An Alternative Low-Cost Process for Deposition of MCrAlY Bond Coats for Advanced Syngas/Hydrogen Turbine Applications

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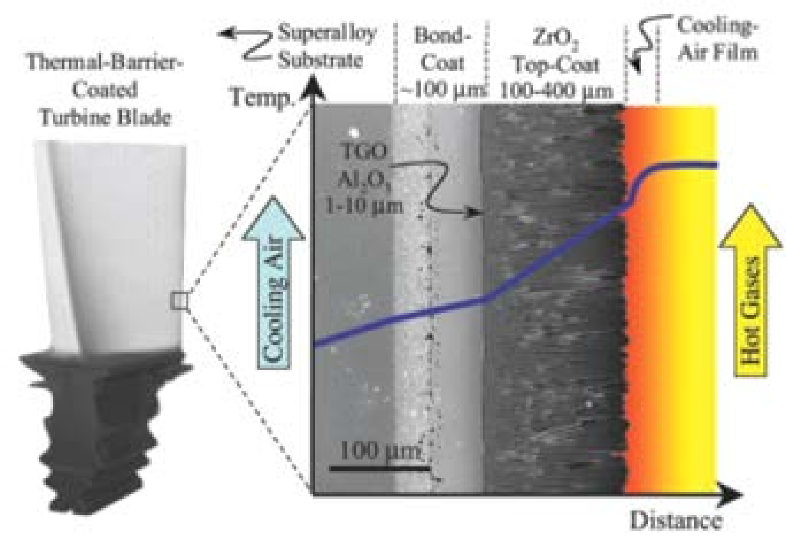
Coating Development Need for IGCC

(Integrated Gasification Combined Cycle)

- One of materials needs for advancement of IGCC power plants is to develop low-cost and effective manufacturing processes for application of new TBC/bond coat architectures with enhanced performance and durability in syngas/hydrogen environments.

(http://www.ge-7fa.com)

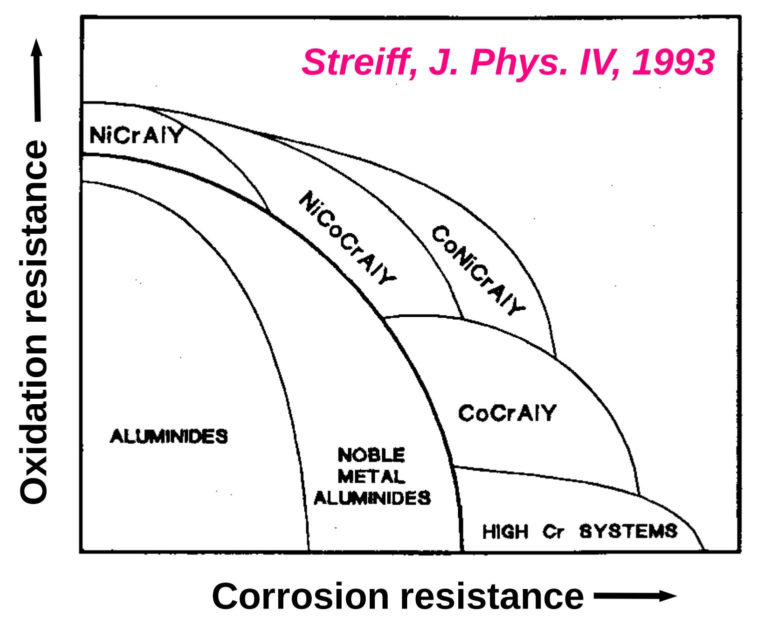
(http://www.aecengineering.com)



(Padture, et al., Science, 2002)

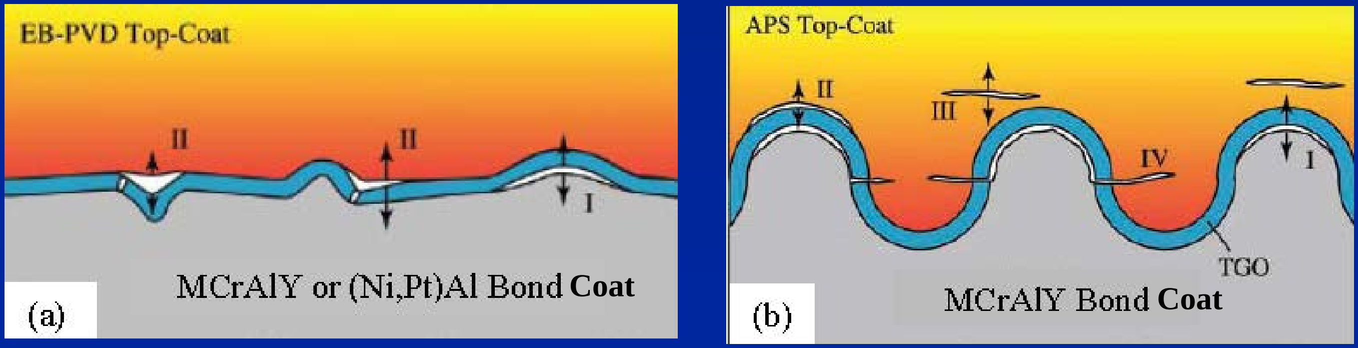
Bond Coat Choices

- Bond coat choices
  - Diffusion aluminide
  - MCrAlY overlay (M = Ni, Co or a mixture of Ni & Co)
    - More independent of the substrate composition
    - Lower ductile-to-brittle-transition temperature



Streiff, J. Phys. IV, 1993

- Depending on the bond coat choice and fabrication process the TBC failure mode can be quite different.



(Padture et al., Science, 2002)

Processes for MCrAlY Bond Coat Fabrication

- **Current fabrication processes**
  - **Low-pressure plasma spray (LPPS)**
  - **Air plasma spray (APS) & high-velocity oxy-fuel (HVOF)**

- **Limitations of thermal spray processes**
  - **Line-of-sight, requiring complex robotic manipulation for complete coverage**
  - **Oxide content can be high in APS and HVOF coatings.**
  - **High porosity level in APS**

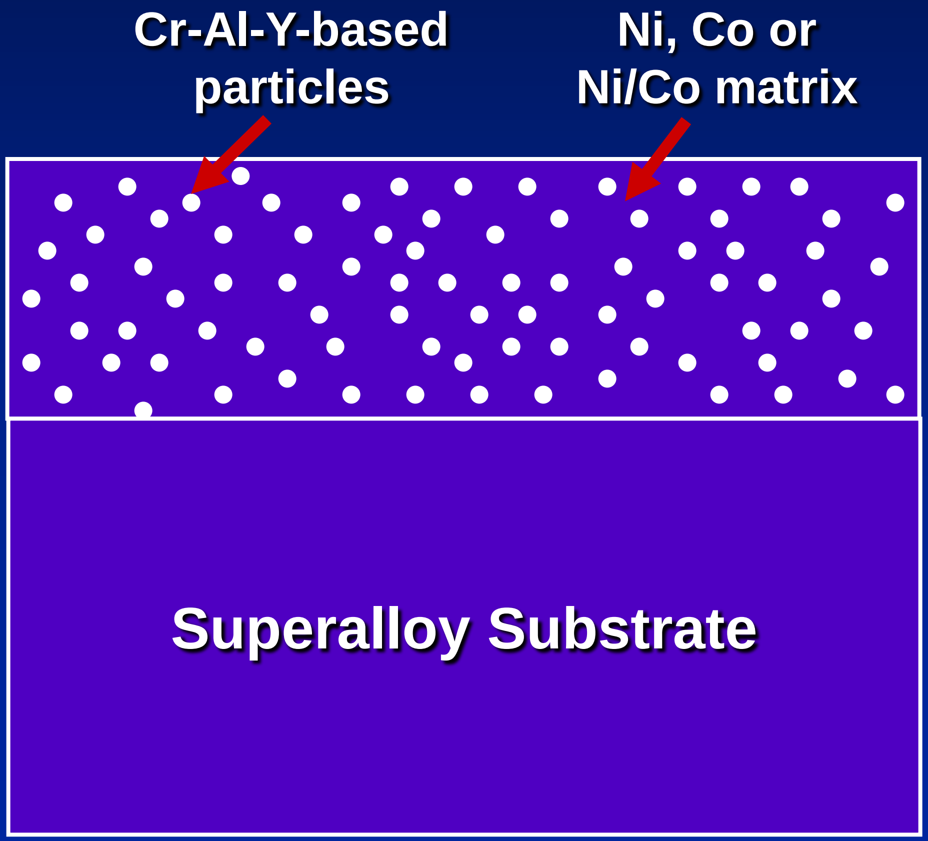
- **Alternative coating processes for bond coat fabrication**
  - **Electrolytic codeposition**
  - **Electrophoresis**
  - **Autocatalytic electroless deposition**

Why Electro-codeposited MCrAlY Coatings?

