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

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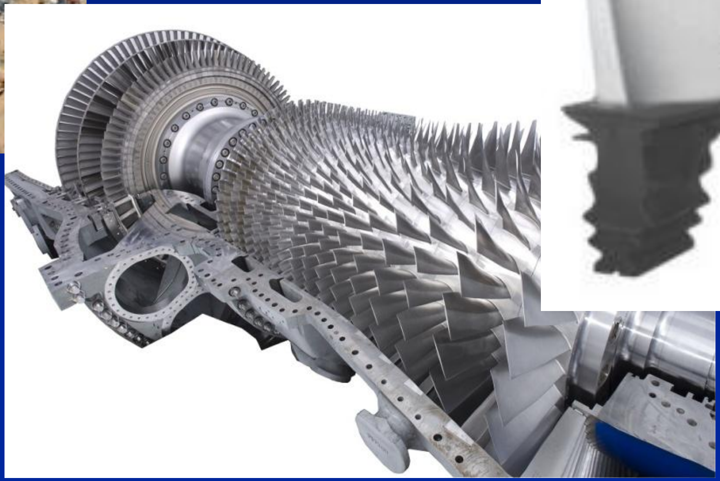
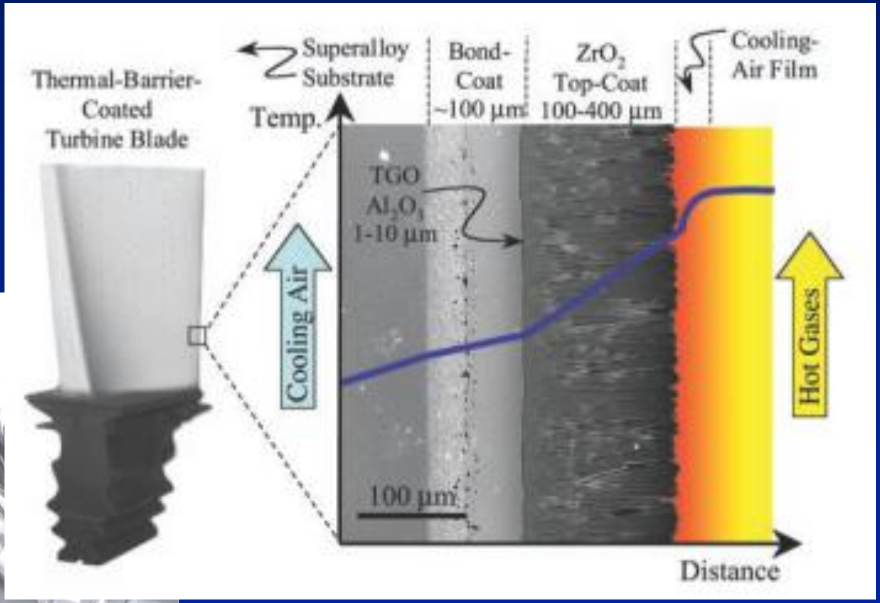
Coating Development Need for IGCC
(Integrated Gasification Combined Cycle)

- **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.aecengineering.com)



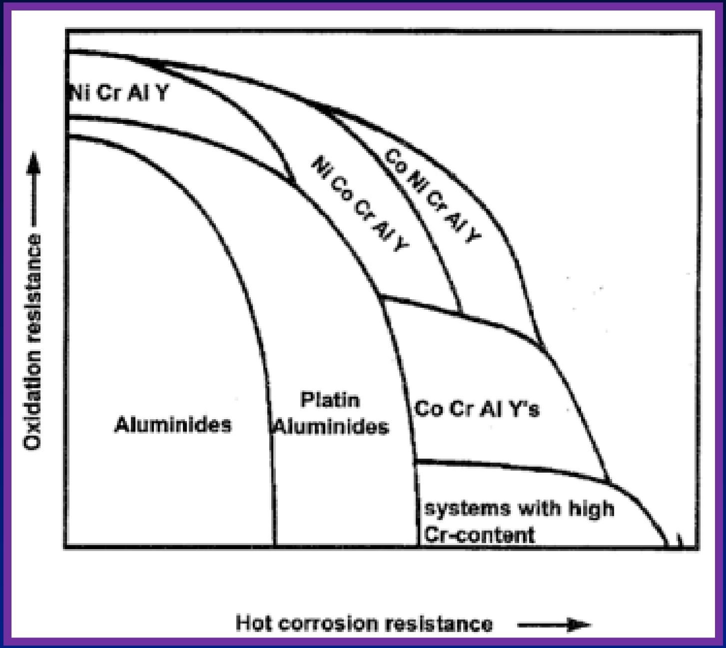
(http://www.ge-7fa.com)



(Padture, et al., Science, 2002)

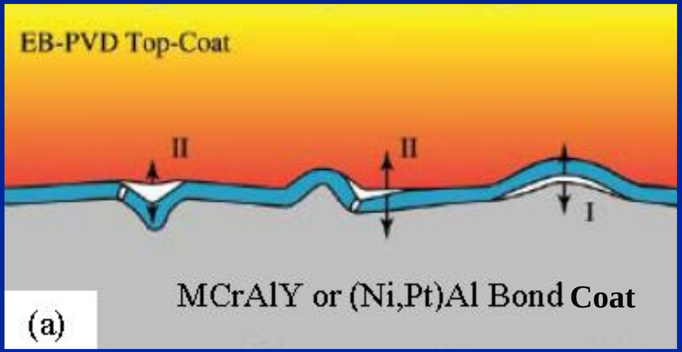
Bond Coat Choices

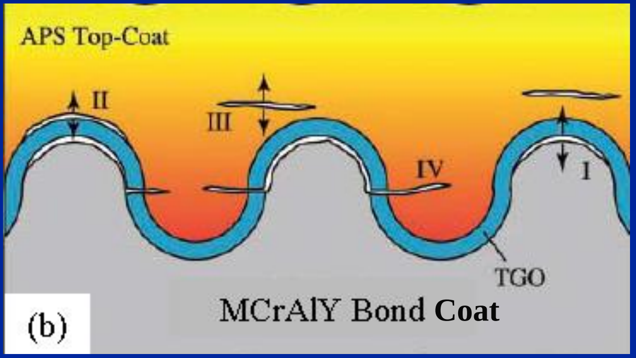
- Bond coat choices
  - — Diffusion aluminide
  - — MCrAlY overlay (M = Ni, Co or a mixture of Ni & Co)
    - ➢ More flexibility with regard to composition
    - ➢ Lower DBTT



