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

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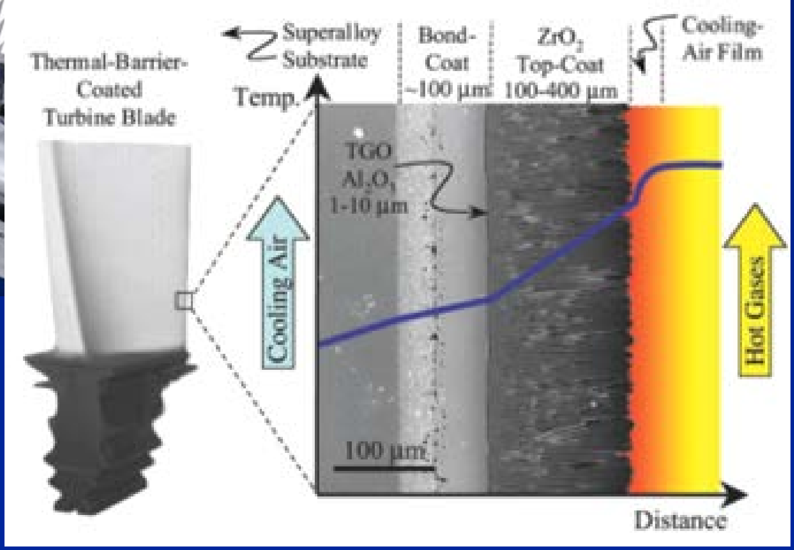
Coating Development Need for IGCC
(Integrated Gasification Combined Cycle)

- **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)

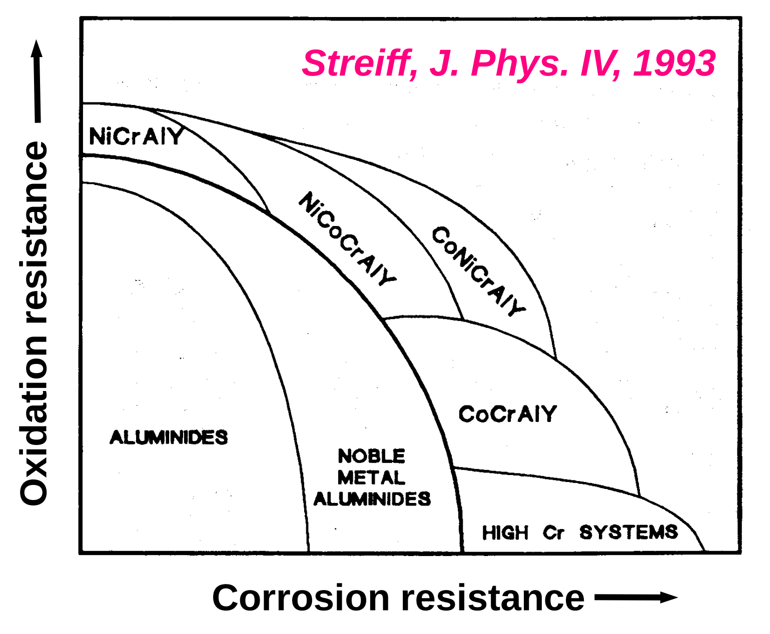
(http://www.aecengineering.com)



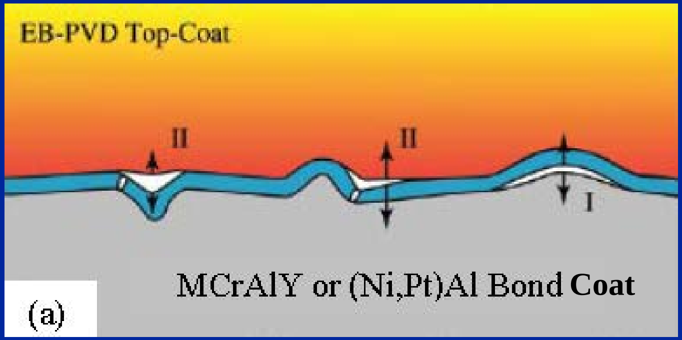
(Padture, et al., Science, 2002)

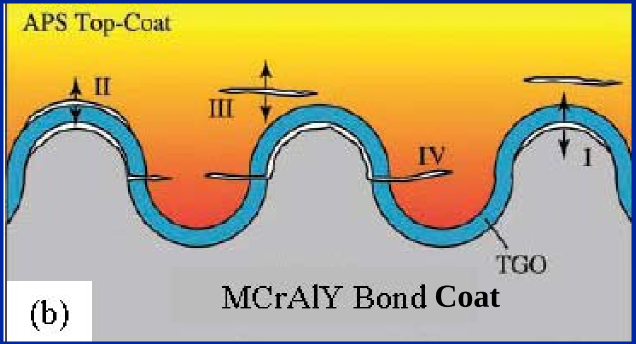
Bond Coat Choices

- 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



- 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

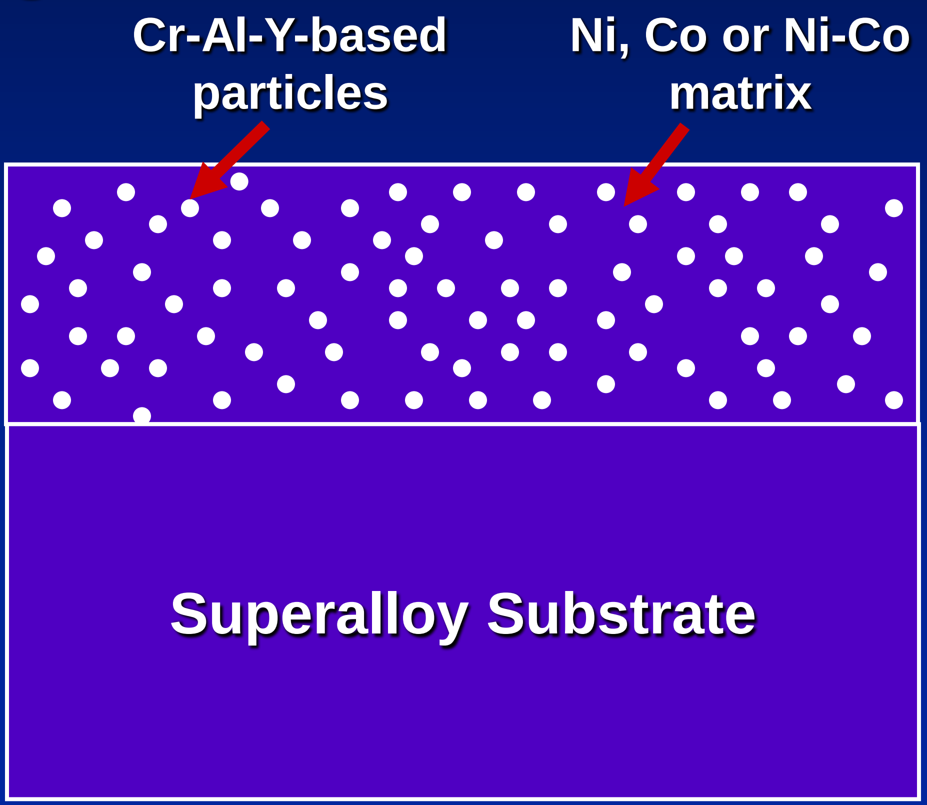
- Current fabrication processes
  - Low-pressure plasma spray (LPPS)
  - Air plasma spray (APS) & high-velocity oxy-fuel (HVOF)
- Limitations of thermal spray processes
  - Line-of-sight, requiring complex robotic manipulation for complete coverage
  - Oxide content can be high in APS and HVOF coatings.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