- **Electrolytic codeposition ("composite electroplating"):**

  Fine powders dispersed in an electroplating solution codeposit with the metal onto the cathode to form a multiphase coating.

  - **Non-line-of-sight**
  - **Low cost (capital investment, energy consumption, powder waste)**
  - **Ability of producing homogeneous and dense coatings**



Very Limited Research on Electrolytic Codeposited MCrAlY Coatings

- Codeposition of CrAlY powder and a metal matrix of Ni, Co, or Ni-Co, followed by a post-plating heat treatment

  (Foster et al., Trans. Inst. Met. Finish; 1985, Honey et al., J. Vac. Sci. Technol., 1986)

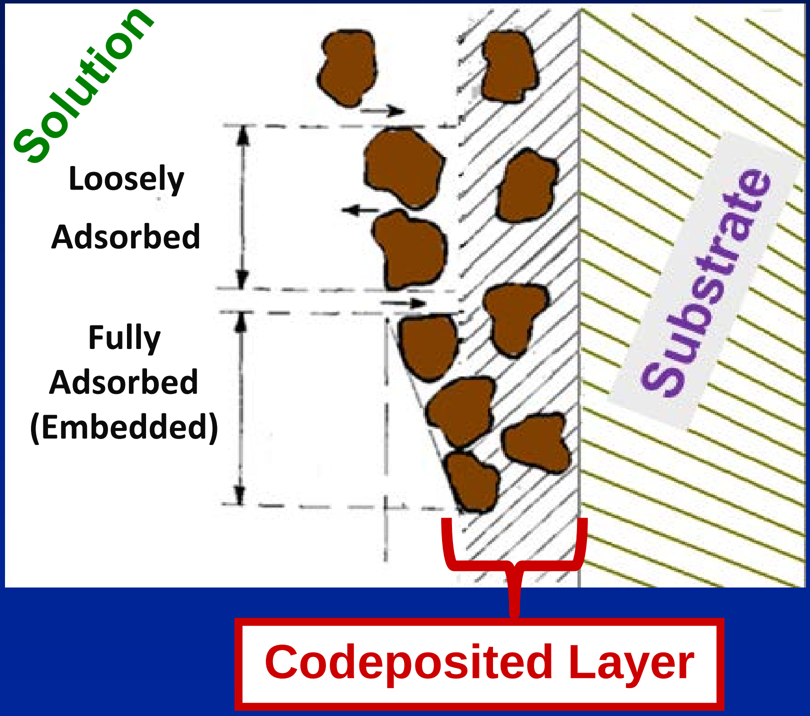
- A dense MCrAlY coating of ~125μm thick was reported.
- The process was later patented by Praxair, known as *Tribomet*, and has been applied as the abrasive tip coating on first stage turbine blades.

- Lack of systematic studies
- No evaluation in syngas/hydrogen turbine environments

Electrolytic codeposition is a more complex process than conventional electroplating

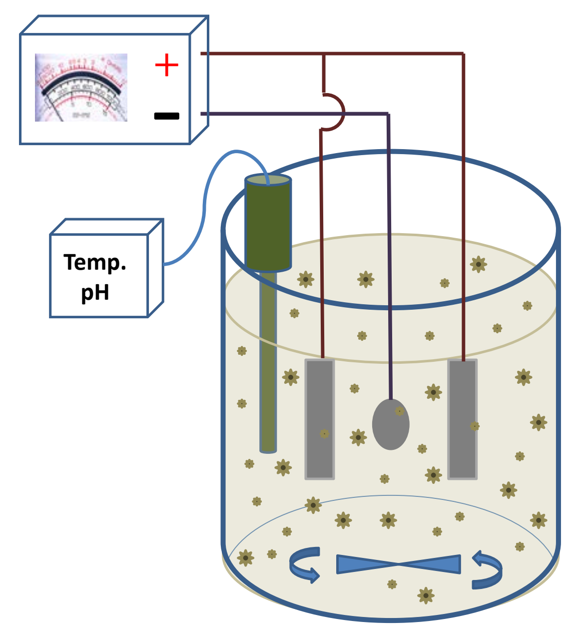
- **It is believed that five consecutive steps are engaged during the electrolytic codeposition process:**

1. **Formation of ionic clouds on the particles**
2. **Convection towards the cathode**
3. **Diffusion through a hydrodynamic boundary layer**
4. **Diffusion through a concentration boundary layer and finally**
5. **Adsorption at the cathode where the particles are entrapped within the metal deposit**



(Guglielmi, J. Electrochem. Soc., 1972)

Synergistic Effects of Codeposition Parameters



- Codeposition parameters
  - Type of electrolyte
  - Current density
  - pH
  - Temperature
  - Agitation
  - Particle composition/size/volume
  - Cathode position (plating configuration)
  - Post-plating heat treatment
- Lack of systematic studies, need to establish a knowledge base

Project Objectives

- Develop and optimize MCrAlY bond coats for syngas/hydrogen turbine applications using a low-cost electrolytic codeposition process
- Improve coating oxidation performance by reducing the sulfur impurity levels and by employing reactive element co-doping
- Evaluate the oxidation behavior of the new bond coat in water vapor environments
- Understand the failure mechanism of the new TBC/bond coat architecture

Key Research Components

#1: Selection of Substrate Alloys More Relevant to IGCC Applications

CMSX-486 (a revised version of CMSX-4)

#2: Development & Optimization of Electro-codeposited Coatings

- Electrolyte selection for Ni-/Co-matrix deposition
- Optimization of particle composition & volume
- Control of other codeposition parameters
- Microstructural evolution during post-plating heat treatment

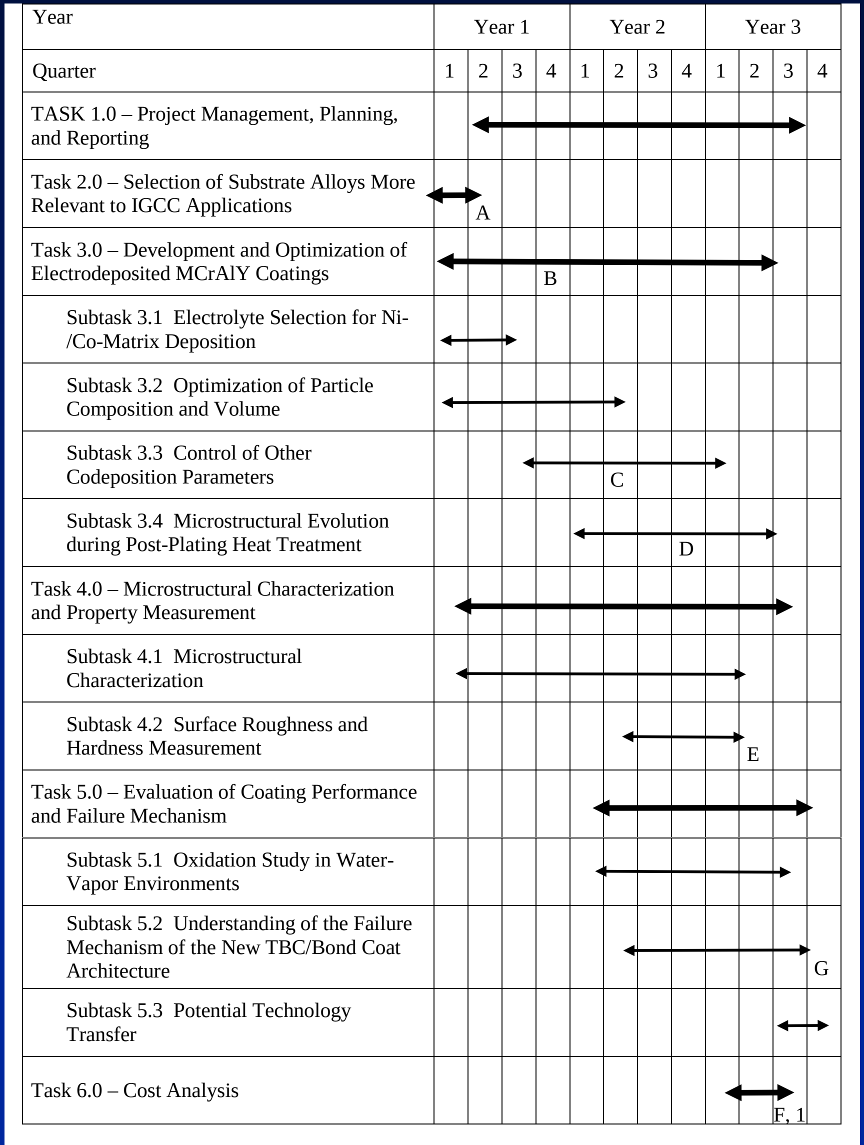
#3: Microstructural Characterization & Property Measurement

- Microstructure
- Surface roughness & hardness measurement

#4: Evaluation of Coating Performance & Failure Mechanism

- Oxidation in water vapor
- Understanding of failure mechanism
- Potential technology transfer

