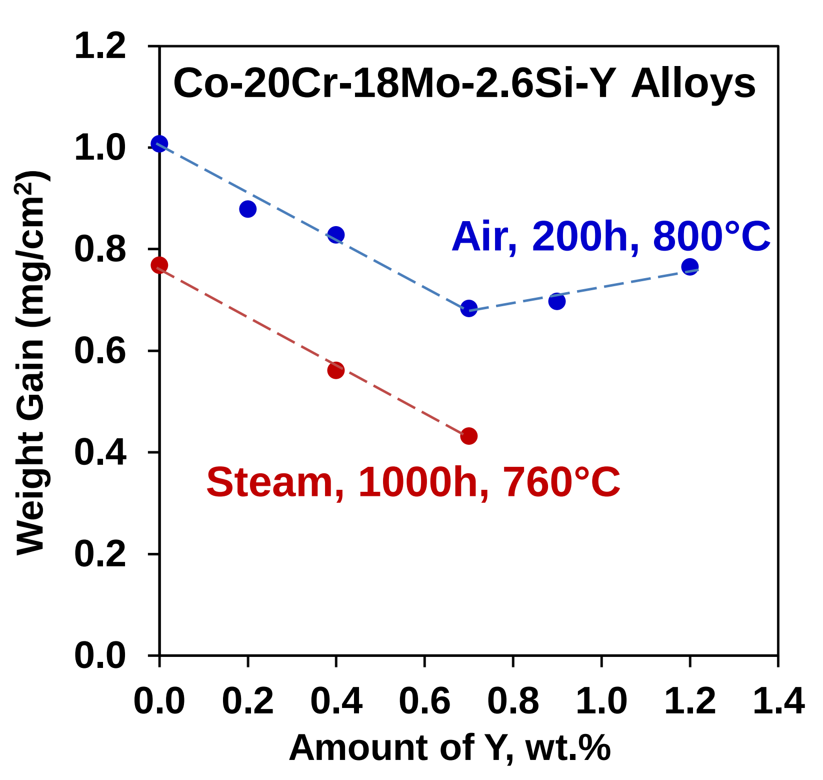
200-h Oxidation in Air at 800°C

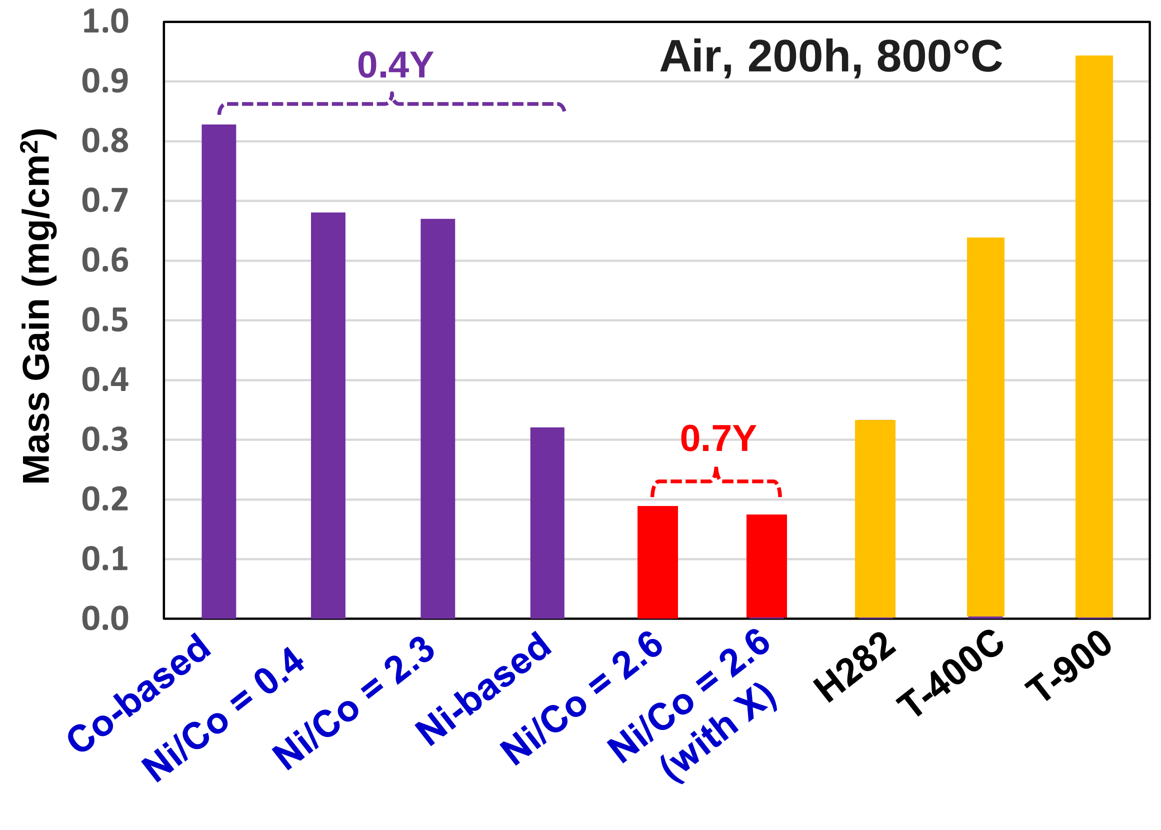


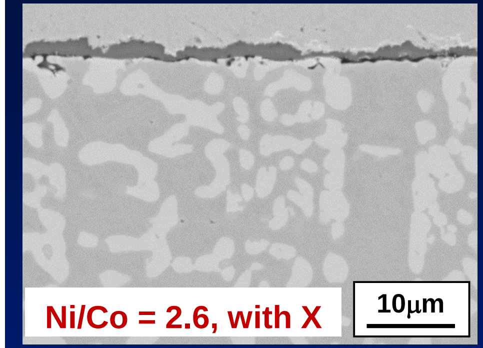


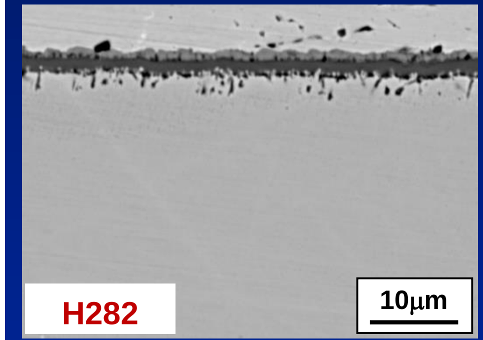
- Mo < 20%: adherent oxide scales
- Mo ≥ 20%: spallation, mainly at the Cr_2O_3/SiO_2 interface