(Eskner, M., PhD. Thesis, 2004)

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





(Padture et al., Science, 2002)

Processes for Bond Coat Fabrication

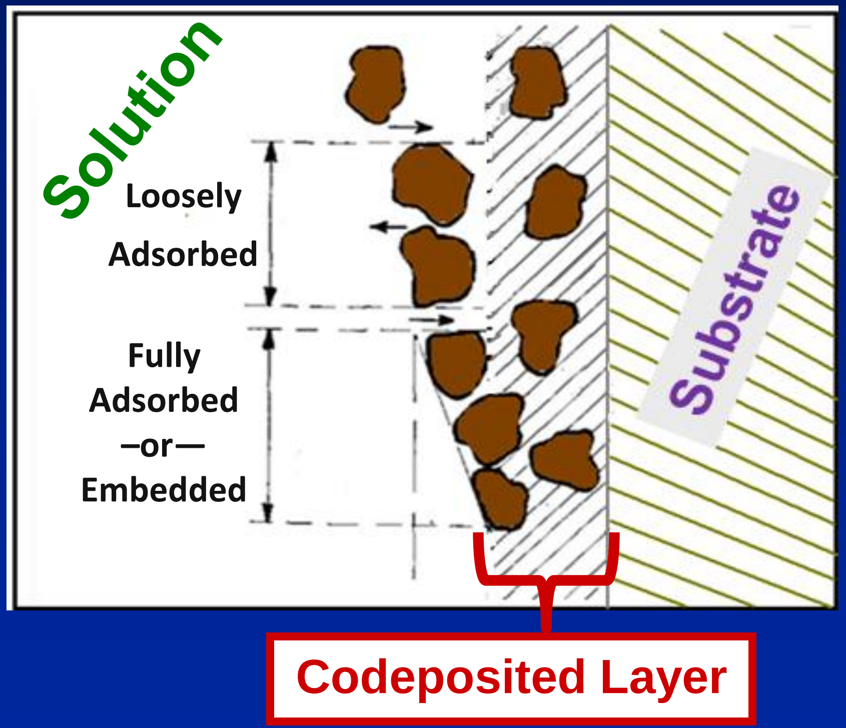
- Current fabrication processes
  - Low-pressure plasma spray (LPPS)
  - Air plasma spray (APS) & high-velocity oxy-fuel (HVOF)
- Limitations of thermal spray processes
  - Line-of-sight, requiring complex robotic manipulation for complete coverage
  - Oxide content can be high in APS and HVOF coatings
  - 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.

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



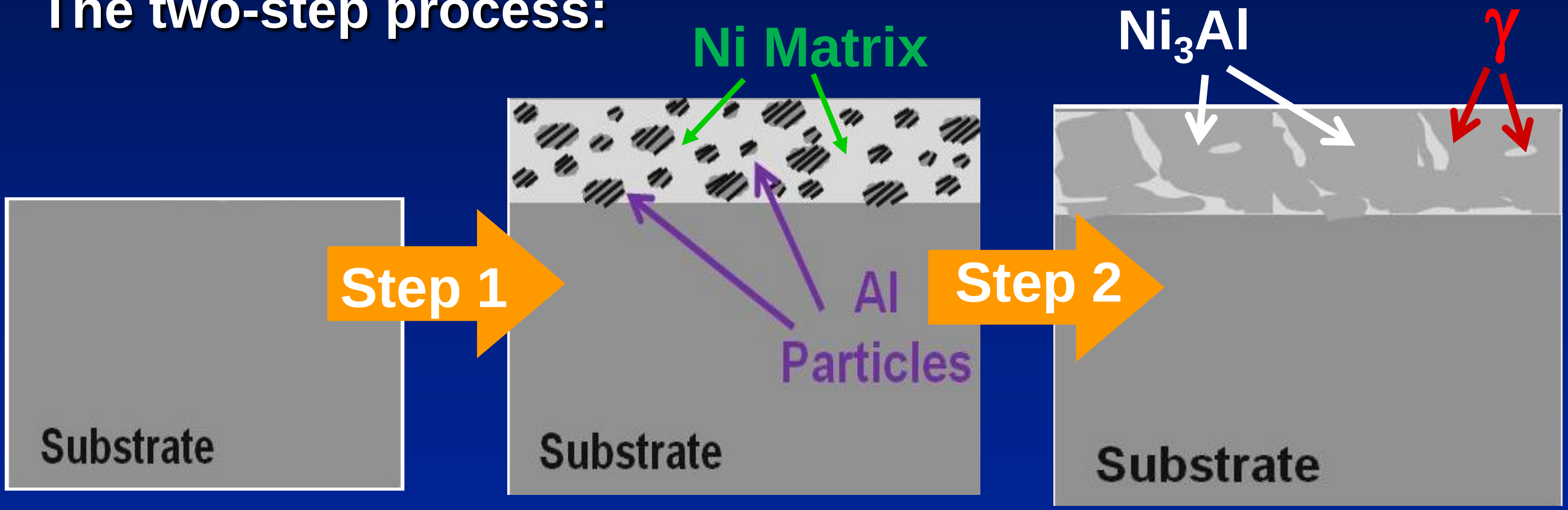
(Guglielmi, J. Electrochem. Soc., 1972)

Extensive studies have been conducted on Ni-Al based coatings via electrolytic codeposition

- **Ni-Al based coatings with Al or Al_2O_3 particles**

  (Susan et al., Thin Solid Films, 1997; Susan & Barmak, Oxid. Met.2002; Liu & Chen, Corros. Sci., 2007)

- **The two-step process:**



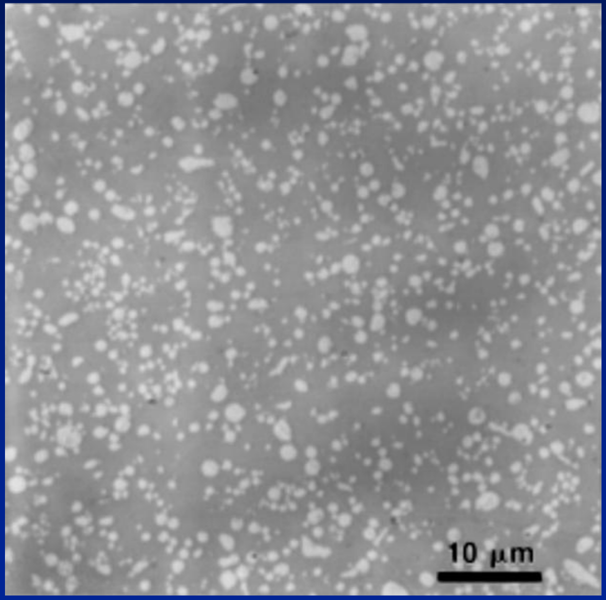
Step 1: Electrodeposition
(Ni matrix with embedded Al particles)