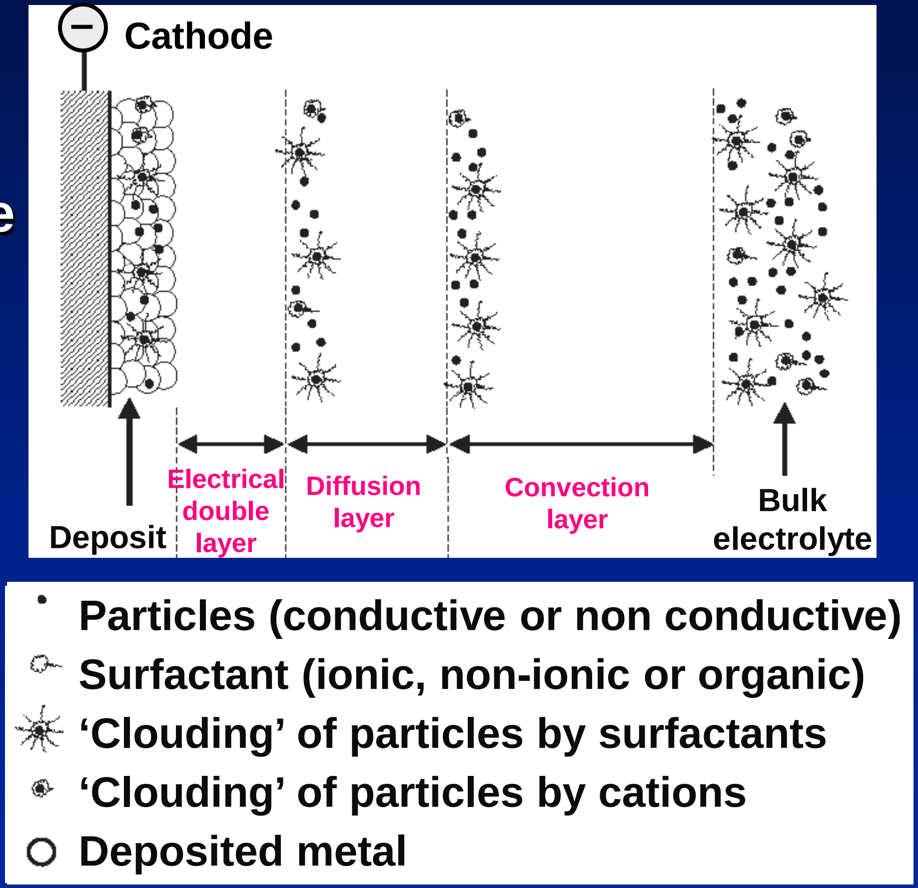
- A dense MCrAlY coating of ~125μm thick was reported.
- The process was later patented by Praxair, known as "Tribomet", and has been applied as the abrasive tip coating on first stage turbine blades.

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

Electrolytic codeposition is a more complex process than conventional electroplating

It is generally believed that five consecutive steps are engaged:

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
5. **Adsorption** at the cathode where the particles are entrapped within the metal deposit



(Celis, et al., J. Electrochem. Soc., 1987; Low et al., Surf. Coat. Technol., 2006)

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 codeposition parameters
- Microstructural evolution during post-plating heat treatment

#3: Microstructural Characterization & Property Measurement

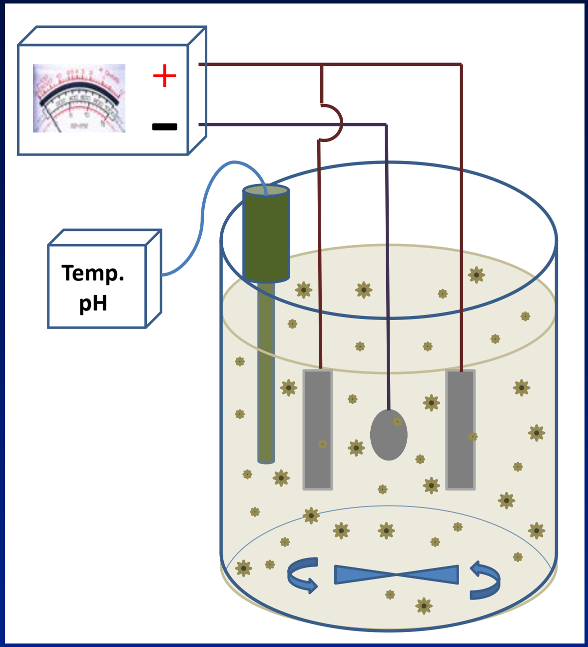
- Microstructure
- Surface roughness & hardness measurement

#4: Evaluation of Coating Performance & Failure Mechanism

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

Synergistic Effects of Electro-codeposition Parameters

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



Electro-codeposition Experiments

- Substrate:

  Ni-200 or René 80 discs

  (17 mm in diameter, 1.8 mm thick)
  - ground to 600 grit
  - grit blasted with #220 Al_2O_3
- Anode: pure Ni plate
- Temperature: 50°C
- pH: 3.5
- Time: 2h

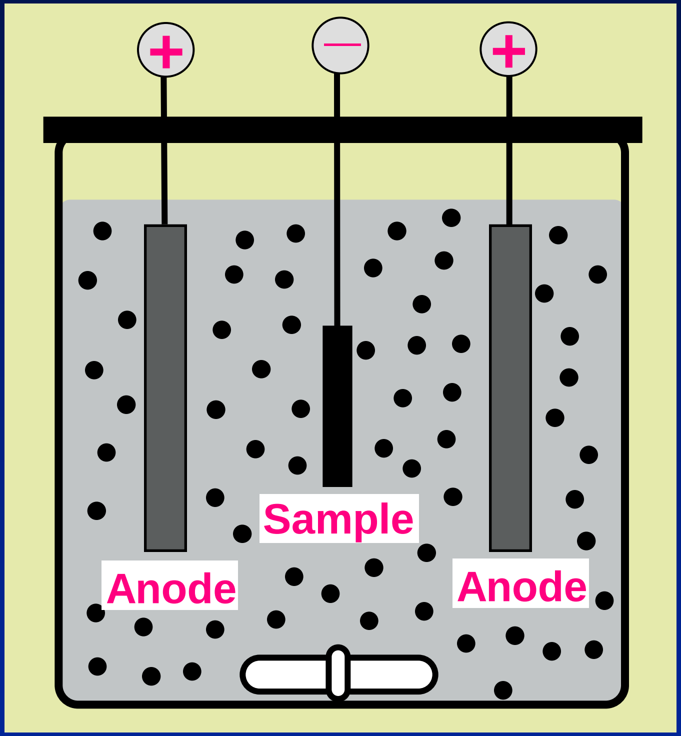
- Watts plating solution

Constituent	(g/L)
Nickel sulfate	210-310
Cobalt sulfate	0-12
Nickel chloride	45-50
Boric acid	30-40
Sodium lauryl sulfate	2.0

- Pre-alloyed powder
  - Laboratory: ball-milled CrAlY-based powder
  - Commercial: atomized CoNiAlY