Major Activities Planned in 36 Months



Year	Year 1				Year 2				Year 3			
Quarter	1	2	3	4	1	2	3	4	1	2	3	4
TASK 1.0 – Project Management, Planning, and Reporting												
Task 2.0 – Selection of Substrate Alloys More Relevant to IGCC Applications		A										
Task 3.0 – Development and Optimization of Electrodeposited MCrAlY Coatings				B								
Subtask 3.1 Electrolyte Selection for Ni-/Co-Matrix Deposition												
Subtask 3.2 Optimization of Particle Composition and Volume												
Subtask 3.3 Control of Other Codeposition Parameters						C						
Subtask 3.4 Microstructural Evolution during Post-Plating Heat Treatment								D				
Task 4.0 – Microstructural Characterization and Property Measurement												
Subtask 4.1 Microstructural Characterization												
Subtask 4.2 Surface Roughness and Hardness Measurement										E		
Task 5.0 – Evaluation of Coating Performance and Failure Mechanism												
Subtask 5.1 Oxidation Study in Water-Vapor Environments												
Subtask 5.2 Understanding of the Failure Mechanism of the New TBC/Bond Coat Architecture												G
Subtask 5.3 Potential Technology Transfer												
Task 6.0 – Cost Analysis											F, 1	

A, B, C, D, E, F, G – Milestones from Milestone Log; 1– Decision Point

- **A. Material Selection/Procurement (02/15/2012):** Complete selection and procurement of substrate alloys as well as electro-codeposition supplies and start initial experiments on electro-codeposition of MCrAlY coatings
- **B. Initial Coating Process Development (08/15/2012):** Demonstrate initial success of the electrolytic codeposition of the MCrAlY coatings
- **C. Optimization of Codeposition Process (02/15/2013):** Identify optimized parameters of the codeposition process
- **D. Post-Plating Heat Treatment (08/15/2013):** Finalize the post-plating heat treatment procedure that produces the desired coating microstructure
- **E. Property Characterization (02/15/2014):** Complete surface roughness and hardness measurement
- **F. Cost Analysis (06/15/2014):** Complete cost analysis and provide a cost comparison between the proposed coating technique and the current techniques such as APS and HVOF
- **G. Performance & Failure Assessment (08/15/2014):** Complete both the oxidation testing and failure mechanism study for the developed coatings

Research Progress

(Since Last UTSR Workshop in October 2011)

- Preparation of Cr-Al-Y powder
  - Fabrication of Cr-Al-Y alloy via arc melting
  - Ball milling and sieving

- Electro-codeposition experiments
  - Effect of current density
  - Vertical and horizontal configurations

No commercial Cr-Al-Y powder is currently available with the specific composition required

Gas Atomized

- **Commercial powder suppliers**
  1. CEAC
  2. American Elements
  3. READE Advanced Materials
  4. LPW Technology
  5. Sandvik
  6. ARCMELT
  7. Stellite
  8. Flame Spray
  9. HAI
  10. Shinwa Bussan (Japan)
  11. Sulzer Metco
  12. Praxair
  13. AEE
  14. HC Stark
  15. Powder Alloy Corp

Ball Milled

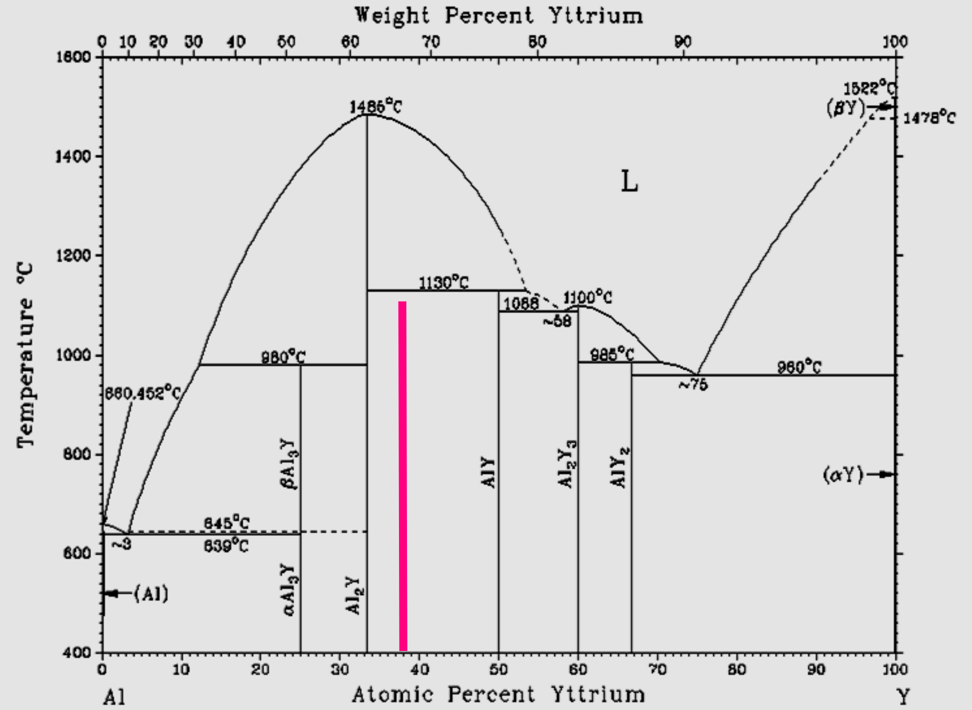
- Arc melting of Cr-Al-Y alloys, followed by ball milling at TTU
- Metals purchased for arc melting
  - Al – 99.99%
  - Cr – 99.995%
  - Y - 99.9%

Fabrication of Cr-Al-Y Alloy — Problems with the Initial Arc Melting Process

- Target alloy composition: Cr-37Al-1.7Y (wt.%)
  - High weight loss of ~4% in initial arc melting
  - Brittleness of the intermetallic phases leads to cracking & loss of material into the arc melter chamber if the turn-over speed is not well controlled.

Improvement in the Arc Melting Process

- Careful control of the **turn-over speed** to prevent material loss
- Instead of using pure Y, **an Al-Y master alloy** was made first for Y incorporation.
  - Reduce oxidation of Y
  - More accurately control the Y level in the Cr-Al-Y alloy



Al-Y Master Alloy

Al-66.7Y (wt.%)

(Al-37.8Y in at.%)

Weight loss of < 0.5% was achieved for the arc-melted Cr-Al-Y alloys

- Weight loss of the new alloys is in the range of 0.04 to 0.44%.

Alloy	Total Weight (g)		ΔW (g)	ΔW%
	Before	After		
#1 (initial)	75.00	71.70	-3.30	-4.0
#2	99.96	99.89	-0.07	-0.07
#3	79.99	79.72	-0.27	-0.34
#4	79.97	79.94	-0.03	-0.04
#5	79.97	79.62	-0.35	-0.44

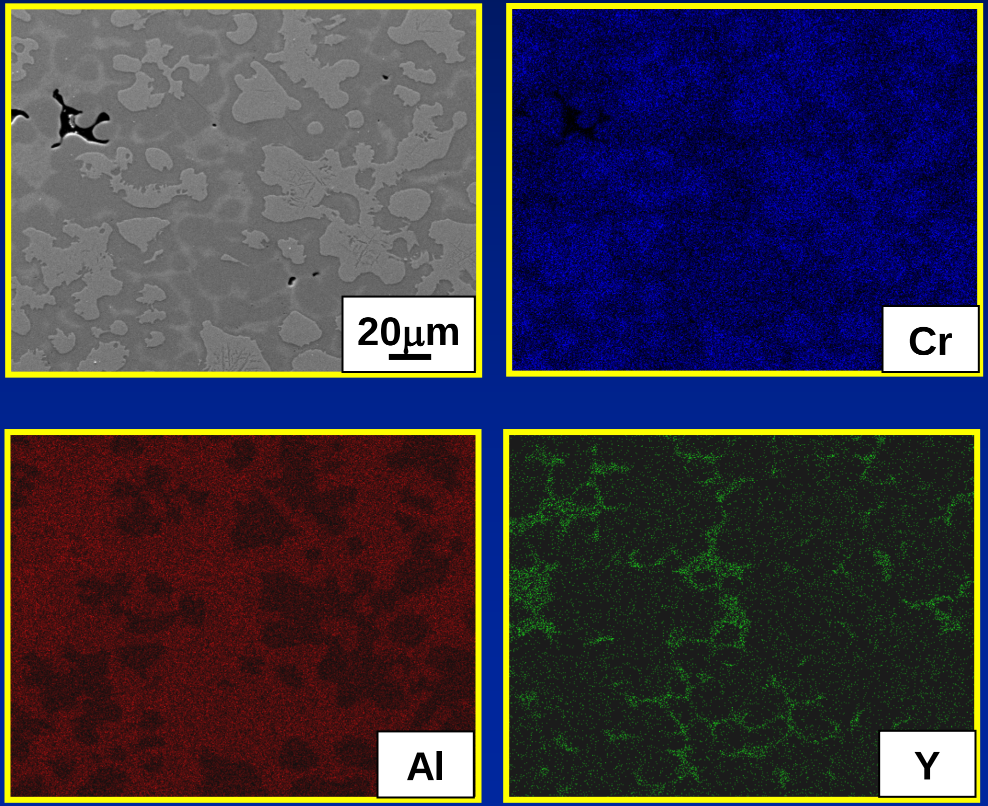
Accurate Composition Control of Cr-Al-Y Alloy

- The concentrations of major alloying elements are very close to the target composition.
- The levels of impurity elements (S and O) are extremely low.