Step 2: Diffusion treatment
(Ni alloy coating containing Ni_3Al intermetallic phase)

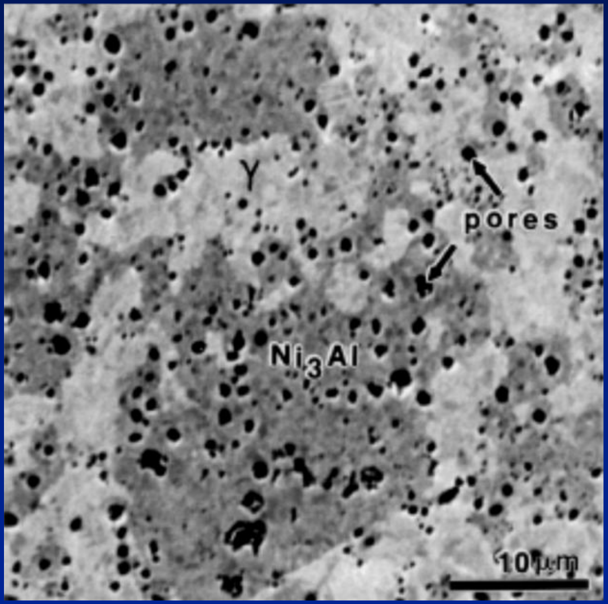
Kirkendall Porosity in the Ni-Al Coating due to Different Intrinsic Diffusivities between Ni and Al

- After heat treatment, a coating with a mixture of γ (Ni) + γ' (Ni_3Al) was formed with significant Kirkendall porosity.

(Susan et al., Metall. Mater. Trans. A, 2001)



As-deposited Ni-Al coating



After heat treatment (850ºC/10h)

- As a result of high porosity, the NiAl-based coatings showed poor oxidation performance.

Very Limited Research on 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

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, a knowledge base needs to be established

Electro-codeposited MCrAlY Coatings: Critical Issues

- **Sulfur Impurities, Y Reservoir, & Reactive Element Co-doping**
  - **Traditional electrolyte used to deposit Ni/Co matrix involves either sulfate- or sulfamate-based solution.**

    ONERA (France): an electroless process using a S-free solution (pure nickel electroless bath and CrAlYTa powder)

    (Mercier et al., Surf. Coat. Technol., 2006)
  - **Y/S ratio in the coating**
  - **RE co-doping**

Critical Issues (Cont'd)

- Surface Roughness
  - Ra of ~10 μm for APS TBC top coat
- Coating Performance Assessment
  - As an abrasive tip coating: in-depth evaluations have been reported with regard to its thermal expansion behavior.
  - For syngas/hydrogen turbines: The levels of water vapor are considerably higher than in natural gas.

Project Objectives

- Develop and optimize MCrAlY bond coats for syngas/hydrogen turbine applications using the 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

Substrate Alloys Relevant to IGCC Applications

- Successful coating development involves consideration of the substrate composition
  - — Generally negligible during deposition, however in service interdiffusion can modify the composition and microstructure

Alloy	Composition (wt.%)									
	Cr	Co	W	Mo	Re	Ta	Al	Ti	Hf	Other
PWA 1484	5	10	6	1.9	3	—	5.6	—	0.1	8.7 Nb
René N5	7	8	5	2	3	7	6.2	—	0.2	200 ppm Y
CMSX-4	6.5	10	6	0.6	3	6	5.6	1.0	0.1	—
CMSX-486	5	9.3	8.6	0.7	3	4.5	5.7	0.7	1.2	0.015 B, 50 ppm Zr

- CMSX-486:
  - — Similar to CMSX-4 in composition
  - — More adapted to large castings
  - — Good stability at temperatures between 982 and 1093°C (1800~2000°F)

- Less expensive Ni-based alloys may be used in the initial coating development stages

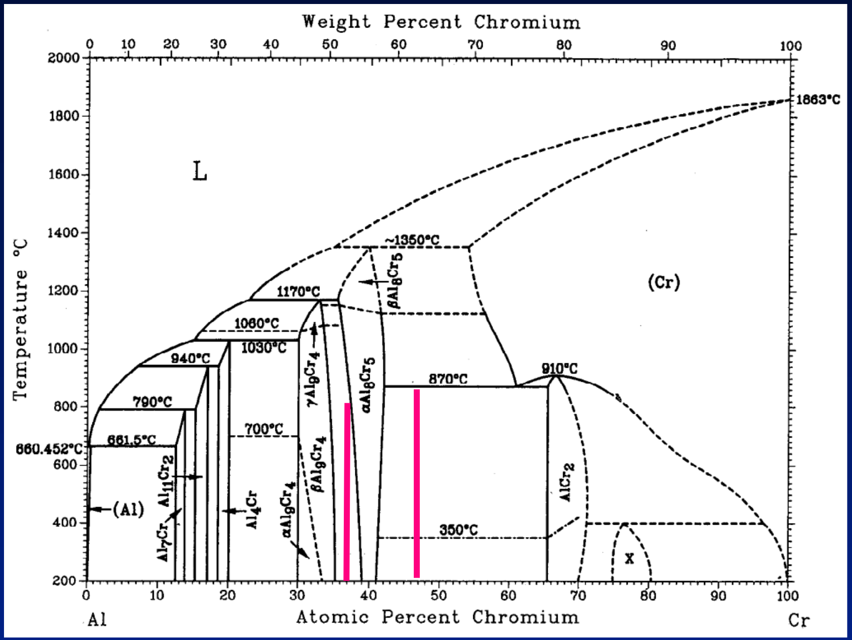
Sulfur-free Ni plating solution will be explored

- **In addition to conventional Watts bath, S-free fluoborate electrolyte will be studied.**
- **It is 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

Cr/Al Ratio and Y Level in the Coating

- Cr/Al ratio and Y level in electro-codeposited MCrAlY coatings are controlled by the CrAlY powder composition.
- Easily adaptable to a RE Co-doping additions