Effect of Reactive Element Additions and Ni/Co Ratio on Oxidation Resistance of Tribaloy-based Alloys



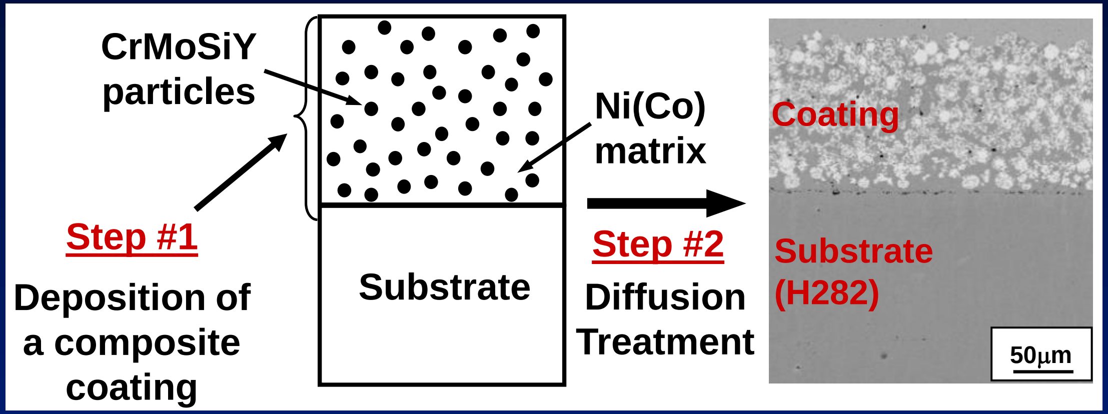




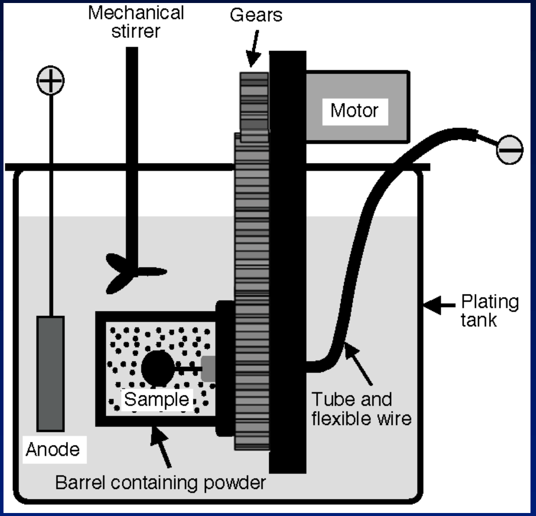


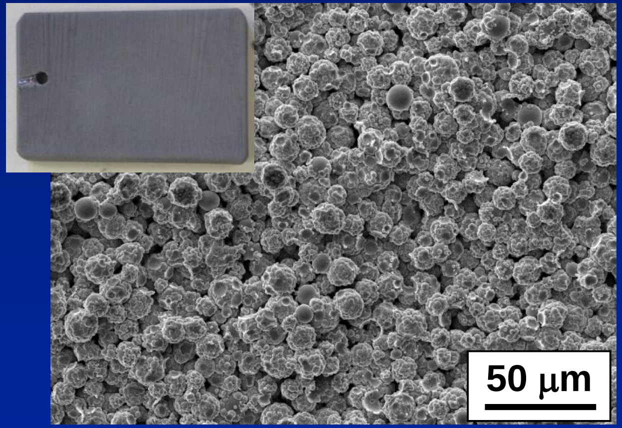
- The optimal Y content in Co-based alloys was 0.6-0.7%.
- Coating costs could be reduced by reducing the Co content in the coating, which also lowered the mass gain after oxidation.
- With 0.7% Y, good oxidation resistance was obtained for alloys with a Ni/Co ratio of 2.6.

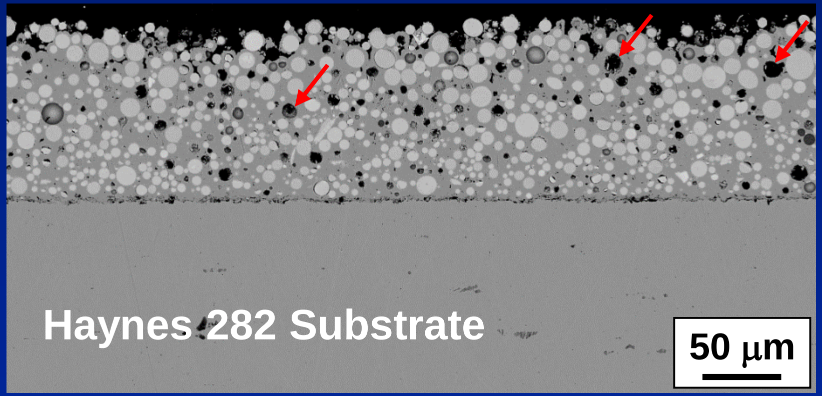
Subtask 3.2 Optimization of Electro-codeposition Coating Process and Post-plating Heat Treatment (TTU & ORNL)



- Type of electrolyte
- pH
- Current density
- Temperature
- Particle loading
- Particle composition/geometry/size
- Cathode position (configuration)
- Post heat treatment







- Electro-codeposition parameters were varied to optimize coating microstructure.
- Uniform and adherent coatings without blisters/cracks or other defects were achieved on the entire specimen.

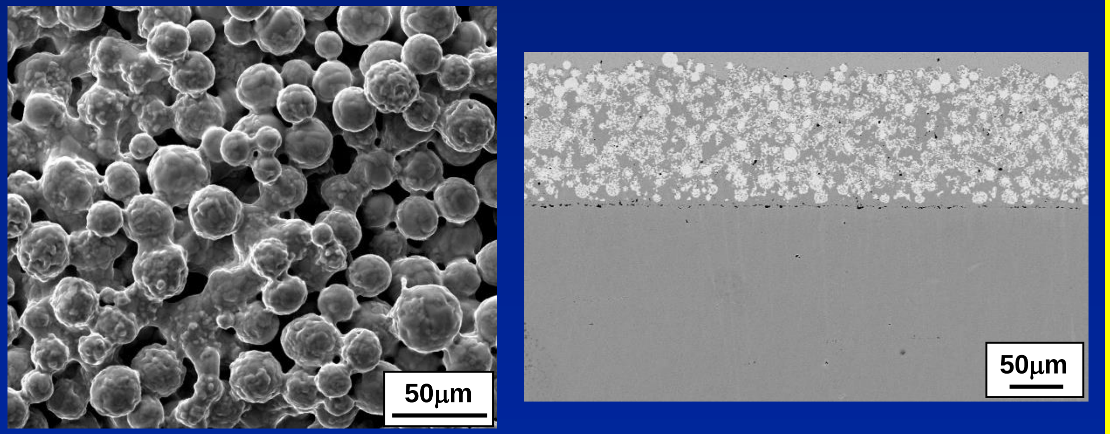
Effect of Post-Deposition Heat Treatment