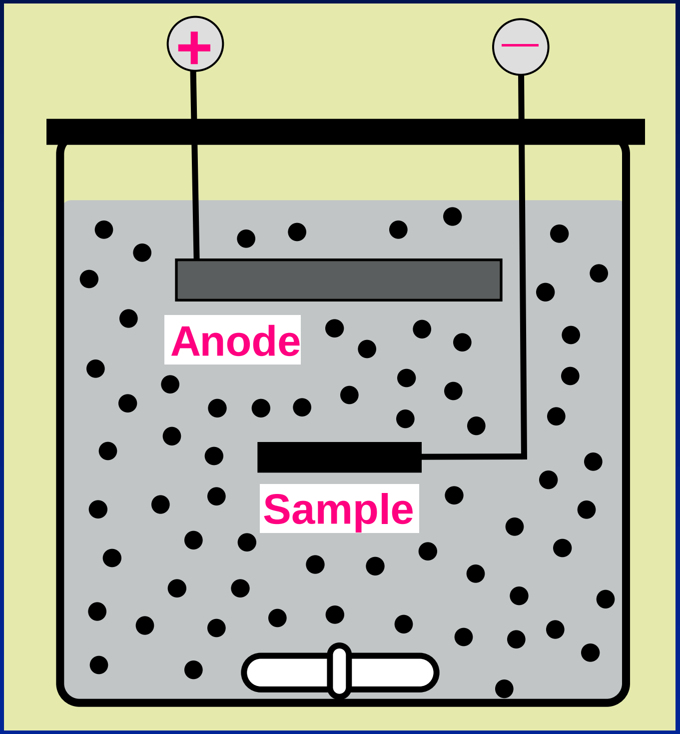
Conventional Configurations in Electro-codeposition

Vertical (Traditional Electroplating)



- Simple, more literature data
- Limited particle incorporation

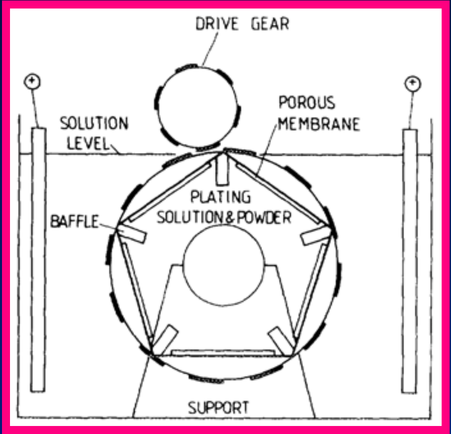
Horizontal (Sediment Codeposition)

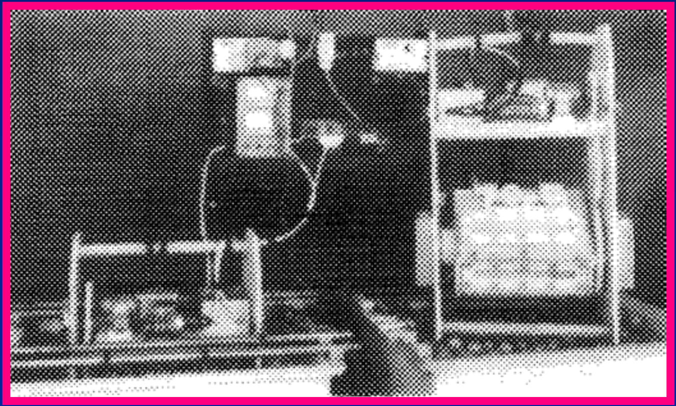


- Increased particle incorporation on the top surface
- Nearly no particles on the bottom surface

Rotating Barrel System

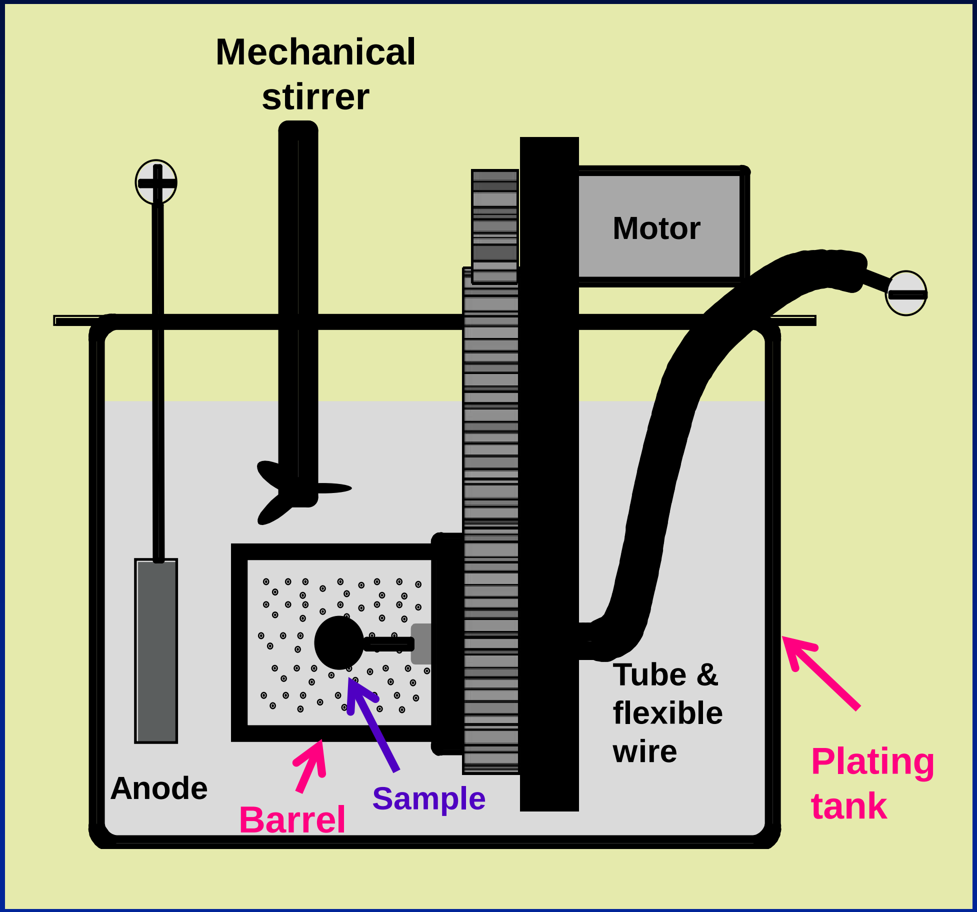
- A semi-permeable barrel that holds the specimen and powder
  - The electrolyte can diffuse through the membrane wall, while the powder is maintained in suspension in the barrel.
  - Uses significantly less powder, allowing a higher concentration if needed
- The barrel rotates along a horizontal axis during plating
  - More uniform coating and particle incorporation

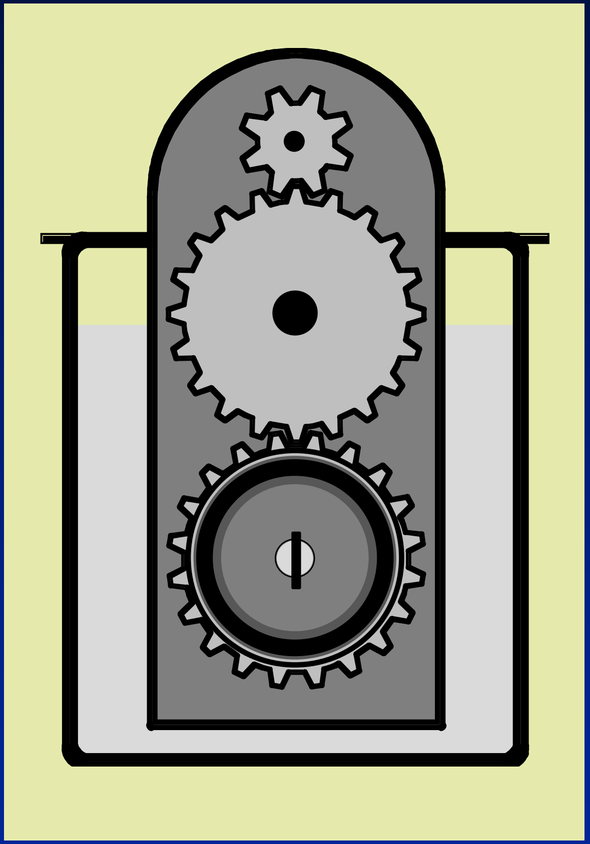




(Honey et al., J. Vac. Sci. Technol., 1986)