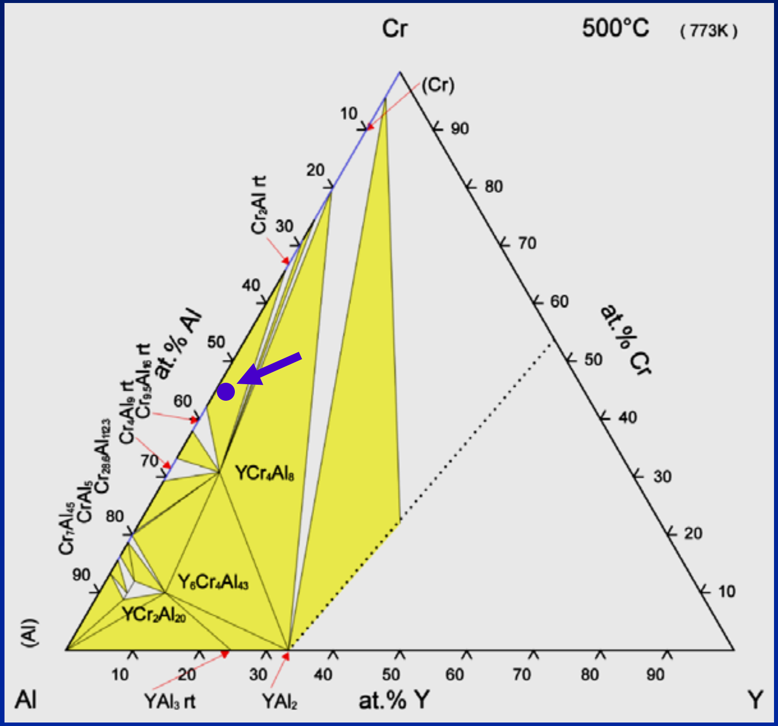
Element	Target Composition (wt.%)	DIRATS Analysis (wt.%)
Cr	61.3	61.25
Al	37.0	37.07
Y	1.7	1.6
Fe	—	0.02
W	—	0.02
Si	—	0.02
P	—	0.005
C	—	0.0008
S	—	<0.0001
O	—	0.0021
N	—	0.0035

Characterization of the Cr-Al-Y Alloy

- **XRD analysis shows that the Cr-Al-Y alloy (Cr-37Al-1.7Y, wt.%) consists of Cr_2Al, Cr_5Al_8, and YCr_4Al_8 three phases.**
- **X-ray mapping also indicates that there are three distinct phases.**



Cr-53Al-0.7Y, at.%

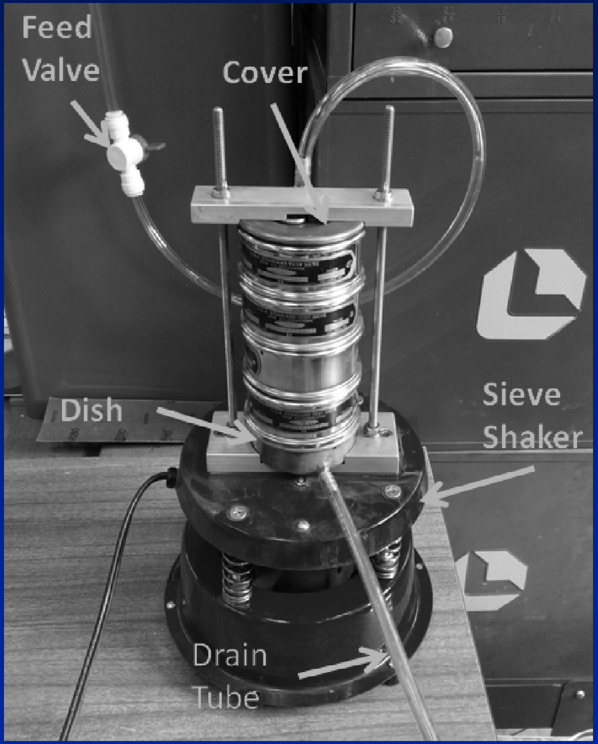


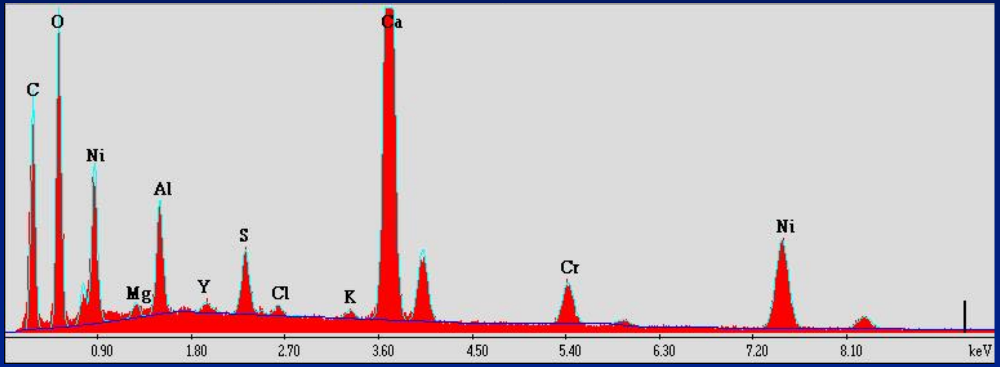
Procedure of Cr-Al-Y Powder Preparation

1. The arc-melted alloy was crushed into small pieces using a mortar and pestle.
2. Sieved through #10 mesh (2 mm) to exclude large pieces
3. Ball milling for 1-3 hours
4. Sieving (wet vs. dry)
5. SEM examination
6. Particle analysis

Wet Sieving vs. Dry Sieving

- **Wet sieving was first selected due to agglomeration of particles (<44 μm) during dry sieving.**
- **Contamination was found in the powder after wet sieving.**





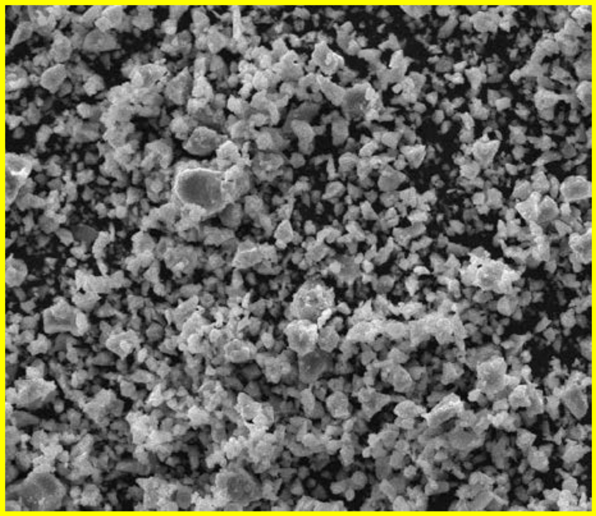
Impurity elements (Mg, Cl, K, and Ca) were introduced during wet sieving

- **Dry sieving (up to 44 μm) was used in powder preparation.**

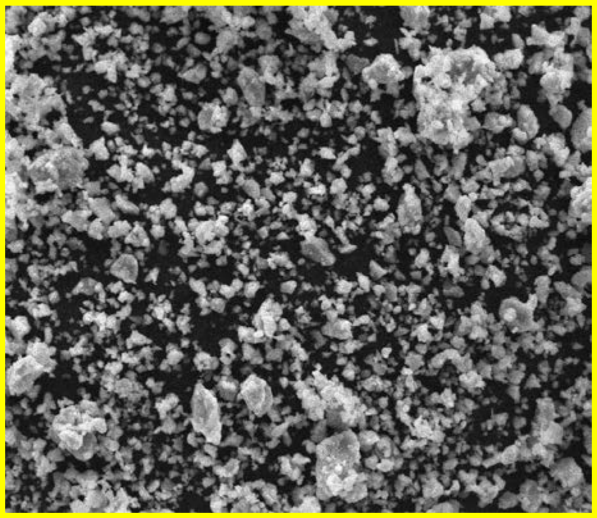
Effect of Ball Milling Time

- **Ball milling followed by dry sieving**
- **Sieving through #170 mesh (90 µm) and #325 mesh (44 µm)**