- Post-deposition heat treatment facilitates interdiffusion between CrMoSi particles and the (Co,Ni) matrix to form phases of γ, Laves, etc.
- Ideally, to combine the coating & substrate heat treatment

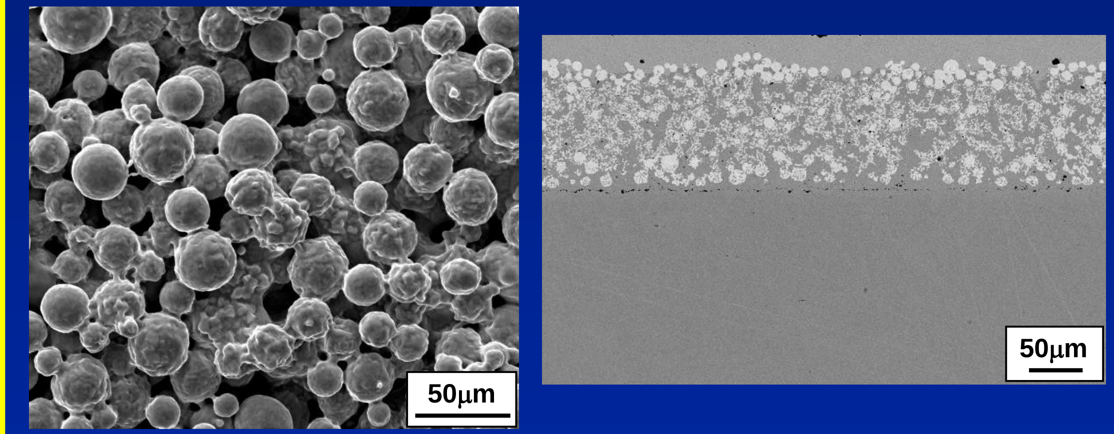
  H282: solution treatment (1121-1149°C) + two-step aging treatment (1010°C/2h/air cool + 788°C/8h/air cool)

Element	Phase Composition after 6h at 1080°C (wt.%)	
	γ-phase matrix	Laves phase
Cr	25.3	10.8
Mo	7.3	43.4
Si	0.9	5.3
Co	19.3	13.9
Ni	47.2	26.6

6h at 1080°C



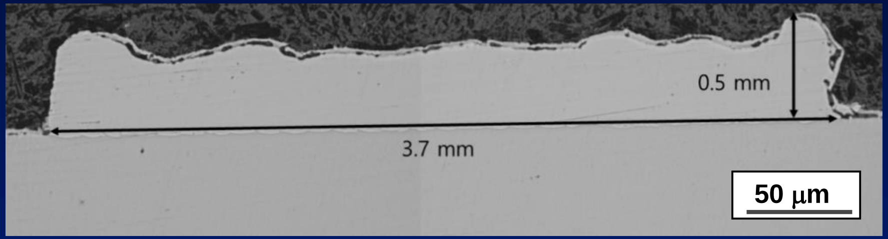
2h at 1149°C



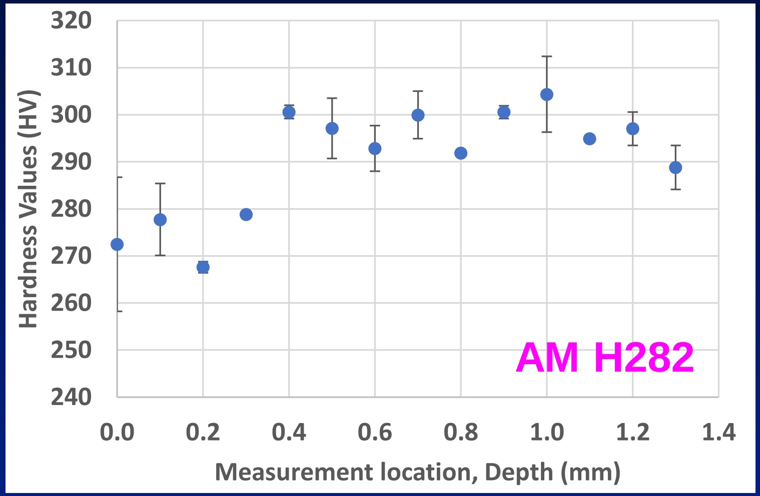
- Both 1080°C x 6h and 1149°C x 6h treatments resulted in the desired coating microstructure.

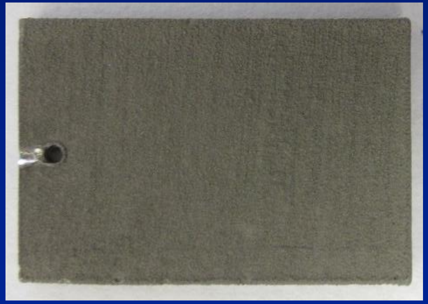
Subtask 3.3 Coating Development on AM Ni-Base alloys (TTU & Purdue)

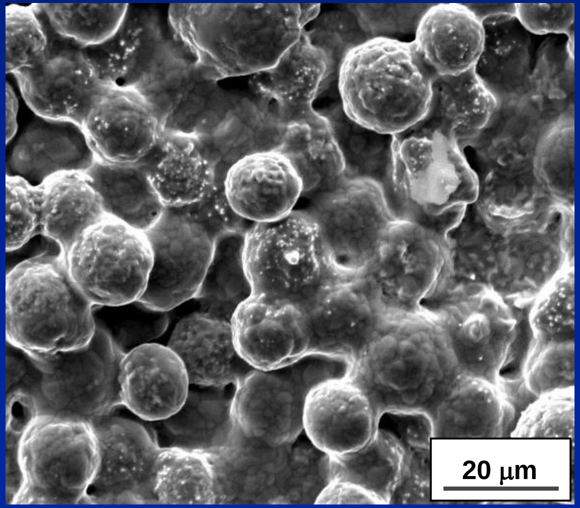
- To demonstrate that electro-codeposition is a viable coating process for AM alloys