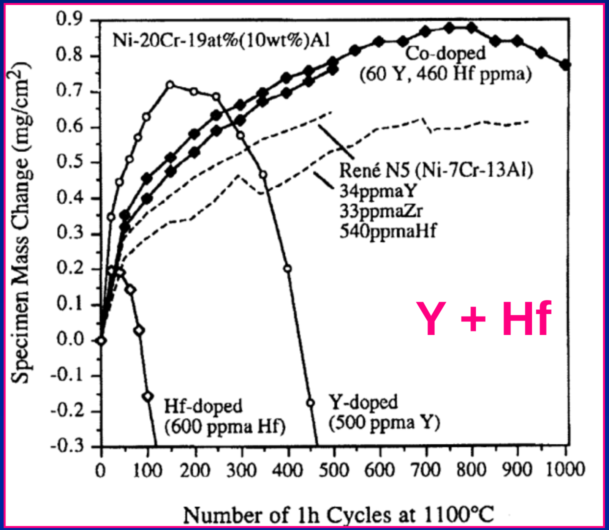


(Foster et al., US Patent 4,789,441, 1988)

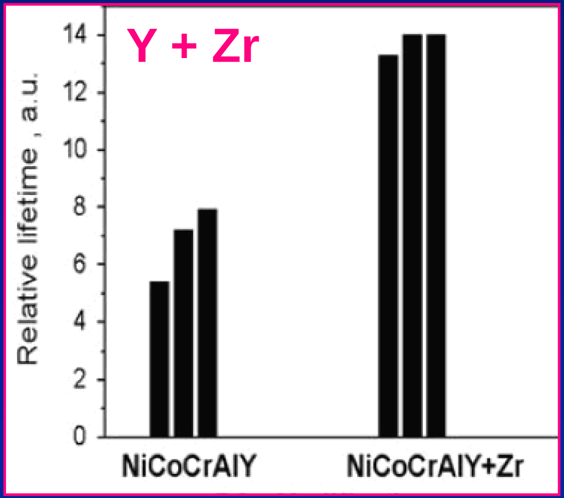
Designation	Plating Solution	Particle Composition (at.%)
Coating #1	Co-Ni	Cr-53Al-0.7Y
Coating #2	Co	Cr-63Al-0.7Y
Coating #3	Co	Cr-53Al-0.7Y

Optimum Y Reservoir and RE Co-doping

- Even though Y (~0.5 wt.%) is commonly incorporated into the MCrAlY coatings, a ratio of Y/S > 1 is needed to effectively getter excess sulfur.
- The optimum Y reservoir needs to be defined to maximize its beneficial effect on extending TBC lifetimes.
- Possible RE co-doping to further enhance oxidation performance



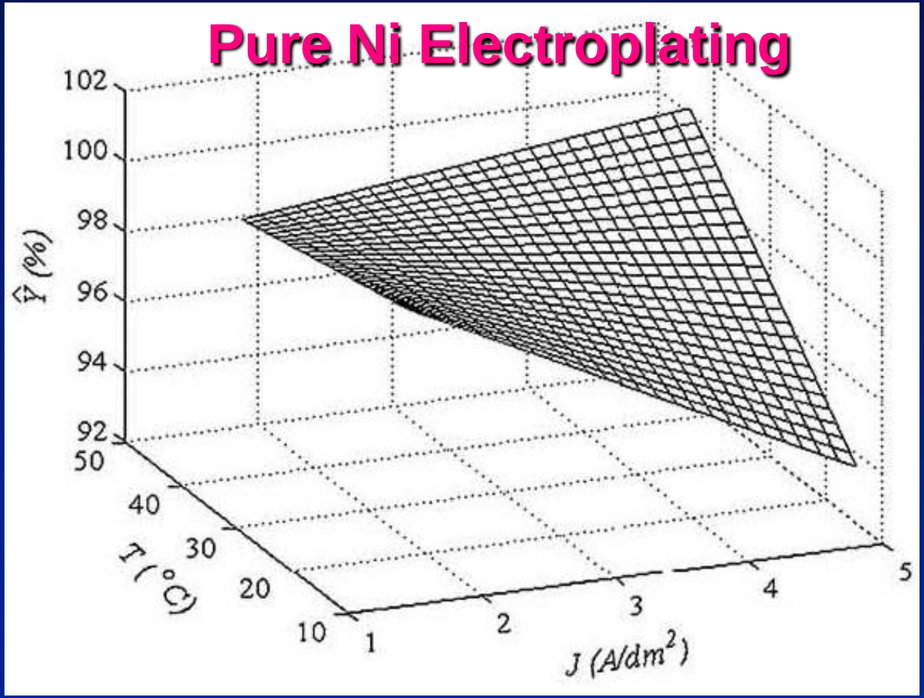
(Pint et al., Mater. High Temp., 2003)



(Naumenko et al., J. Mater. Sci., 2009)

A DoE approach will be used to investigate and optimize codeposition parameters

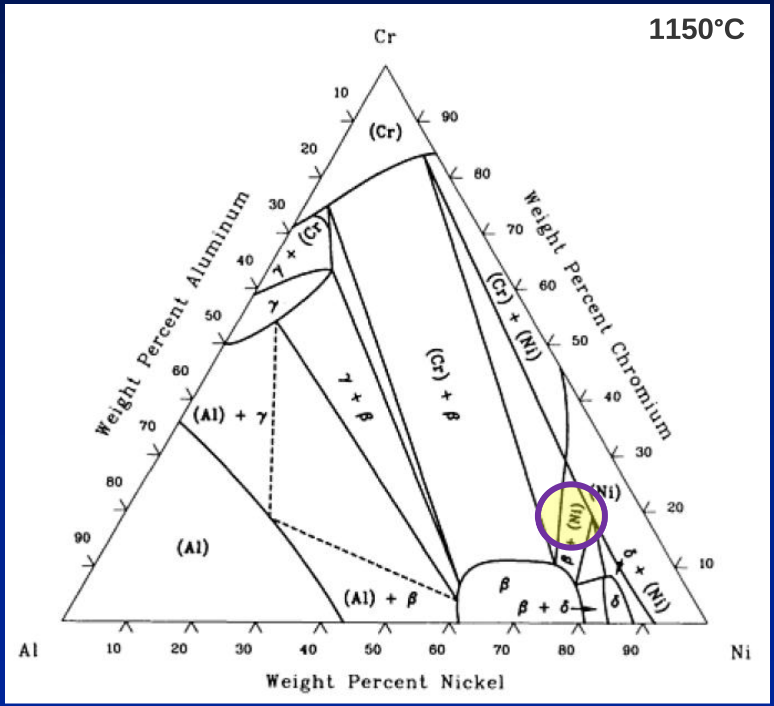
- **A two-level full factorial experimental design uses all possible factor levels in determining its model.**
- **6 Factors**
  - — Current density
  - — pH
  - — Temperature
  - — Particle loading
  - — Particle size
  - — Agitation
- **3 Responses**
  - — Cathode efficiency
  - — Coating uniformity
  - — Particle incorporation