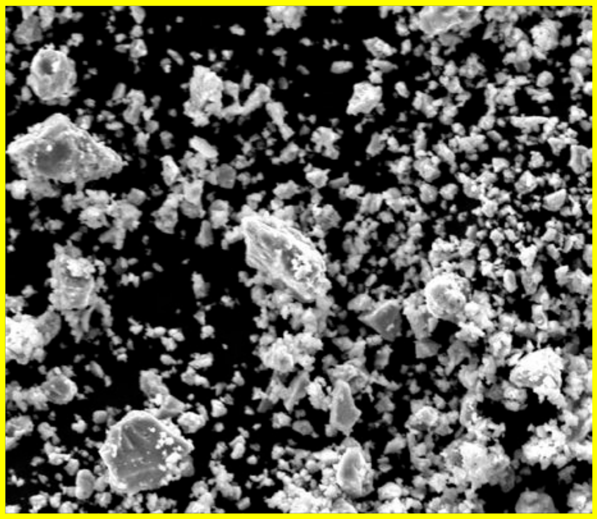
1hr



2hr



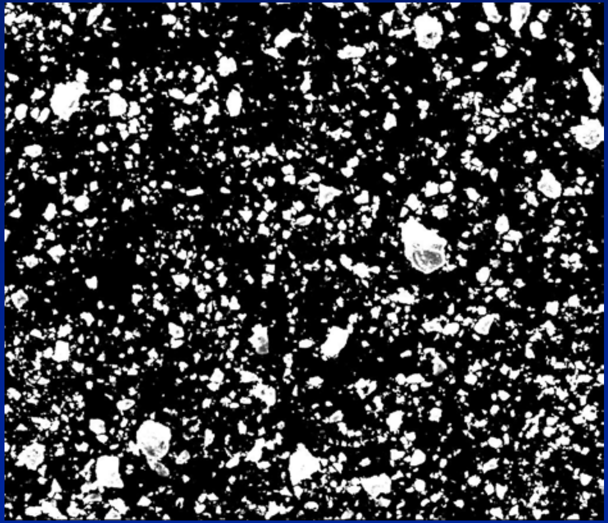
3hr



10µm

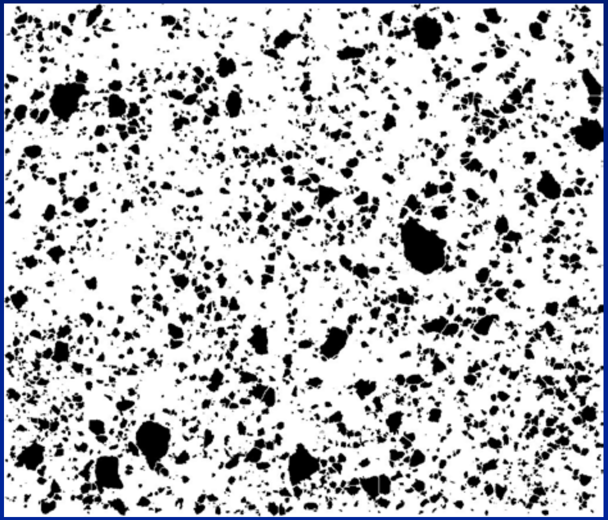
Particle Size Analysis by ImageJ

- High-contrast SEM images were taken at various locations to include >10,000 particles for quantitative particle analysis.
- Particle size analysis was conducted using ImageJ.
- The projected area of each particle was measured and converted to the diameter by assuming the particles as spheres.



20μm

High-Contrast SEM Image



Converted binary Image

Particle Size Distribution Table

- The majority of particles are < 5 µm after 1-3h of ball milling.

Size (µm)	Percentage Frequency			Percentage Cumulative Under		
	1h	2h	3h	1h	2h	3h
<1	0.37	0.30	0.34	0.37	0.30	0.34
1-2	0.30	0.36	0.42	0.67	0.66	0.76
2-3	0.17	0.21	0.17	0.84	0.87	0.94
3-4	0.08	0.08	0.05	0.92	0.94	0.98
4-5	0.04	0.03	0.01	0.96	0.97	1.00
5-6	0.02	0.01	0.00	0.98	0.98	1.00
6-7	0.01	0.01	0.00	0.99	0.99	1.00
7-8	0.00	0.00	0.00	0.99	0.99	1.00
8-9	0.00	0.00	0.00	0.99	1.00	1.00
9-10	0.00	0.00	0.00	1.00	1.00	1.00
>10	0.00	0.00	0.00	1.00	1.00	1.00

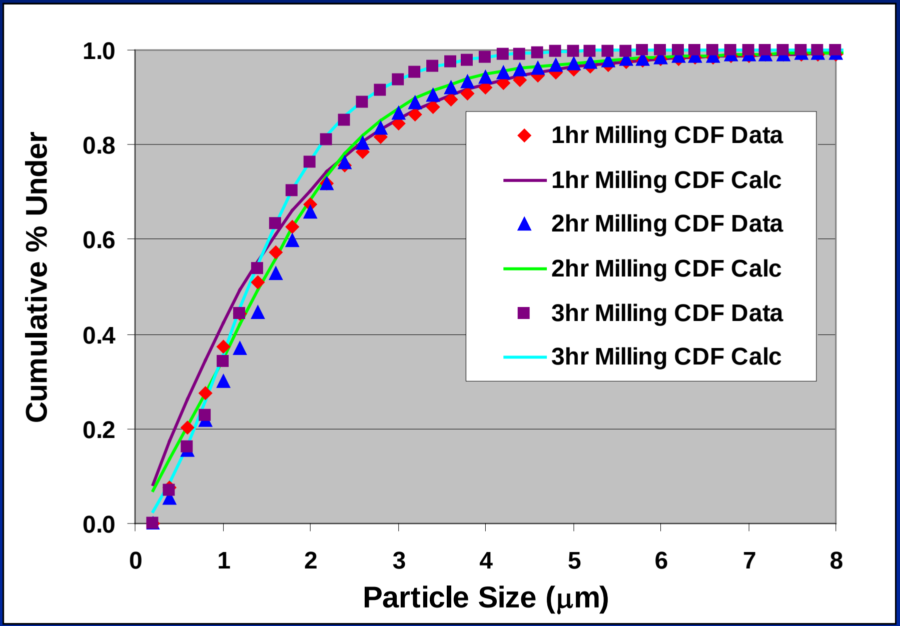
The Probability Density Function

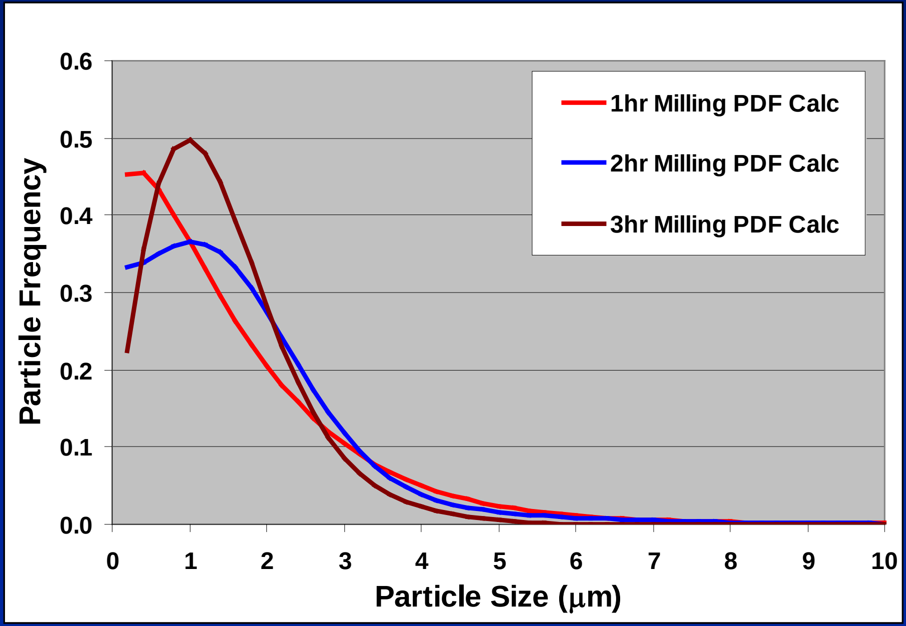
- **To obtain the probability density function, the cumulative under vs. particle size curve was fitted using bimodal Weibull distribution.**

$$F(x) = 1 - \alpha_1 e^{-(\frac{x}{\lambda_1})^{k_1}} - \alpha_2 e^{-(\frac{x}{\lambda_2})^{k_2}}$$