H282 deposited using Purdue's powder bed fusion (PBF) system



	AM H282	Coated AM H282
As-deposited side		
As-ground side		

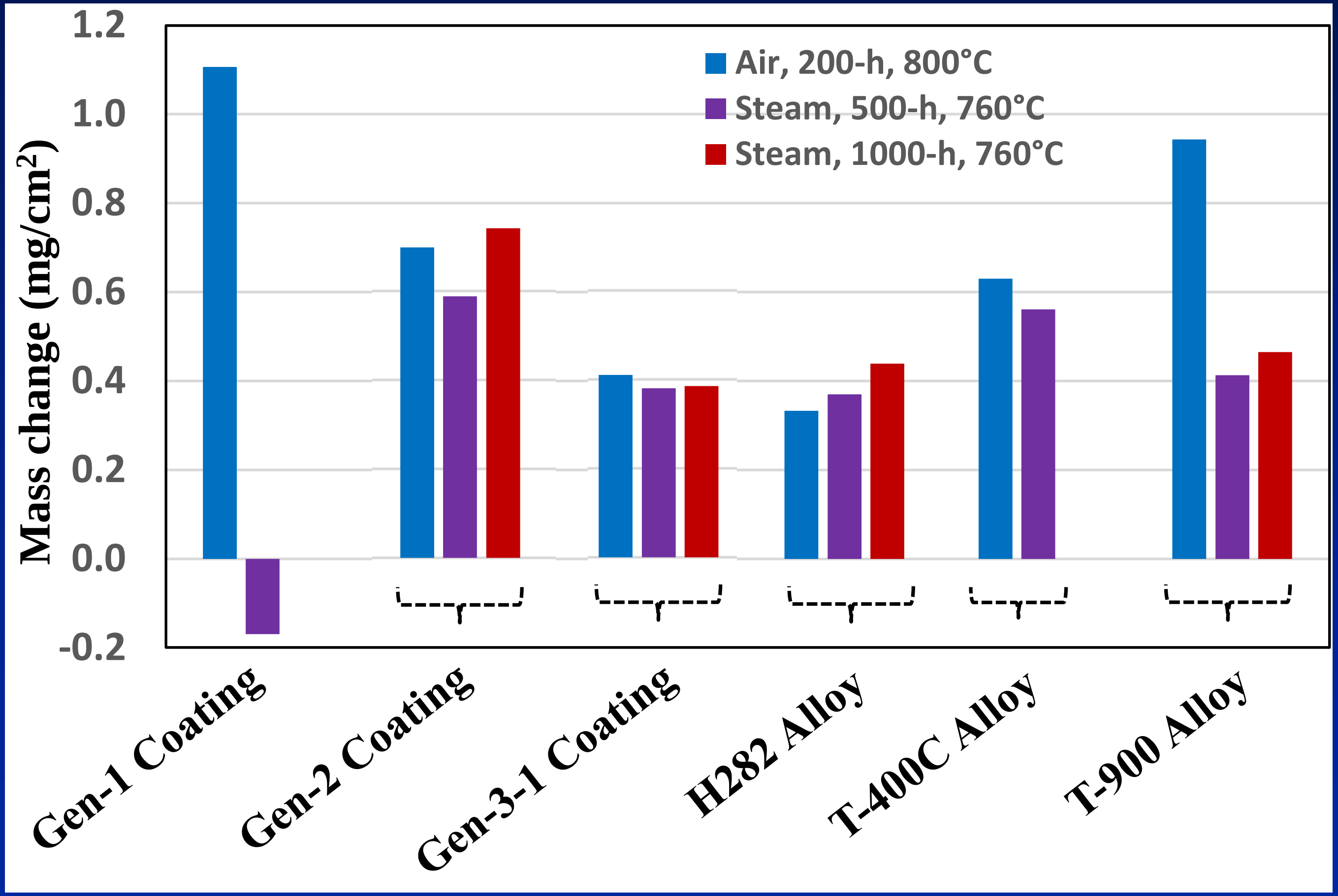


Coated AM H282

(6h at 1080°C)

Task 4.0 – Coating Performance and Property Evaluation

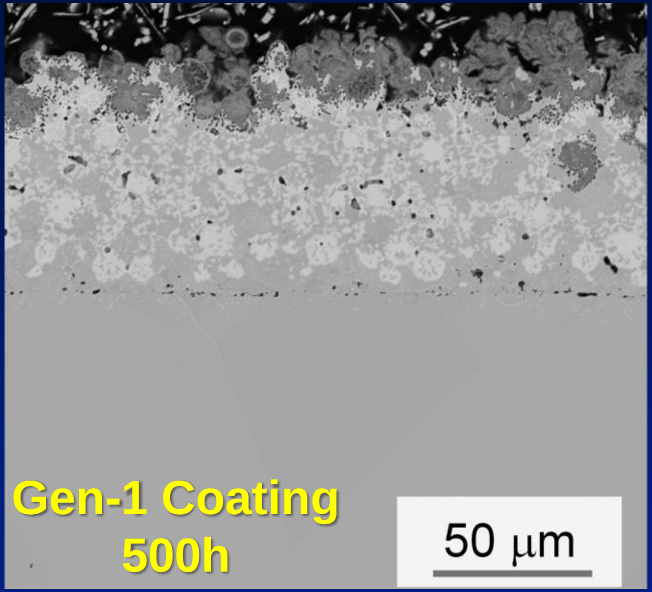
- Subtask 4.1 Coating characterization (TTU & Purdue)
- Subtask 4.2 Oxidation testing in steam at 760°C (ORNL)