Design and Setup of the Rotating Barrel at TTU

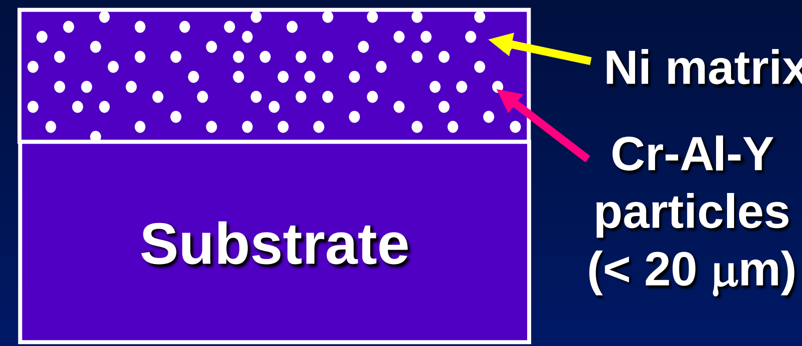




- Polypropylene barrel: 52-mm ID, 70-mm length
- Thin nylon membrane: with ~1 μm mesh size

Two-Step Coating Process to Form MCrAlYs

1. **Form a composite coating:** CrAlY-based particles are electro-codeposited with Ni/Co



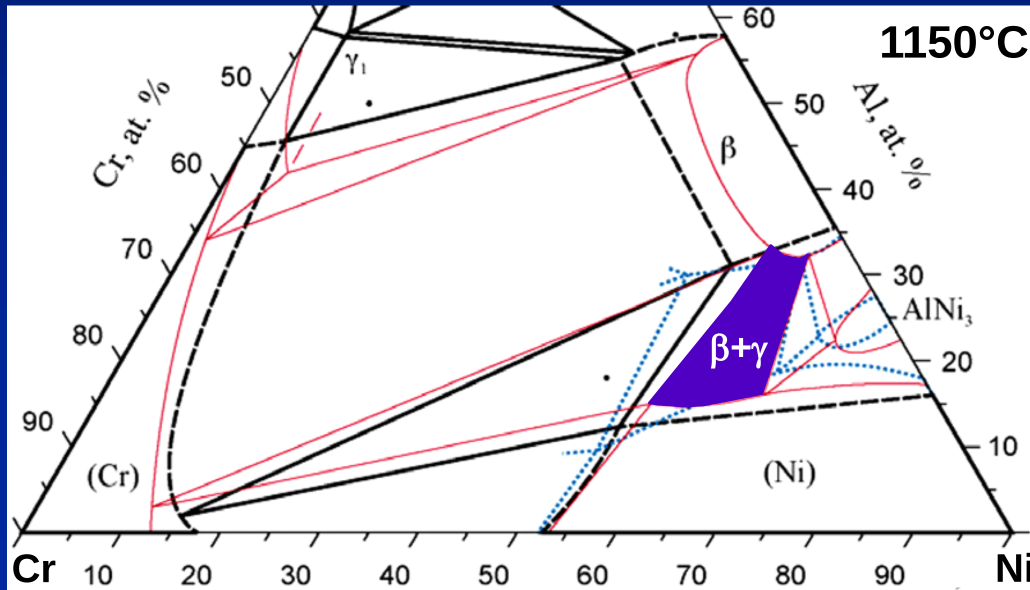
CrAlY powder: Cr-37Al-1.7Y (wt.%) (Cr_2Al, Cr_5Al_8, & YCr_4Al_8)

Need ~40 vol.% in coating

2. **Convert to β + γ:** post-plating diffusion treatment

16-22 Al, 18-22 Cr, 0.3Y, at.%

(8-12 Al, 18-22 Cr, 0.5Y, wt.%)

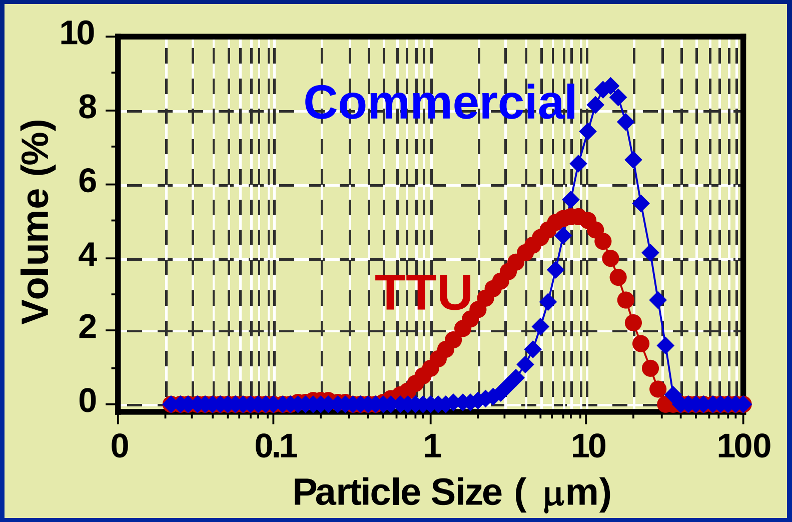


(Grushko et al., J. Alloys Compd., 2008)

Commercial Powder vs. TTU Powder

	Commercial	TTU
Composition (wt.%)	Co-32Ni-21Cr-8Al-0.8Y	Cr-37Al-1.7Y
Processing	Atomizing	Ball milling
Shape	Spherical	Irregular
Size (μm)	12.9	7.1
Density (g/cm^3)	7.5	4.5

Powders with desired composition are not commercially available.