The probability density function

$$f(x) = \alpha_1 \left(\frac{k_1}{\lambda_1}\right)\left(\frac{x}{\lambda_1}\right)^{k_1 - 1} e^{-(\frac{x}{\lambda_1})^{k_1}} + \alpha_2 \left(\frac{k_2}{\lambda_2}\right)\left(\frac{x}{\lambda_2}\right)^{k_2 - 1} e^{-(\frac{x}{\lambda_2})^{k_2}}$$





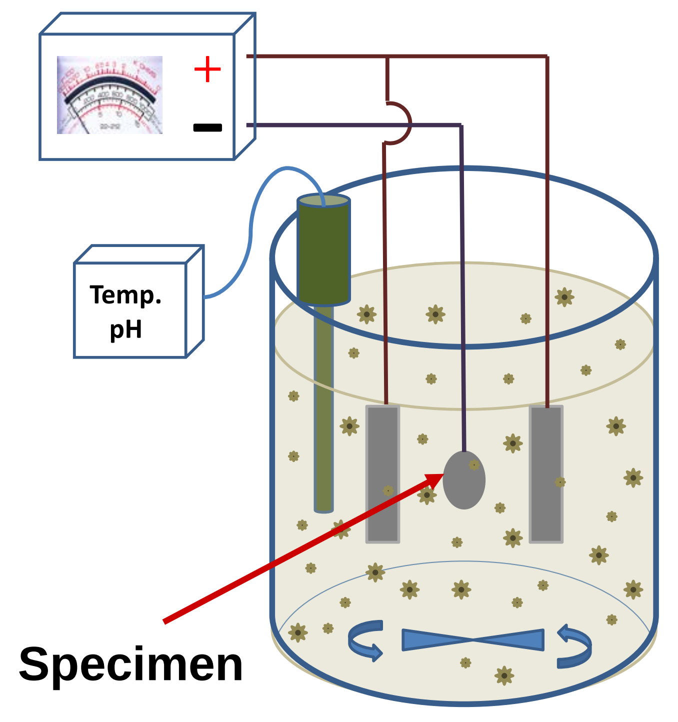
Summary of Particle Size Analysis

Milling Time (h)	Mean (μm)	STD (μm)	Number			Volume
			D_{10} (μm)	D_{50} (μm)	D_{90} (μm)	D_{90} (μm)
1	1.65	1.62	0.2	1.2	3.5	6.0
2	1.67	1.37	0.3	1.4	3.2	5.2
3	1.45	0.90	0.4	1.3	2.7	3.4

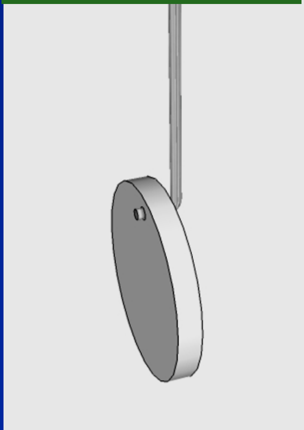
- Out of 100 g powder, ~90 g exhibited a particle size of
  - < 6.0 μm after 1h ball milling
  - < 5.2 μm after 2h
  - < 3.4 μm after 3h
- 1h milling time was selected for fabrication of Cr-Al-Y powder from arc-melted alloys.

Electro-codeposition Experiments

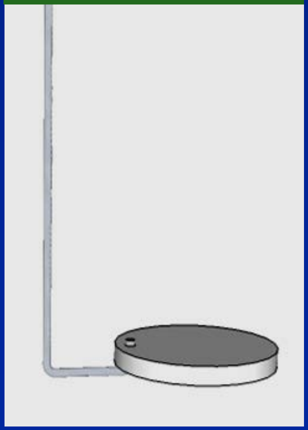
- Substrate: René 80 discs (~17 mm in diameter, ~1.6 mm thick)
  - ground to 600 grit
  - grit blasted with #220 grit
- Watts plating solution
- Anode: pure Ni plate



Vertical



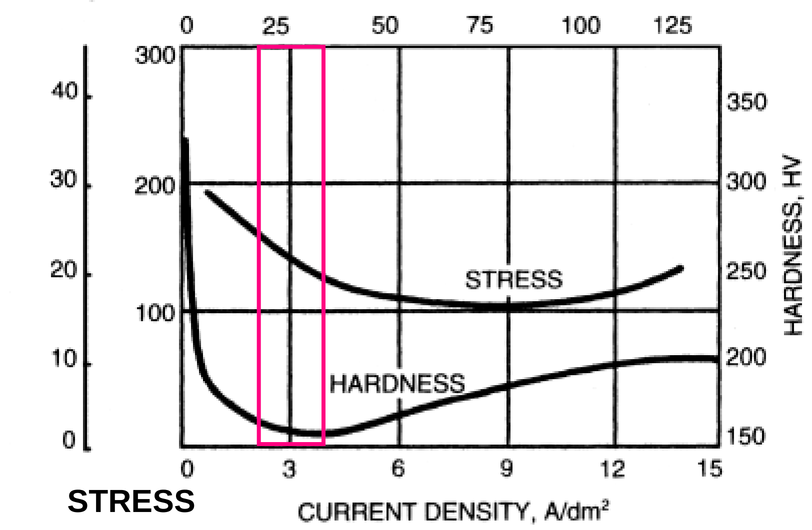
Horizontal

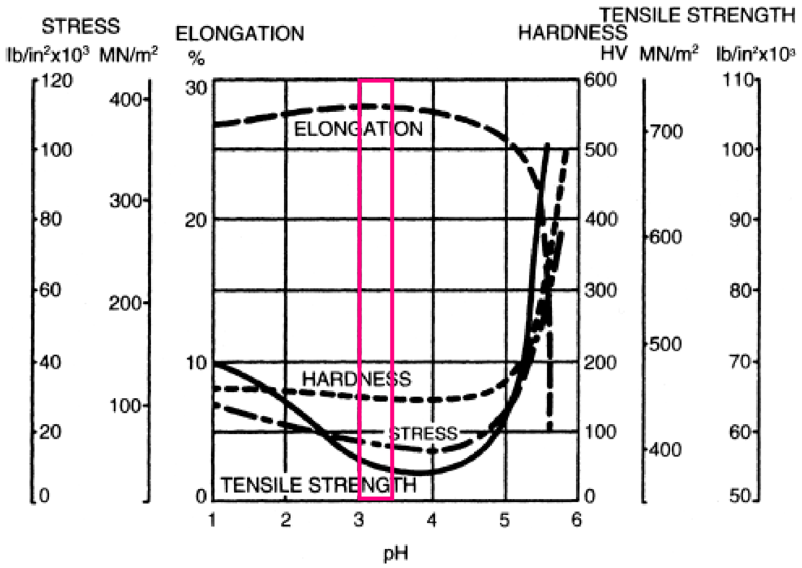


Electro-codeposition Parameters

- **Temperature: 50°C**
- **Current density: 2.0-4.0 A/dm^2**
- **pH: 3.0-3.5**
- **Time: 2h**

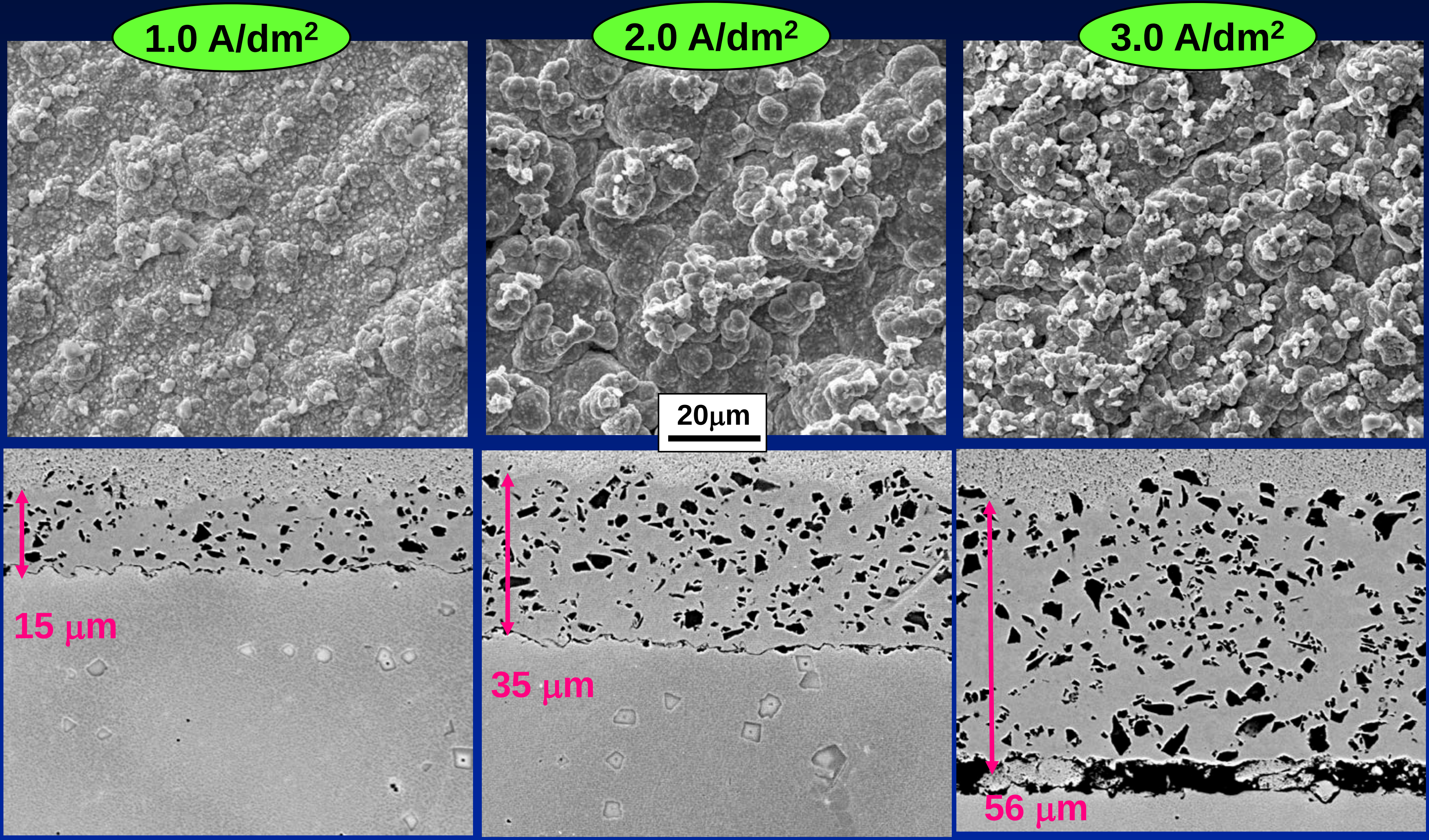
Constituent	**(g/L)**
Nickel Sulfate	**310**
Nickel Chloride	**50**
Boric Acid	**40**
Cr-Al-Y powder	**30**