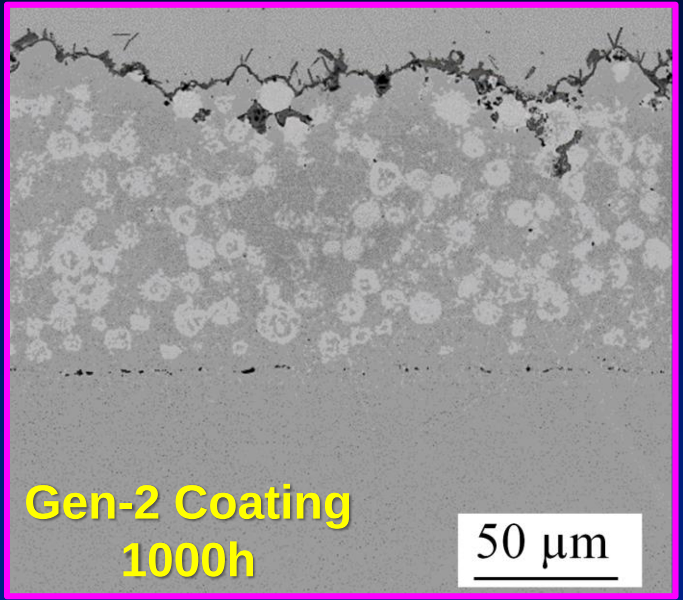


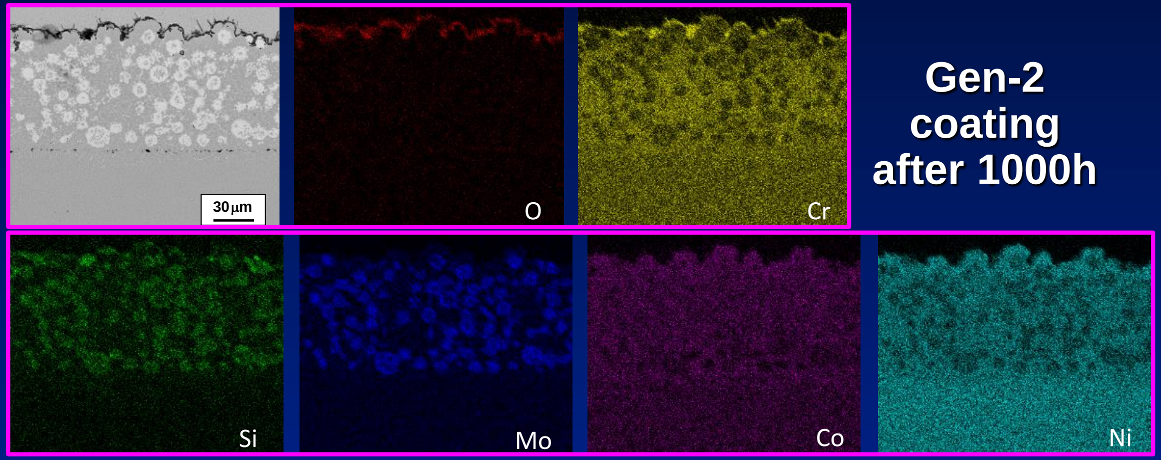
- Gen-1: high Mo (close to T-400C & T-800)
- Gen-2: lower Mo, higher Cr (close to T-900)
- Gen-3: 0.7% Y (to increase erosion resistance while maintaining good oxidation resistance)