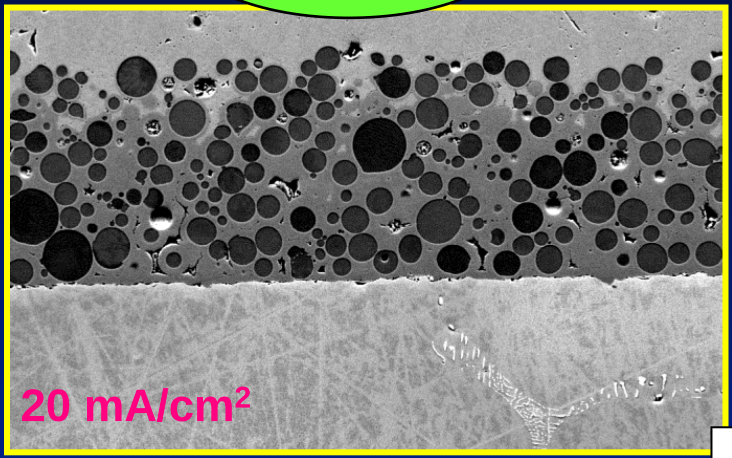


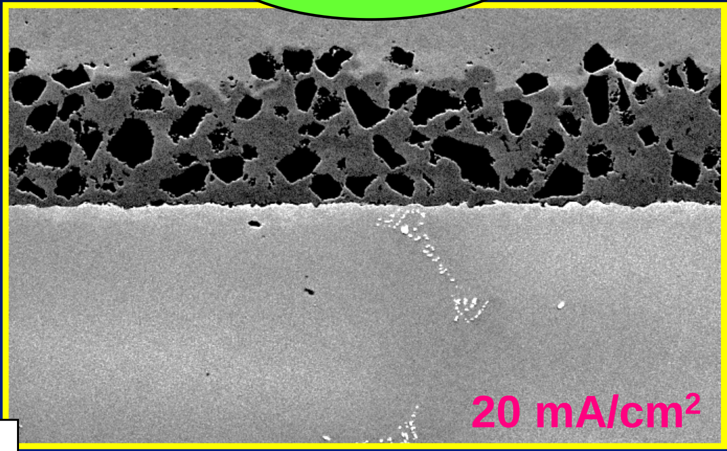
Barrel Codeposition Results

Commercial Powder

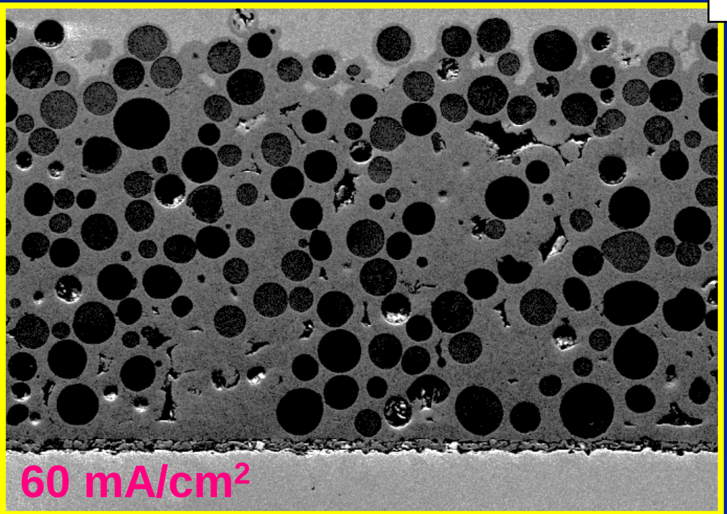
Particle loading: 20 g/L
Rotation speed: 7 rpm