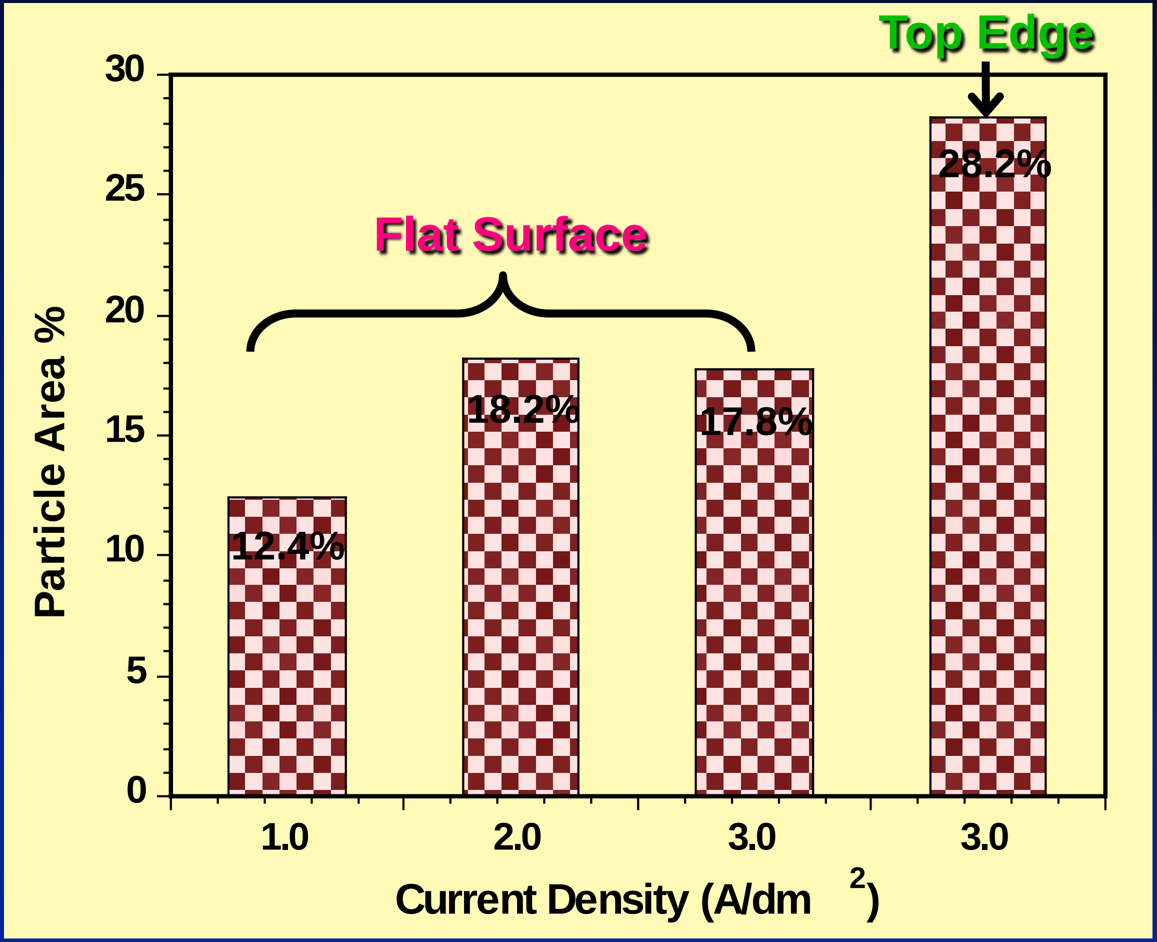
G. A. DI BARI, Modern Electroplating,
John Wiley & Sons, Inc., 2010

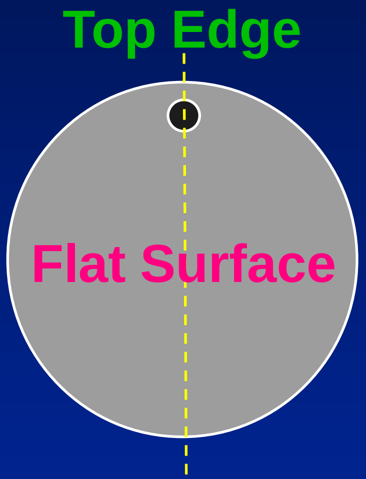
Effect of Current Density



- **The roughness increased as the current density increased.**

Particle Incorporation in Co-deposited Coatings

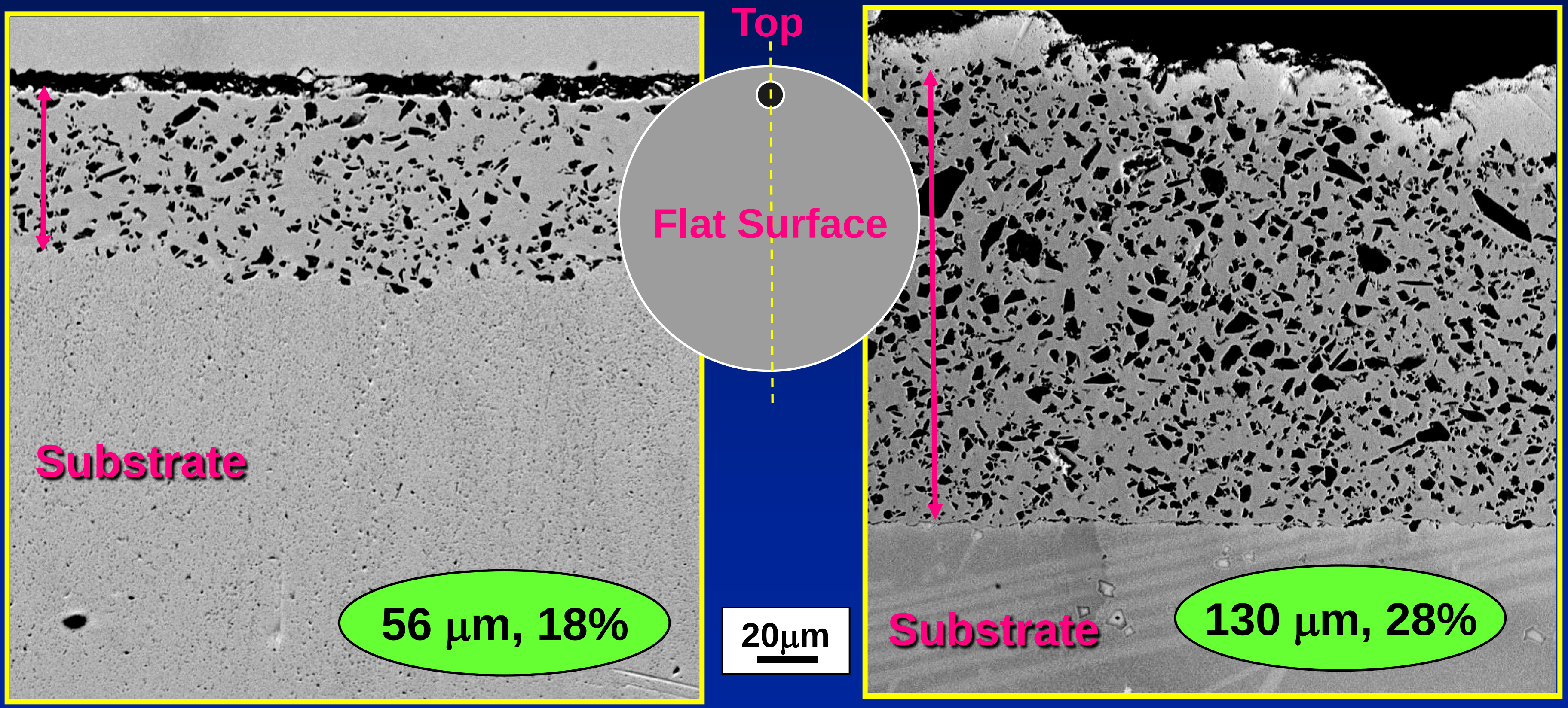




- The current density should be controlled in the range of 2.0-3.0 A/dm^2.