Steam Oxidation Performance of Coated and Uncoated H282

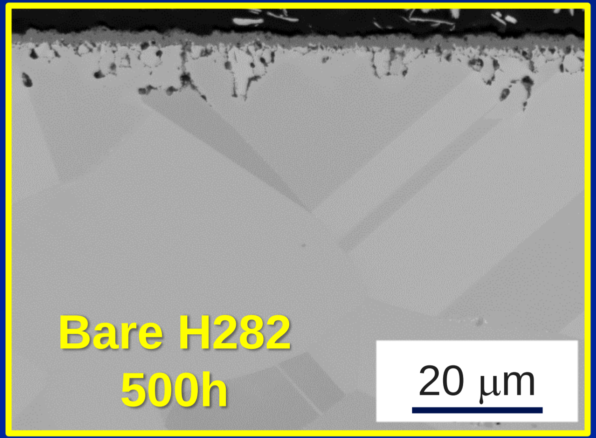
After Oxidation in Steam at 760°C

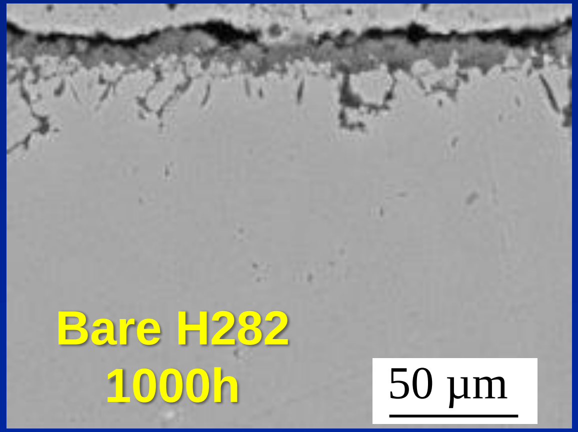


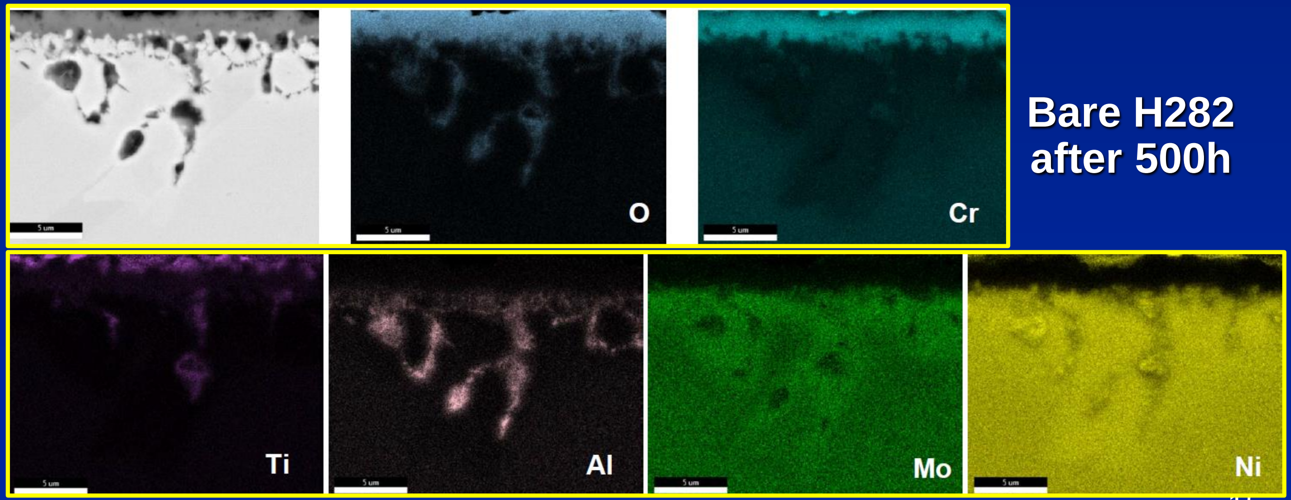




Gen-2 coating after 1000h



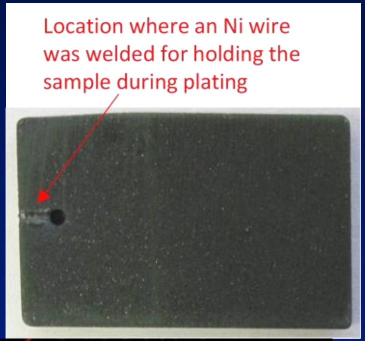


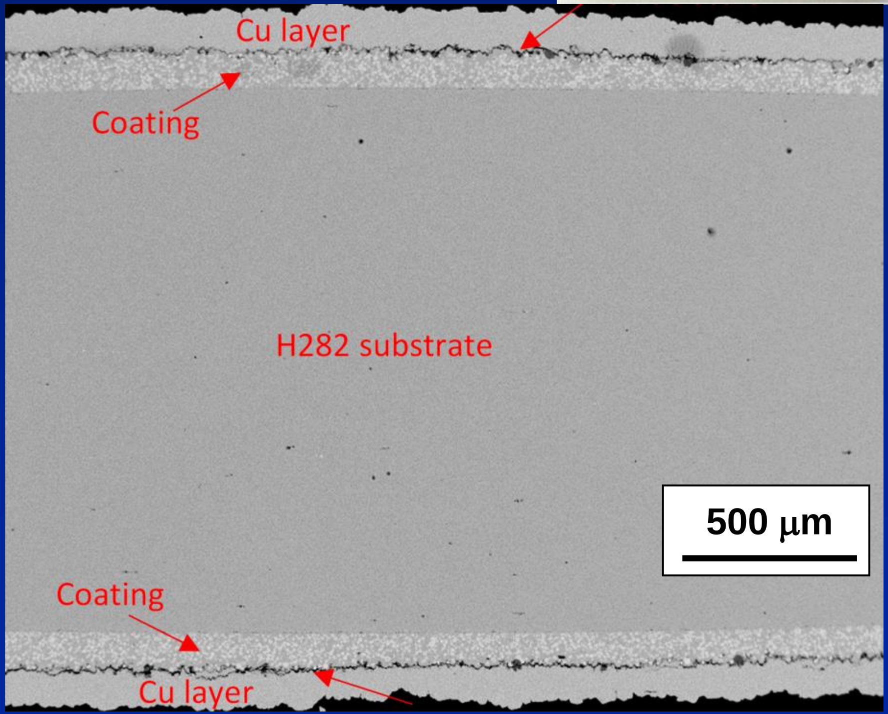


Bare H282 after 500h

Comparison of New Tribaloy Coatings and Coatings Previously Evaluated by the A-USC Consortium

- **Electro-codeposited Tribaloy coating (Gen-2)**
  - **Remained intact**
  - **Free of internal cracks**