Response surface plot of cathode efficiency vs. current density and temperature ***(Seritan et al., Chem. Eng. Res. Des., 2011)***

Evaluation of Microstructural Evolution during Post-Plating Diffusion Heat Treatment

- **Where interdiffusion occurs between the CrAlY particles and the Ni/Co matrix to achieve the final MCrAlY coating consisting of γ and β phases.**
- **The post-plating heat treatment has a significant influence on the TGO growth rate.**
- **Higher temperatures under high vacuum promote oxidation of reactive elements and hence increase TGO growth.**
- **Compatible with superalloy's heat treatment**

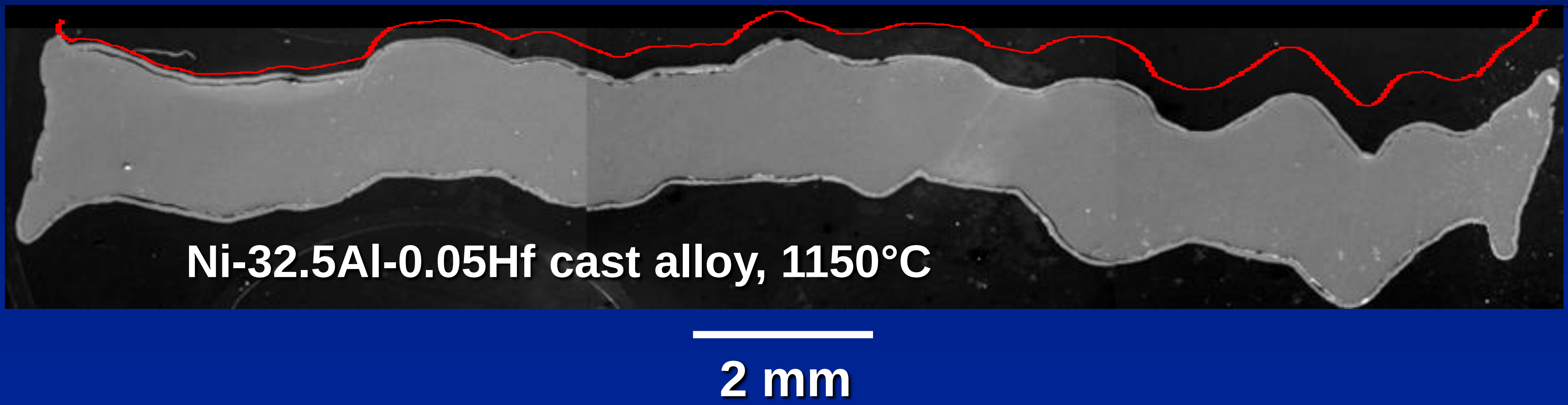


(ASM Handbook, Vol.3, 1992)

The classsic MCrAlY coating:
18-20%Cr, 8-12%Al (wt%)

Coating Characterization

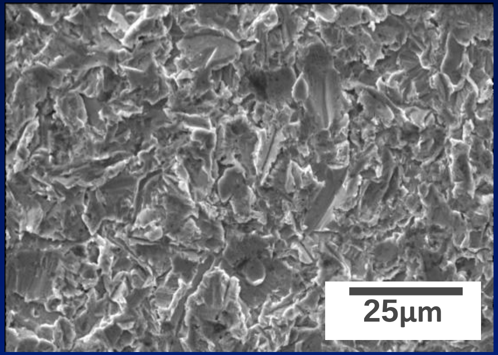
- To provide optimum adherence for an APS TBC top coat, **a surface roughness of ~10μm Ra** is desirable.
- Surface roughness will be examined using **profilometry** in combination with **SEM cross-sectional image analysis**.



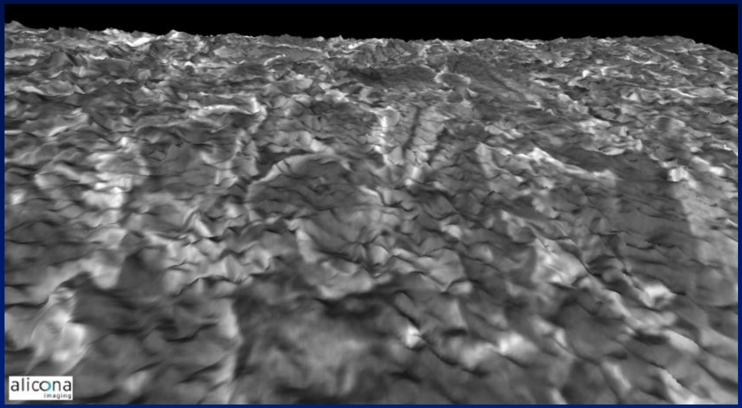
- The effects of codeposition parameters and surface treatment will be investigated.