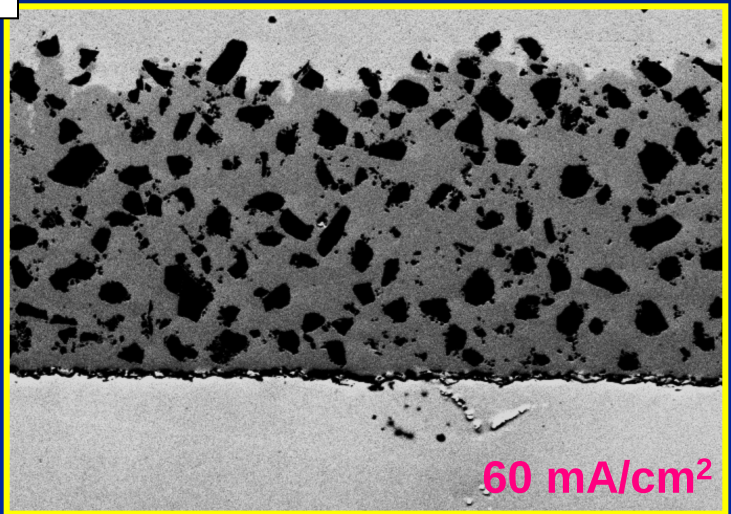
Laboratory Powder



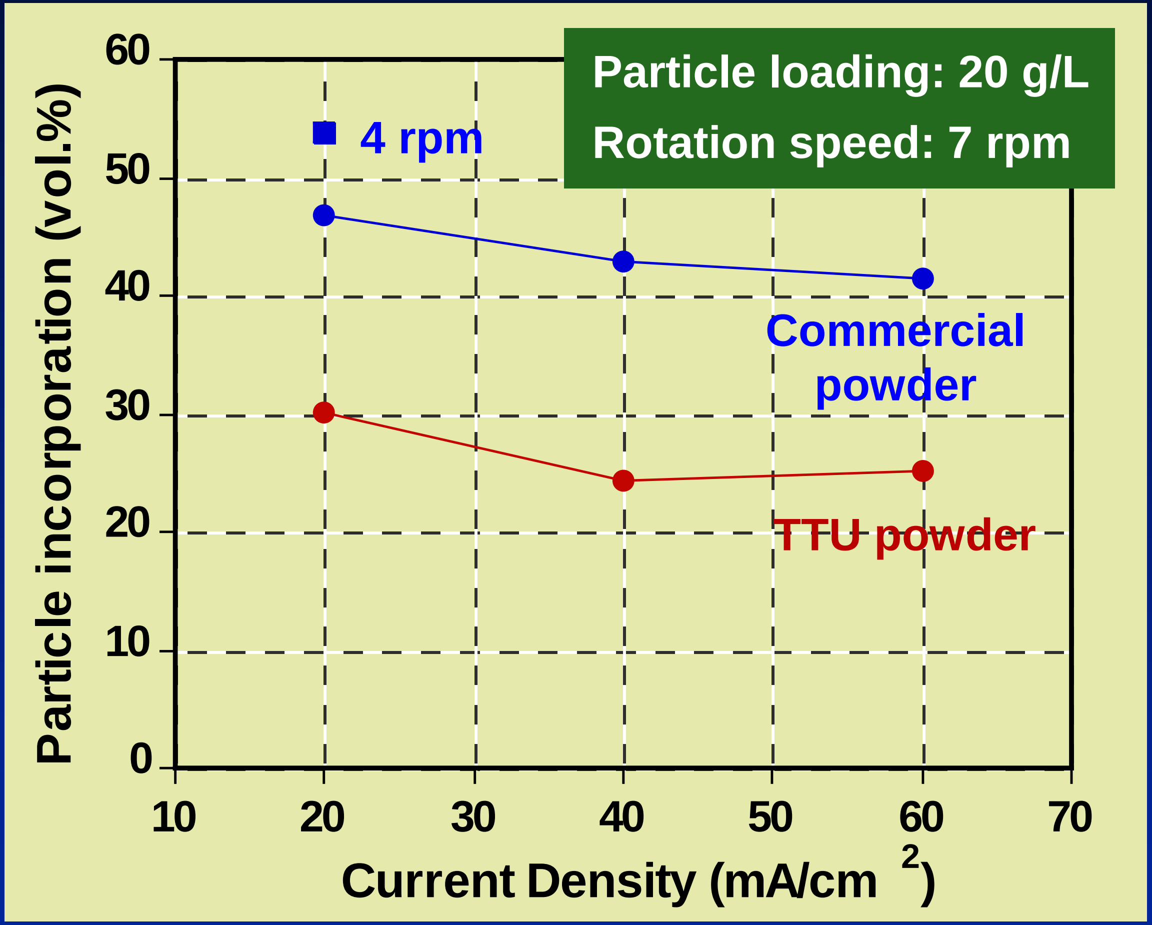


20μm



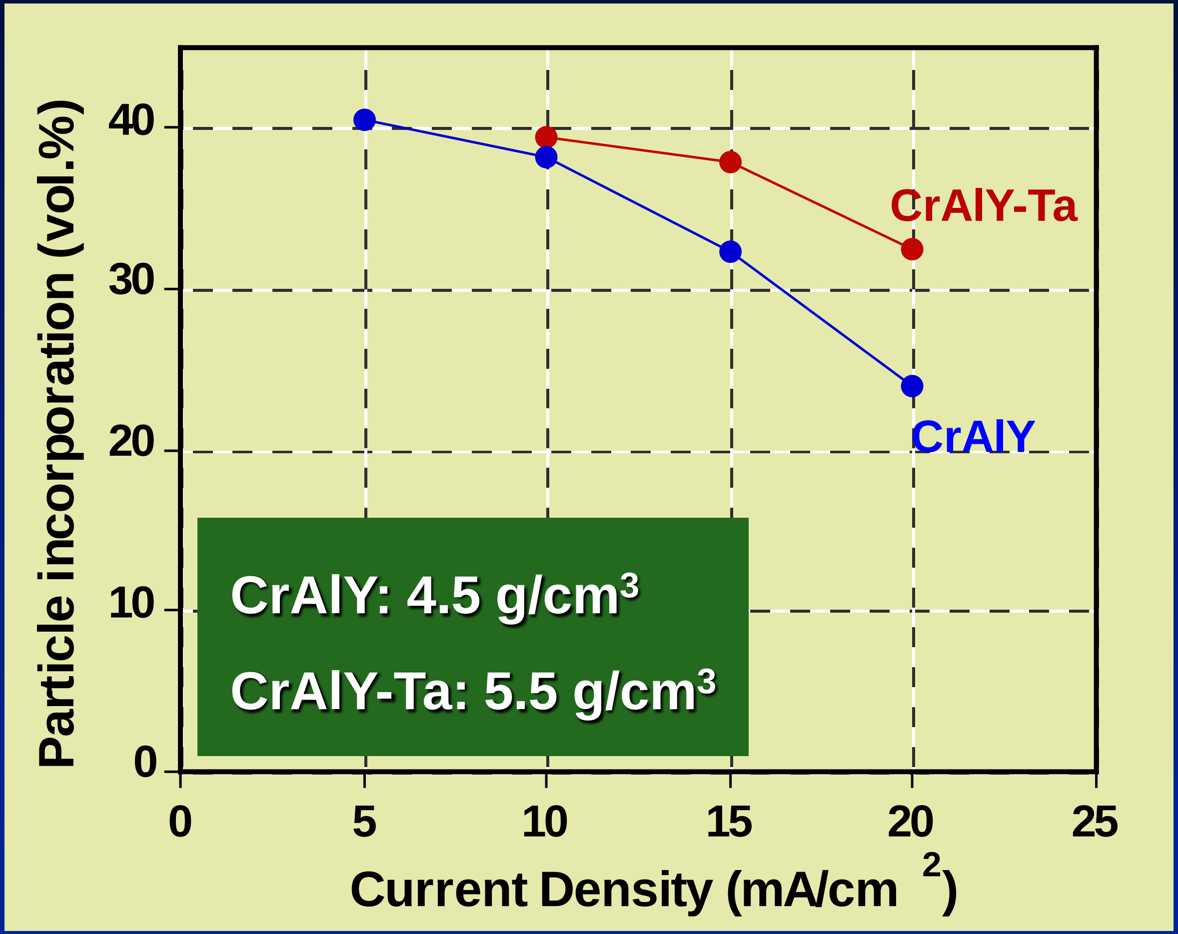


Effect of Barrel Codeposition Parameters



- Higher particle incorporation for atomized powder
- Particle incorporation increased with reduced rotating speed

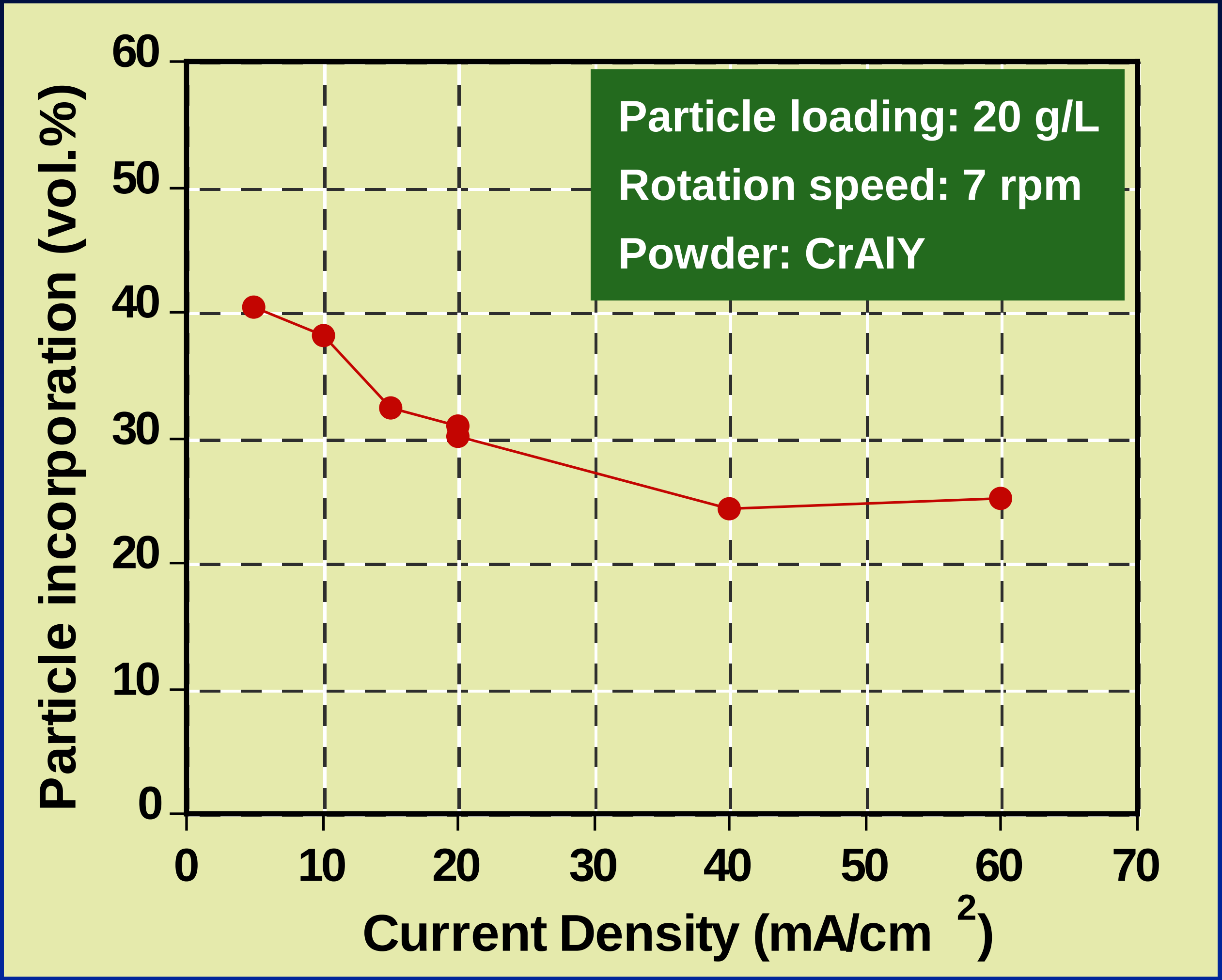
Effect of Particle Density



Cr-25Al-1.5Y-12.6Ta (wt.%)

- Higher particle incorporation for CrAlY-Ta powder
- Ta (0.5-3.4 wt.%) has been added to some MCrAlY coatings
  (A. Vande Put et al., Surf. Coat. Technol., 205, 2010, p. 717)