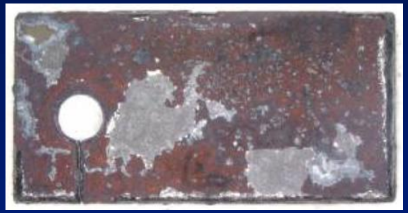




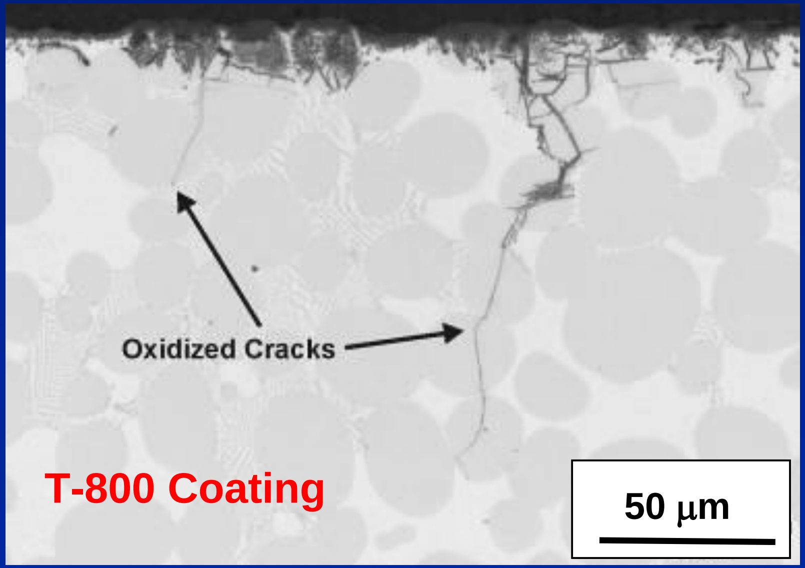
After 1000h in Steam at 760°C

- **Tribaloy coating previously evaluated by the A-USC Consortium**

  R. Viswanathan, et al., Final Technical Report, DE-FC26-05NT42442, 2009.



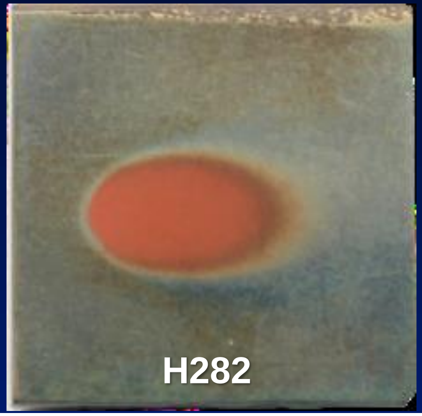
Uncoated side

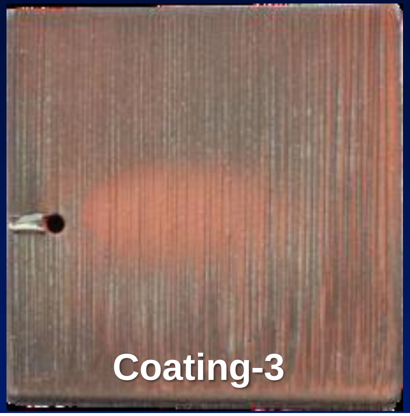


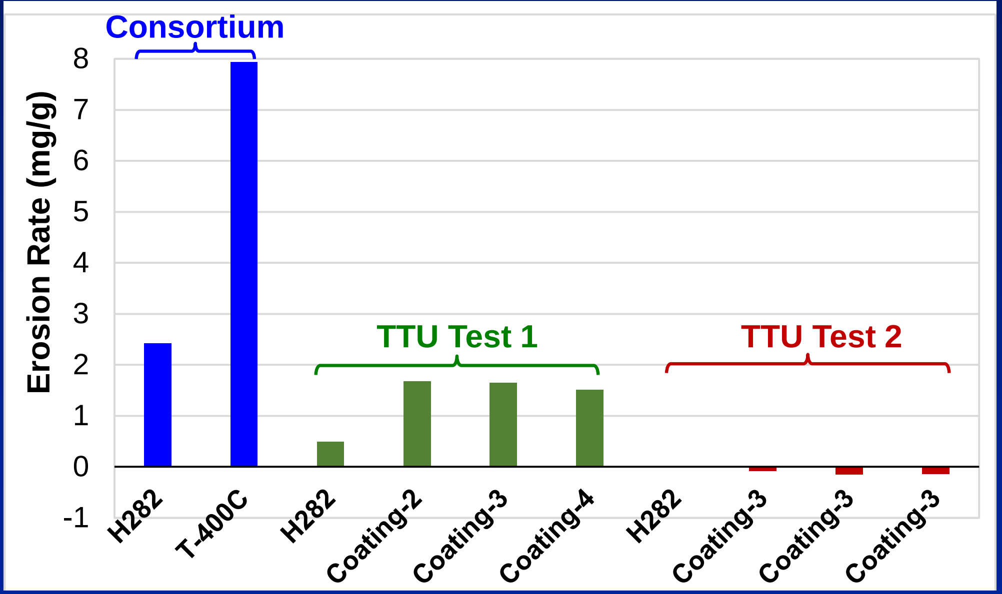
Subtask 4.3 High-Temperature Erosion Testing

- Factors affecting the SPE rate: temperature, environment, erodent, velocity, impact angle, etc.

	Test Facility	Erodent	Velocity (m/s)	Angle (°)	Erosion rate (mg/g)	Erosion rate ratio (Coating vs. H282)
H282	Univ. of Cincinnati (Viswanathan et al.)	Silica (149-850 μm)	274	30	2.42	
T-400C					7.94	3.3
H282	DUCOM	Alumina (50 μm)	150	30	0.49	
Coating-2					1.68	3.4
Coating-3					1.65	3.4
Coating-4					1.51	3.1
H282	DUCOM	Magnetite (<88 μm)	150	30	-0.008 (Net deposit)	–
Coating-3					-0.078 (Net deposit)	–
Coating-3					-0.150 (Net deposit)	–
Coating-3					-0.138 (Net deposit)	–



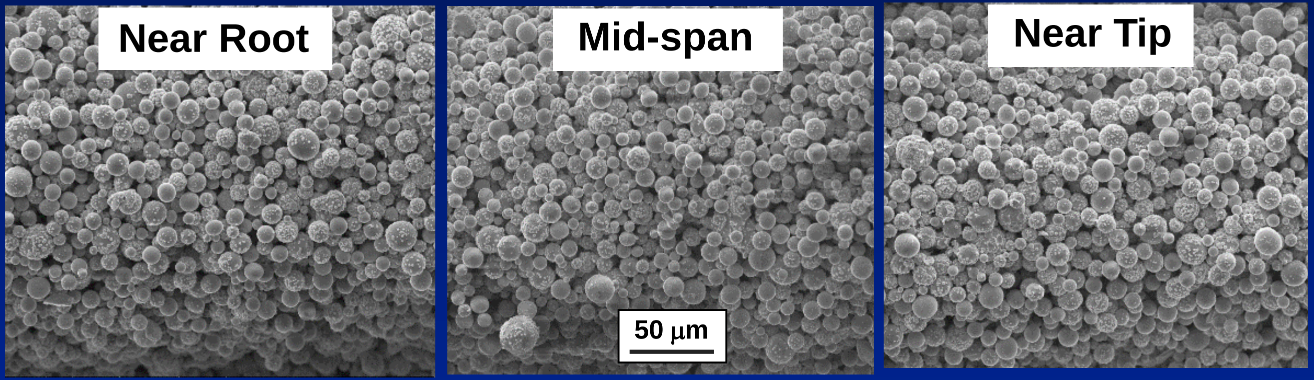


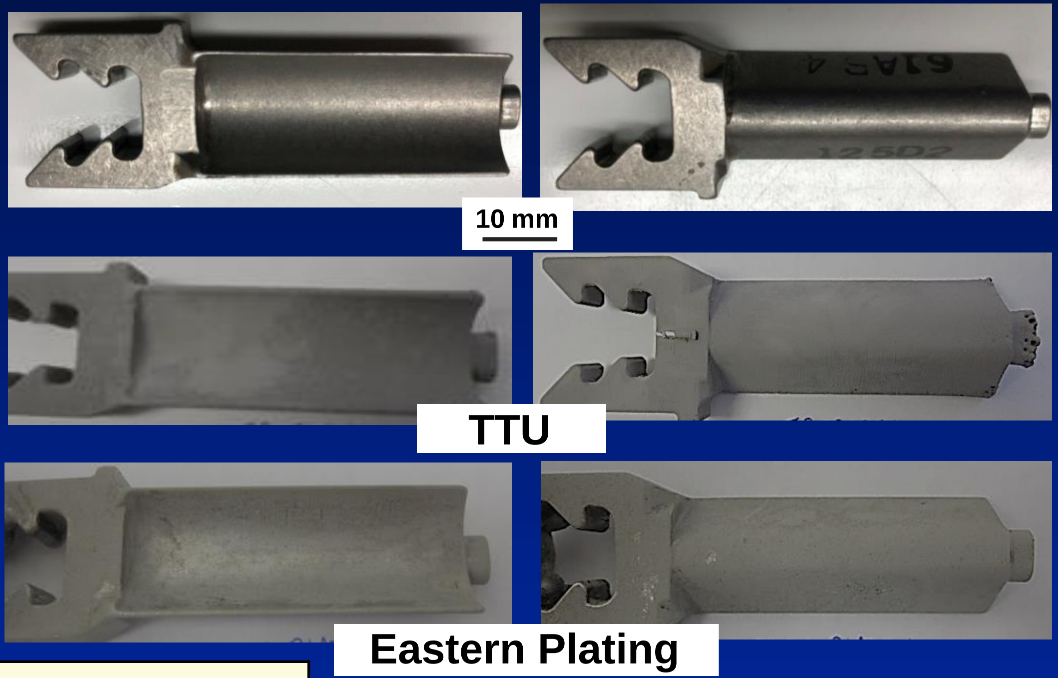


- The erosion resistance of a coating is affected by **microstructure, hardness, and toughness**.
- **Synergistic interactions between erosion and oxidation** at high temperature