Coating Characterization

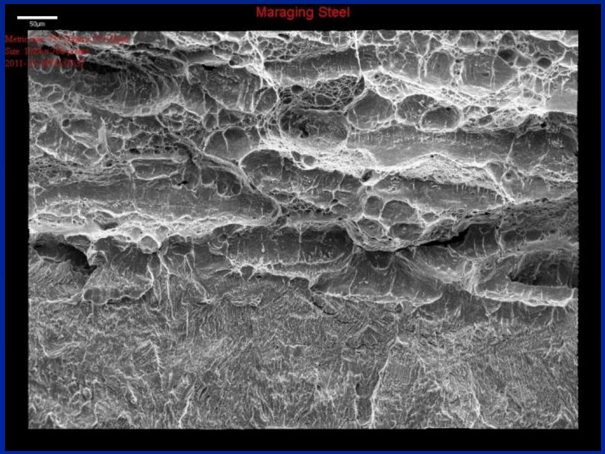
Grit blasted surface of R80 substrate

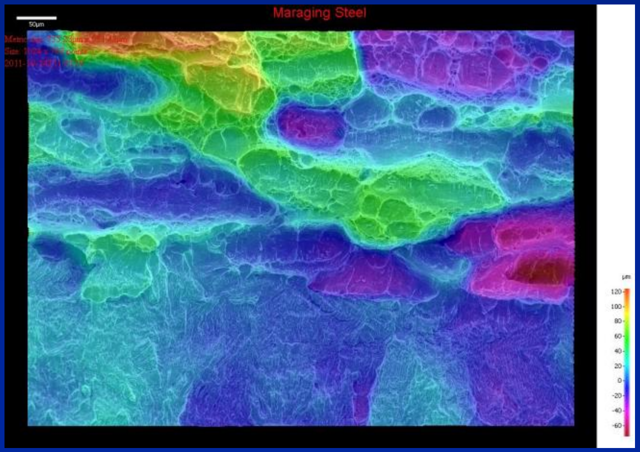


Surface converted to a 3D measurable texture



- **Currently we are evaluating 3D imaging software that will provide surface and area roughness estimates.**





Evaluation of Coating Performance & Failure Mechanisms

- Oxidation testing in water vapor environments
  - Also noting, that the levels of sulfur and particulates can be higher in the syngas/hydrogen combustion than with natural gas-fired turbines

(Alvin et al., The 22nd Annual Conference on Fossil Energy Materials, 2008)

	Syngas Turbine 2010	Hydrogen Turbine 2015	Oxy-Fuel Turbine 2010	Oxy-Fuel Turbine 2015
Combustor Exhaust Temp, °C (°F)	~1480 (~2700)	~1480 (~2700)		
Turbine Inlet Temp, °C (°F)	~1370 (~2500)	~1425 (~2600)	~620 (~1150)	~760 (~1400) (HP) ~1760 (~3200) (IP)
Turbine Exhaust Temp, °C (°F)	~595 (~1100)	~595 (~1100)		
Turbine Inlet Pressure, psig	~265	~300	~450	~1500 (HP) ~625 (IP)
Combustor Exhaust Composition	9.3% CO_2 **8.5% H_2O** 72.8% N_2 0.8% Ar 8.6% O_2	1.4% CO_2 **17.3% H_2O** 72.2% N_2 0.9% Ar 8.2% O_2	17% CO_2 82% H_2O 1.1% N_2 1.0% Ar 0.1% O_2	25-10% CO_2 75-90% H_2O 1.7% N_2, Ar, O_2

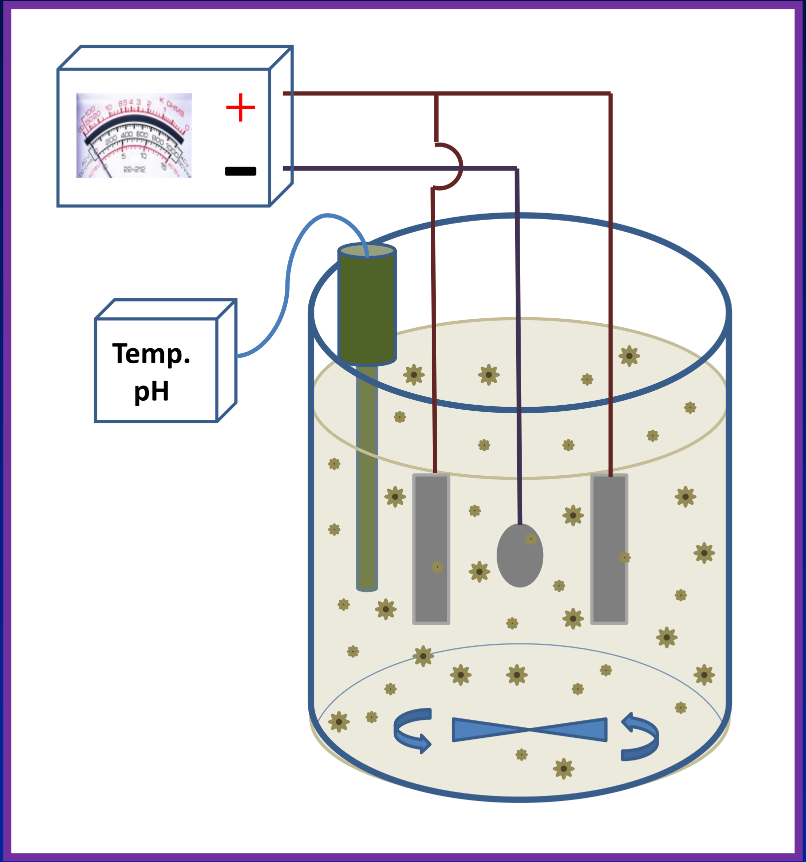
- Understanding of TBC failure mechanism

Industrial Collaboration

- **GE Global Research & GE Energy**
  - Dr. Voramon Dheeradhada and Dr. Warren Nelson
  - Offer guidance on coating development
  - The TBC lifetime will be evaluated and compared to that of the TBCs with the state-of-the-art thermal spray MCrAlY bond coat.
  - Selected coatings with promising oxidation performance will be further assessed by GE.
  - Coatings with superior performance will be recommended for commercial applications.