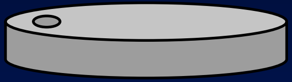
Effect of Sedimentation

- The particle incorporation was much higher on the top edge of the specimen than on the flat surface.
- The coating was also much thicker on the top edge.

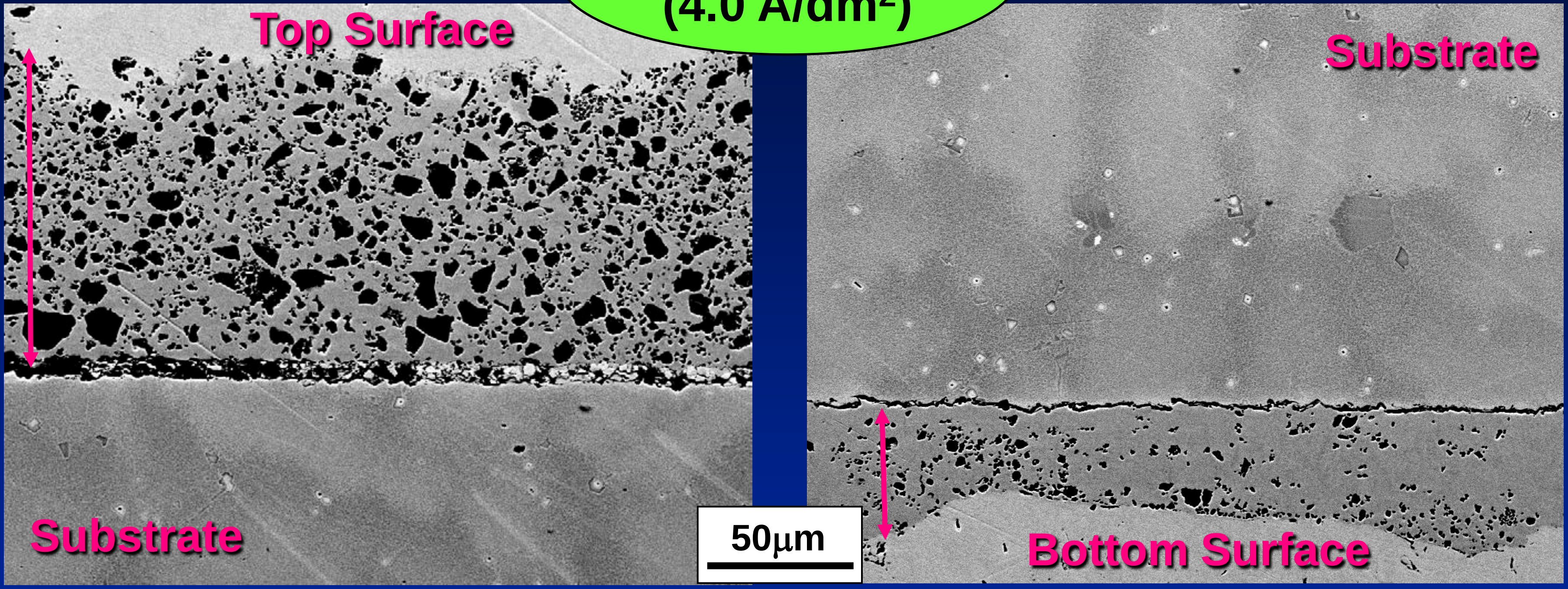


Flat Surface **3.0 A/dm^2** **Top Edge**

Specimens Coated in a Horizontal Position



Horizontal
(4.0 A/dm^2)



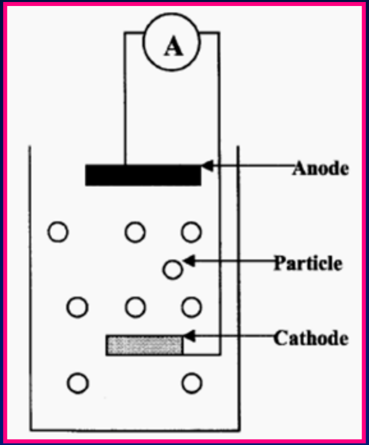
105 μm, 31%

55 μm, 4%

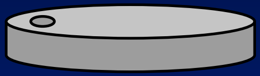
- **An increase of 10% particle incorporation than the vertical position**
- **The process becomes more line-of-sight.**

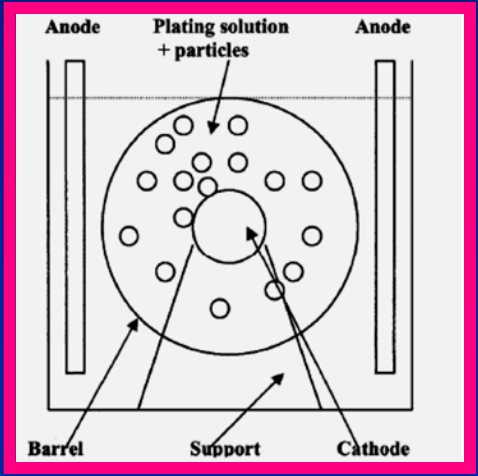
Future Work: Electro-codeposition Configuration

- **Vertical:** more literature data
- **Horizontal:** a transitional setup
- **Rotating barrel:** a semi-permeable rotating barrel that holds the specimen and powder
  - Ultimate design
  - The electrolyte can diffuse through the membrane wall, while the powder is maintained in suspension in the barrel.
  - Uses significantly less powder, allowing a higher concentration if needed



(Liu et al., 2006)





(Honey et al., J. Vac. Sci. Technol., 1986)

Future Work: Effect of Interactive Parameters

- A **Design-of-Experiment (DoE)** approach will be used to understand and optimize codeposition parameters
- Central Composition Design
  - Three factors, three levels (Robin et al., Surf. Coat. Technol., 2010)
  - A total of twelve experiments (including four replicates at the center point)

	Factor	Low	Intermediate	High
		-1	0	1
A	Current density (A/dm^2)	1	2	5
B	Stirring rate (magnetic stirrer)	3	5	7
C	Particle loading	10	30	50

Future Work: Sulfur-Free Ni Plating Solution

- **Fluoborate electrolyte** typically used for heavy nickel applications & electroforming.

Constituent (g/L)	Watts	Sulfamate	High Chloride	All Chloride	Fluoborate
Nickel Sulfate ($NiSO_4 \cdot 6H_2O$)	180-300	—	240	—	—
Nickel Sulfamate $Ni(SO_3NH_2)_2 \cdot 4H_2O$	—	300	—	—	—
Nickel Chloride ($NiCl_2 \cdot 6H_2O$)	45	15	90	240	—
Nickel Fluoborate [$Ni(BF_4)_2$]	—	—	—	—	220
Boric Acid (H_3BO_3)	30-40	30	30-40	30	30
pH Range	4.0-5.0	3.5-4.5	2.0-2.5	0.9-1.1	3.0-4.5
Temperature (°C)	25-65	25-65	40-70	40-65	25-65
Current Density (A/dm^2)	1-6	2-15	1-6	5-11	4-11

Summary

- Milestone A "Material Selection/Procurement" (02/15/12)
- Milestone B "Initial Coating Process Development" (08/15/12)
  - Cr-Al-Y alloys with accurate composition control and low impurity level were fabricated via arc melting
  - Pre-alloyed Cr-Al-Y powder of particle size <5 μm was prepared via ball milling and subsequent dry sieving
  - Electro-codeposited coatings containing 12-30 vol% Cr-Al-Y particles were synthesized, depending on the current density and the sample position.
- Milestone C "Optimization of Codeposition Process" (02/15/13)
  - Effect of electro-codeposition configuration
  - Effect of interactive codeposition parameters
  - Sulfur-free plating solution

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