Task 5.0 – Evaluation of Technology Transfer

- **Subtask 5.1 Scale-up demonstration (TTU, Eastern Plating & Siemens)**
  - Design and construction of larger rotating barrels
  - HP steam turbine blades: 70-350 mm



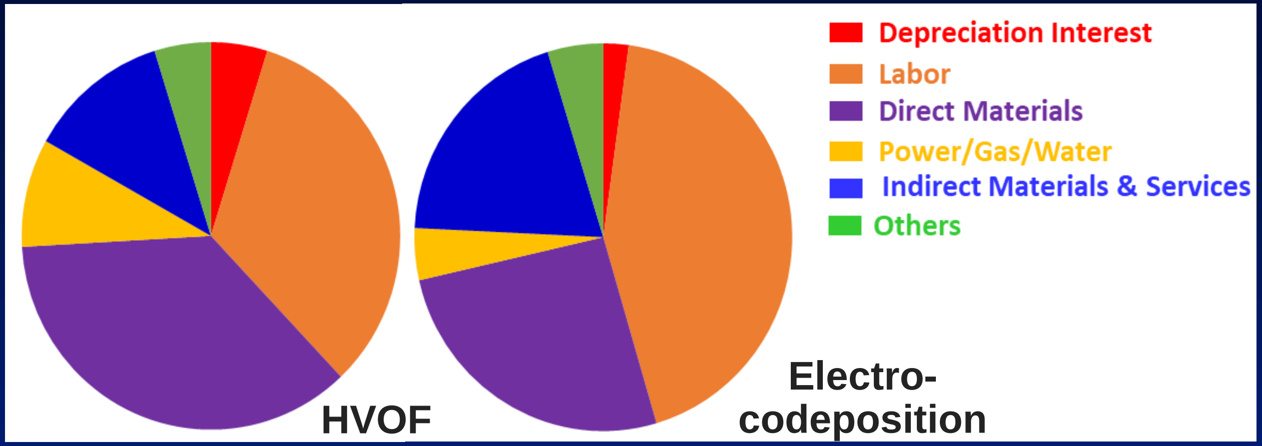


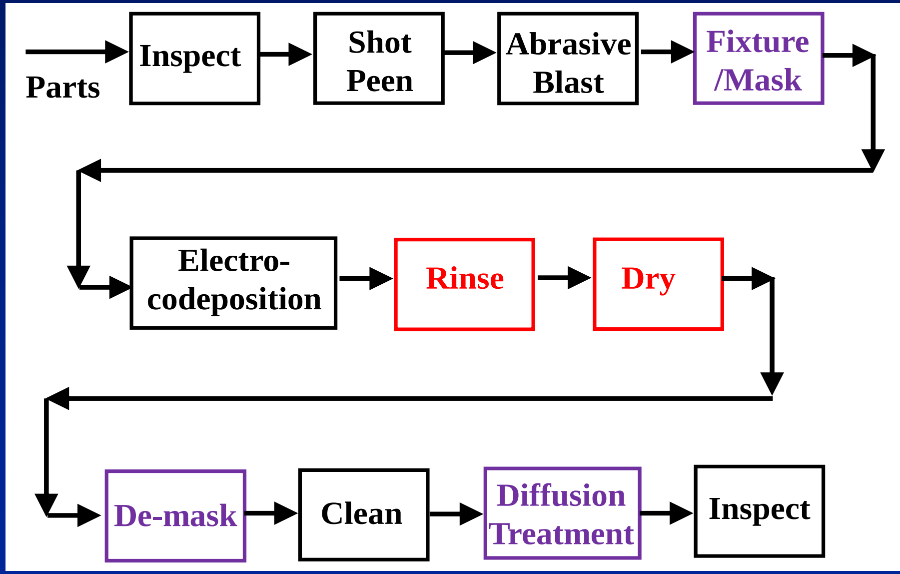
Element (wt.%)	Near Root	Mid-span	Near tip
Si	3.4	4.3	3.9
Mo	24.1	32.0	28.3
Cr	21.9	30.2	25.8
Co	7.4	5.1	5.8
Ni	43.3	28.4	36.1

Subtask 5.2 Techno-Economic Assessment (TTU, Eastern Plating, & Siemens)

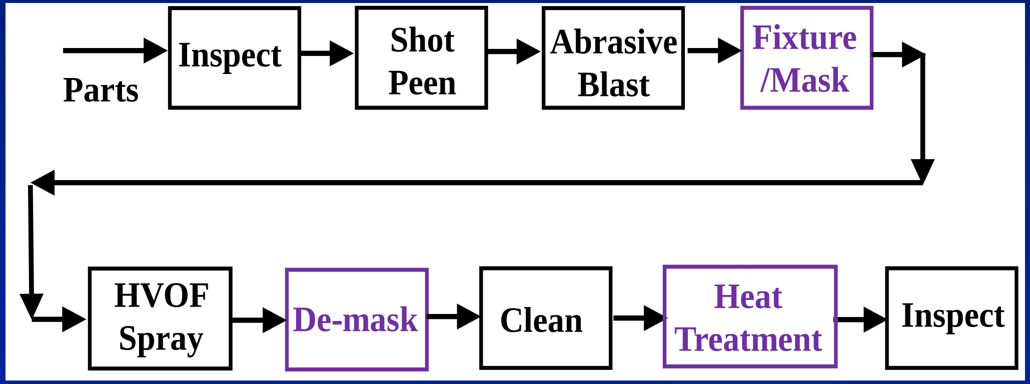
Electro-codeposition:

- Low capital investment
- Minimal powder waste (no overspray) and low energy consumption





Electro-codeposition



HVOF

- ~30% cost reduction could be achieved with the electro-codeposition coating process over the state-of-the-art HVOF spray.

Concluding Remarks

- It is feasible to develop Tribaloy-based coatings with enhanced corrosion and erosion resistance to protect Ni-base superalloy A-USC components (e.g., HP blades and valves).
  - The new electro-codeposited Tribaloy coatings showed excellent steam oxidation performance at 760°C.
  - Initial erosion testing indicates good erosion resistance at 760°C.
  - The electro-codeposition coating process could lead to ~30% cost reduction over the state-of-the-art HVOF spray.
  - Compared to other coating technologies, non-line-of-sight electro-codeposition is more advantageous, particularly for complex-shaped components
- New materials/coatings & manufacturing are the enabling technology for multiple advanced power generation technologies.
  - Transformational sCO_2 power cycles
  - Molten salt heat-transfer and thermal energy storage
  - Centrifugal particle receiver in concentrated solar power plants

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