Preliminary Results

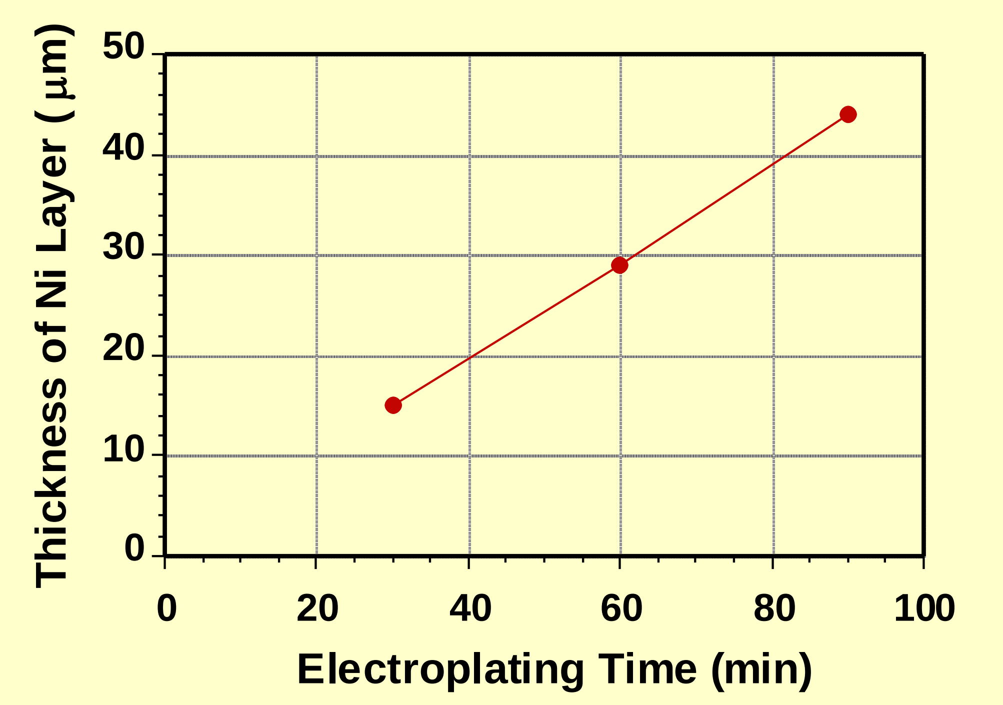
- Experimental setup
  - Substrate: Ni-based superalloys such as René 80
  - Sample preparation:
    - Ground to 600 grit
    - grit blasted with #220 grit
  - Anode: Ni plate



Electroplating of Pure Ni Coating

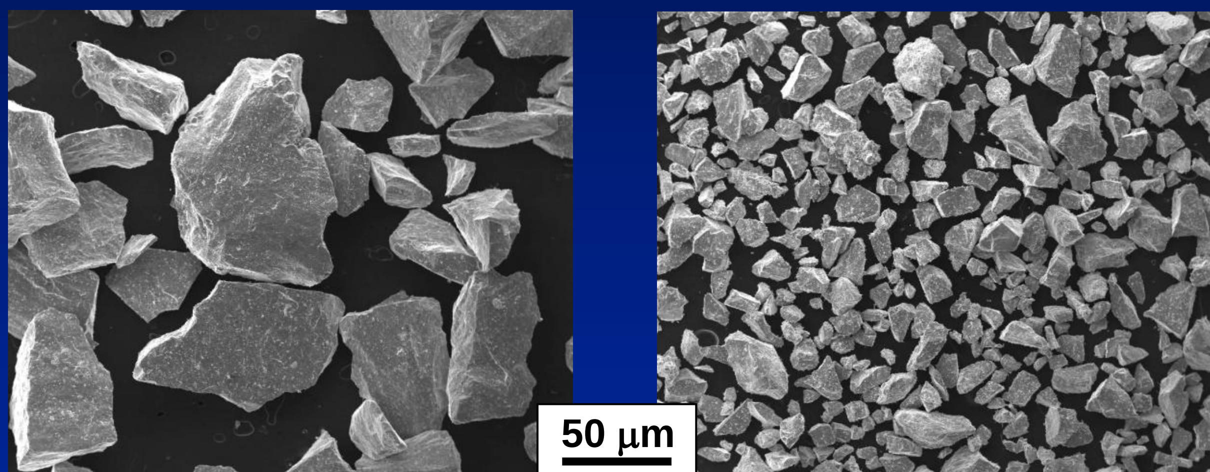
- Watts Ni plating solution
- Current density: 3.1 A/dm^2
- Temperature: 50°C
- pH: 4.0

Constituent	(g/L)
Nickel Sulfate	310
Nickel Chloride	50
Boric Acid	40



High-energy ball milling was used to produce Cr-Al particles of 10-15 μm

- Cr-Al-based particles with ~40 at.% Al
  - Cr-Al alloy made with an arc melter
  - High-energy ball milling in Ar

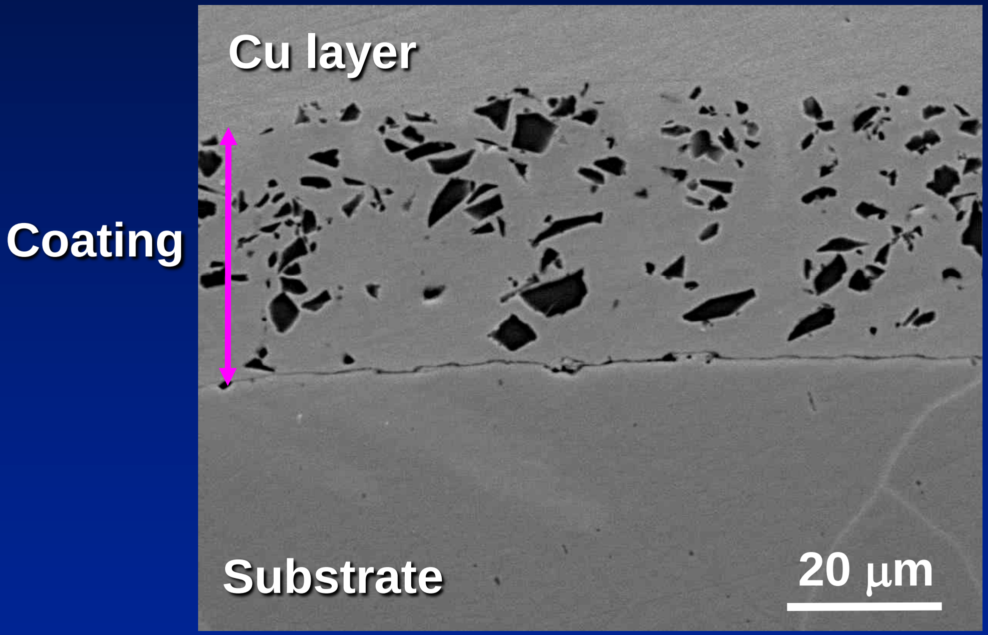


7 min **12 min**

- Particle size was reduced from ~50 μm after 7 min to 10-15 μm after 12 min.

Initial Coating Microstructure

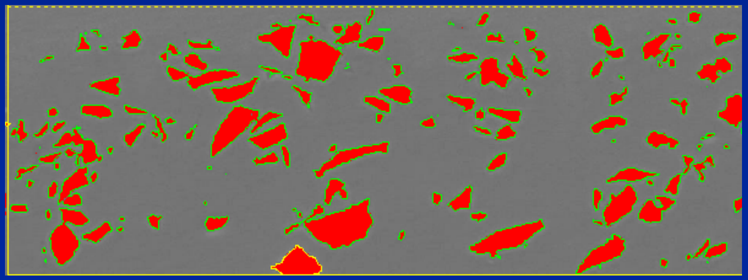
- An adherent Ni coating with Cr-Al particles was deposited.
- The particle incorporation was low, ~15 vol.%.