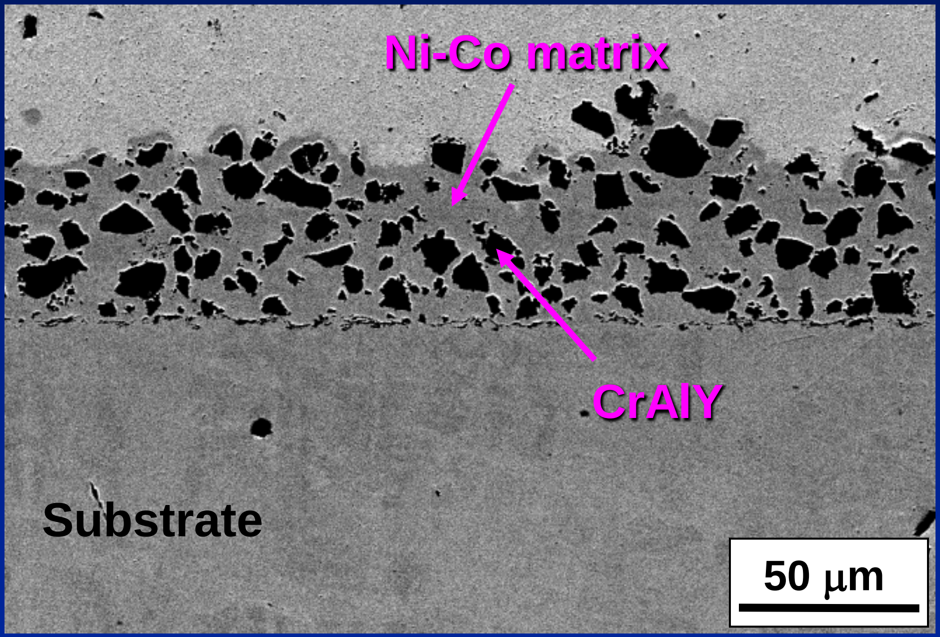
Effect of Plating Current Density



- Decreasing current density led to increased particle incorporation

Composite Coatings with Ni-Co Matrix

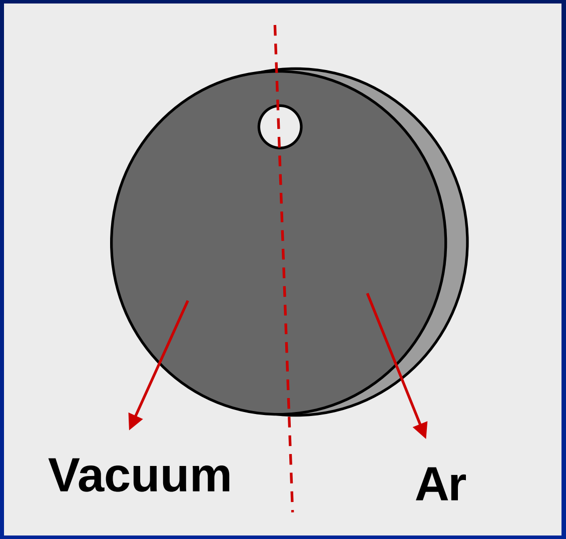
Powder: 20 g/L CrAlY
Current density: 5-20 mA/cm^2
Rotation speed: 7 rpm
Plating time: 2h



- **Coating thickness ~55 μm, CrAlY particle incorporation 30-40 vol.%**

Post-deposition Heat Treatment

- NiCo-CrAlY composite coatings on René 80
- Temperature: 1000, 1100, 1200°C
- Time: 2h
- Environment
  - Vacuum: 10^{-4} Pa
  - Ar: 1 atm