Current density: 3 A/dm^2

Particle load: ~30 g/L

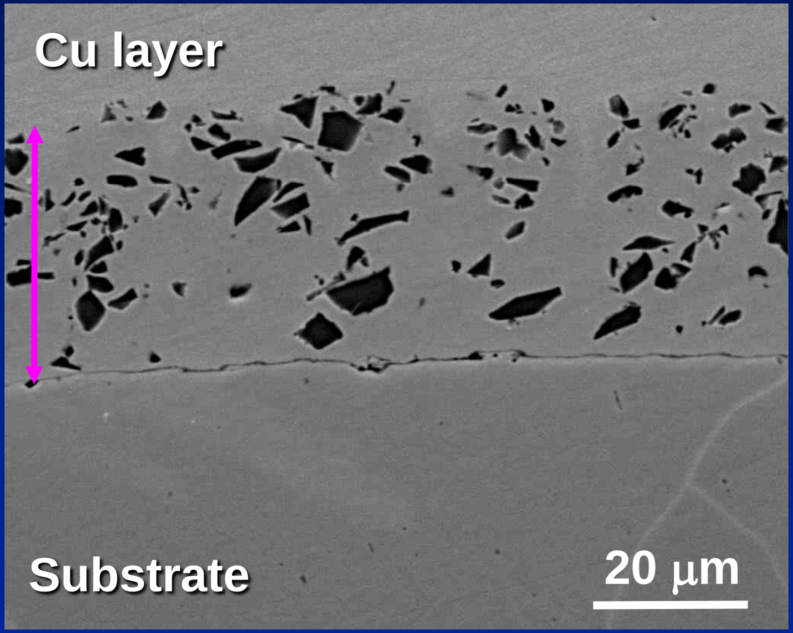
- NIS Elements imaging software was used to calculate the area fraction of the particles.



Improvement in Particle Incorporation

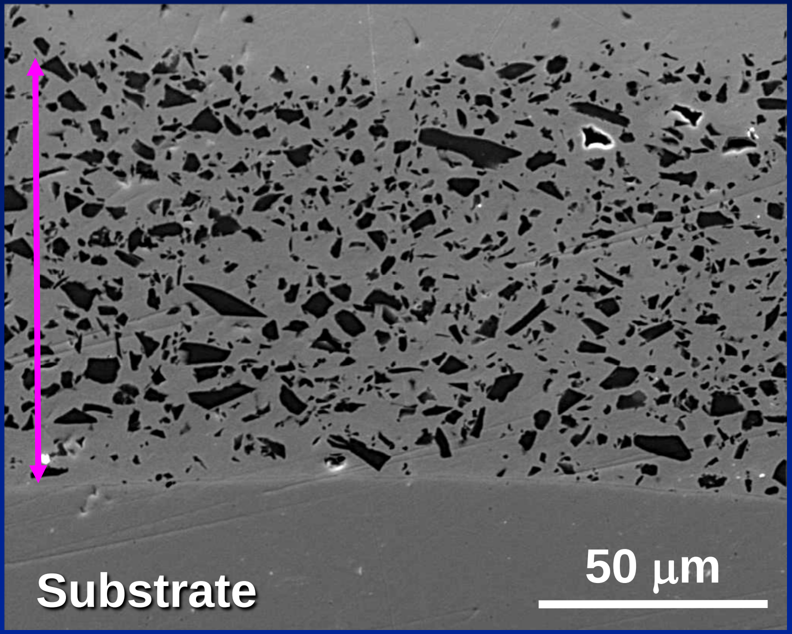
- The particle incorporation can be controlled by modifying the current density, particle loading, stirring, etc.

~15%



Current density: 3 A/dm^2
Particle load: ~30 g/L

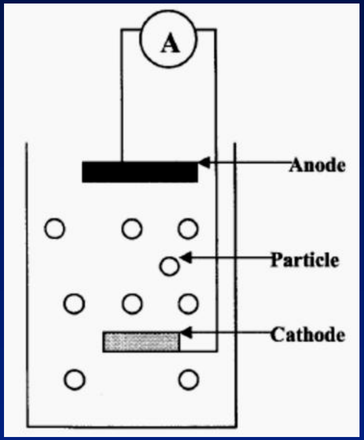
~28%



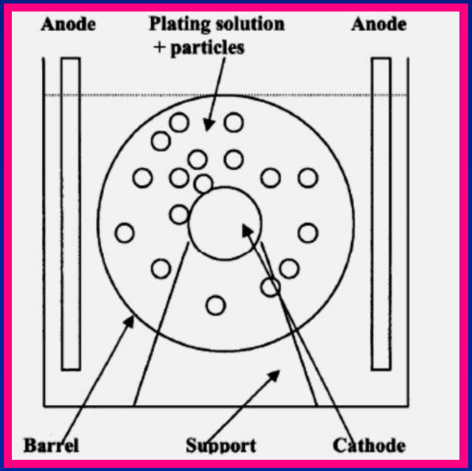
Revised parameters

Electro-codeposition Configuration

- During initial experiments the specimen was positioned vertically
  - — Positioning may limit volume of deposited particles
- Two horizontal arrangements
  - — Particle incorporation is limited on the downward-facing surface
  - — **The barrel unit:** a semi-permeable rotating barrel that holds the specimen and powder
    - ➢ 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)

Summary

- The proposed research is to develop and optimize MCrAlY bond coats for syngas/hydrogen turbine applications using a low-cost electrolytic codeposition process.
- The coating performance will be improved by reducing the impurity levels in the coating and by employing reactive element co-doping.
- The oxidation resistance of the new bond coat will be assessed in the water vapor environments.
- The failure mechanism of the new TBC/bond coat architecture will be studied to provide a knowledge base for further increase of TBC lifetimes.

Acknowledgments

- U. S. Department of Energy - National Energy Technology Laboratory, University Turbine Systems Research, Award No. DE-FE0007332; Project Manager: Dr. Patcharin Burke

- Tennessee Tech University, Center for Manufacturing Research

Thank you