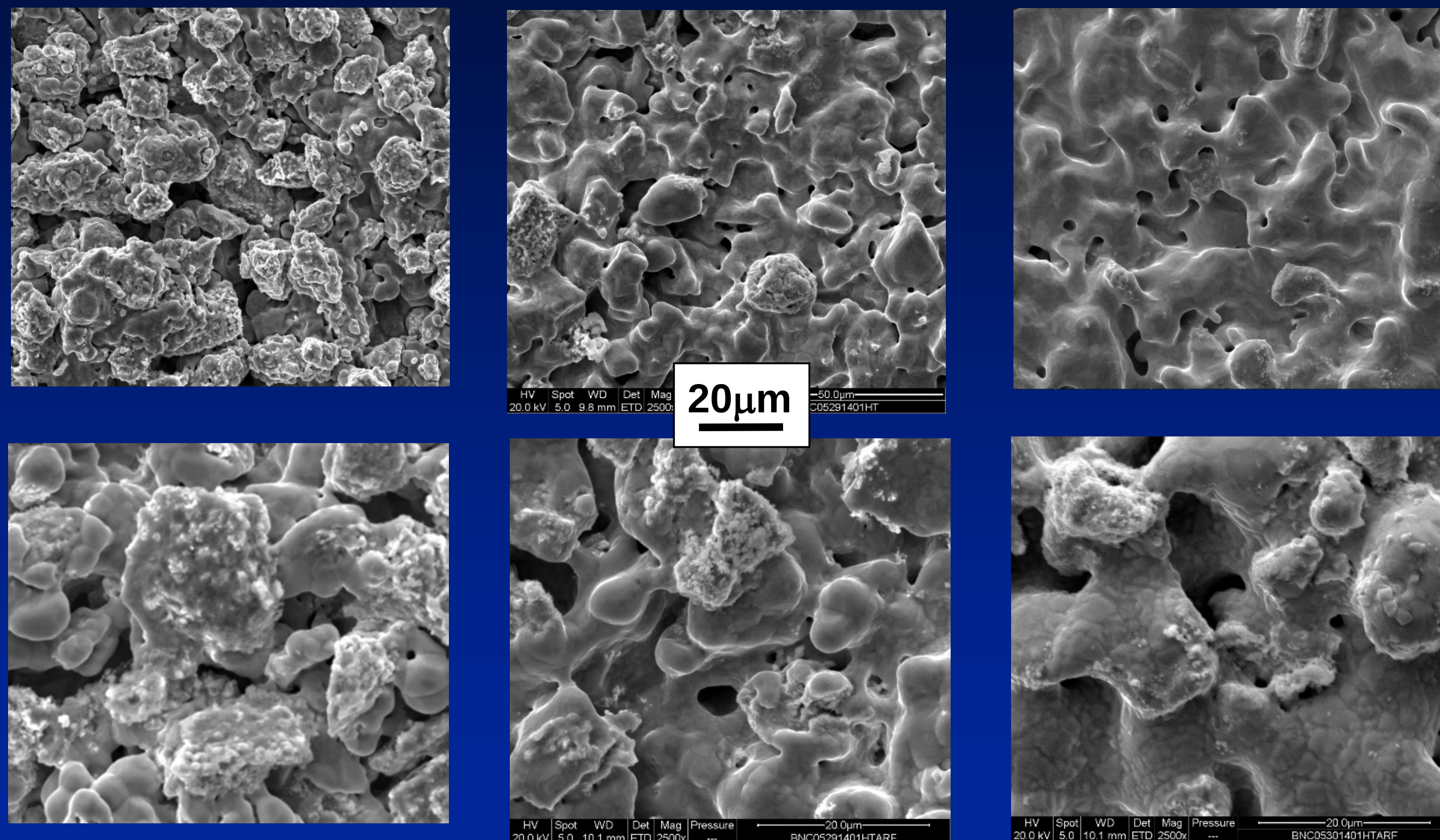


NiCo-CrAlY Coatings after Diffusion Heat Treatment

1000°C | 1100°C | 1200°C

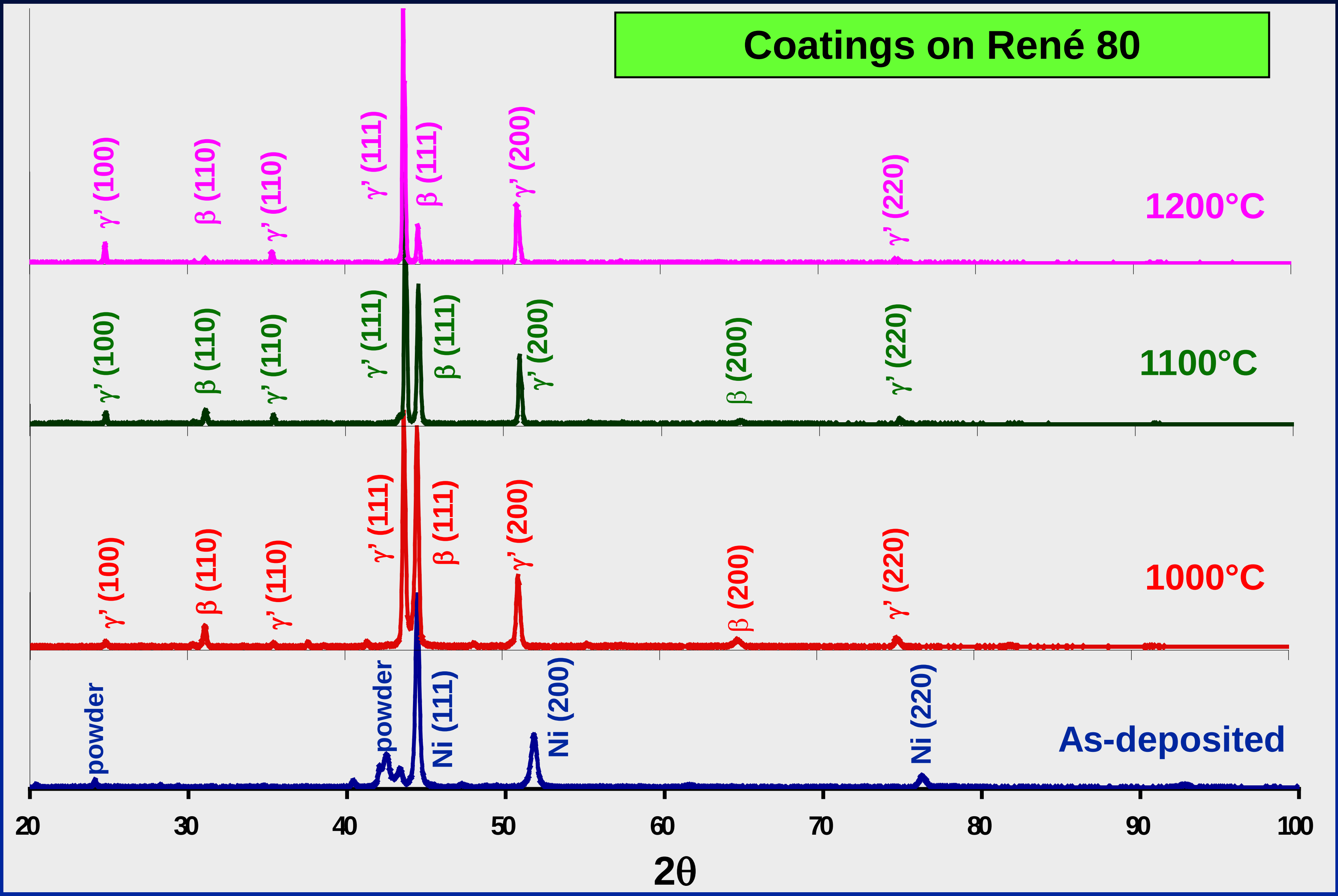
Vacuum

Ar

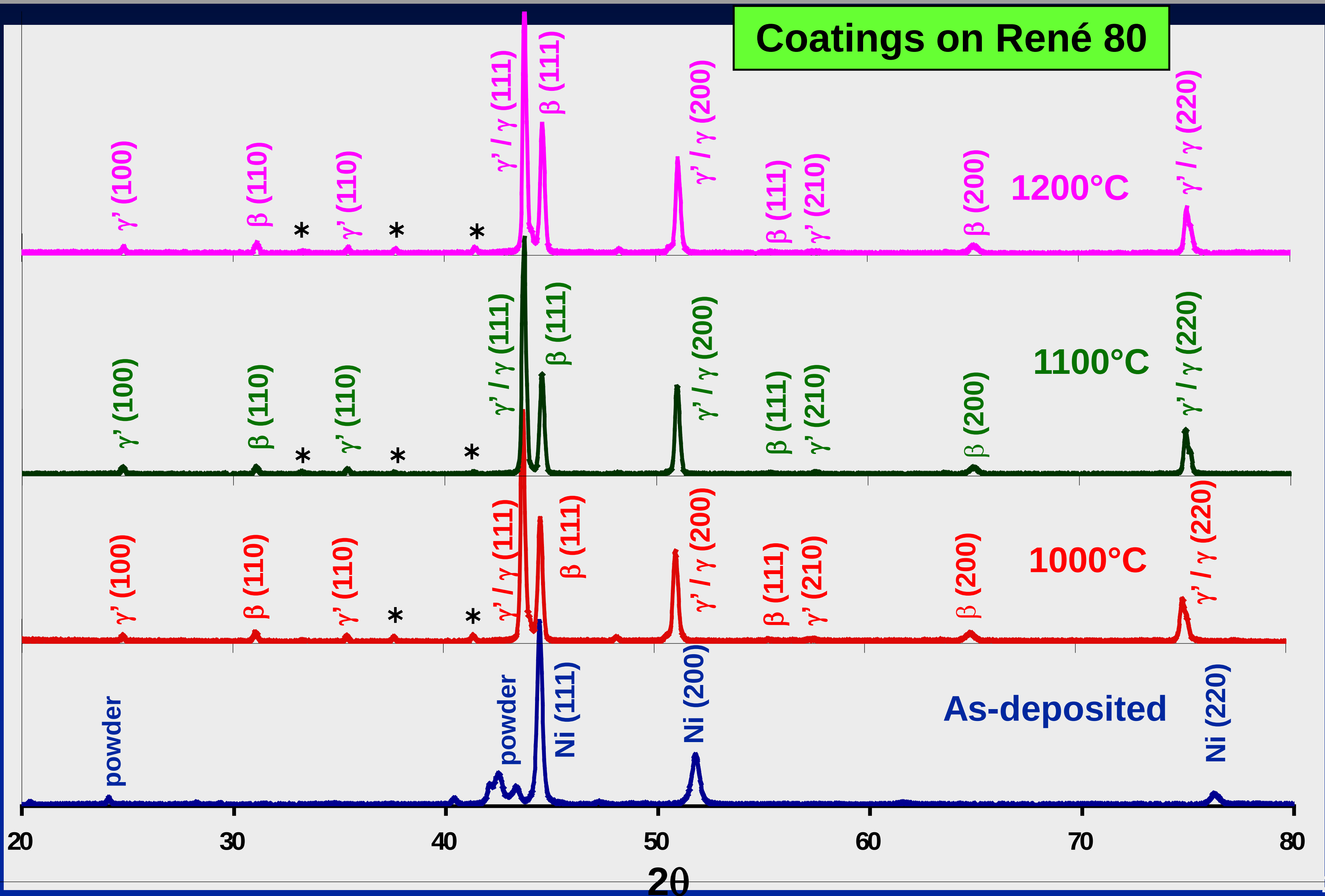


- More interdiffusion at 1100-1200°C
- Cr evaporation at 1200°C in vacuum

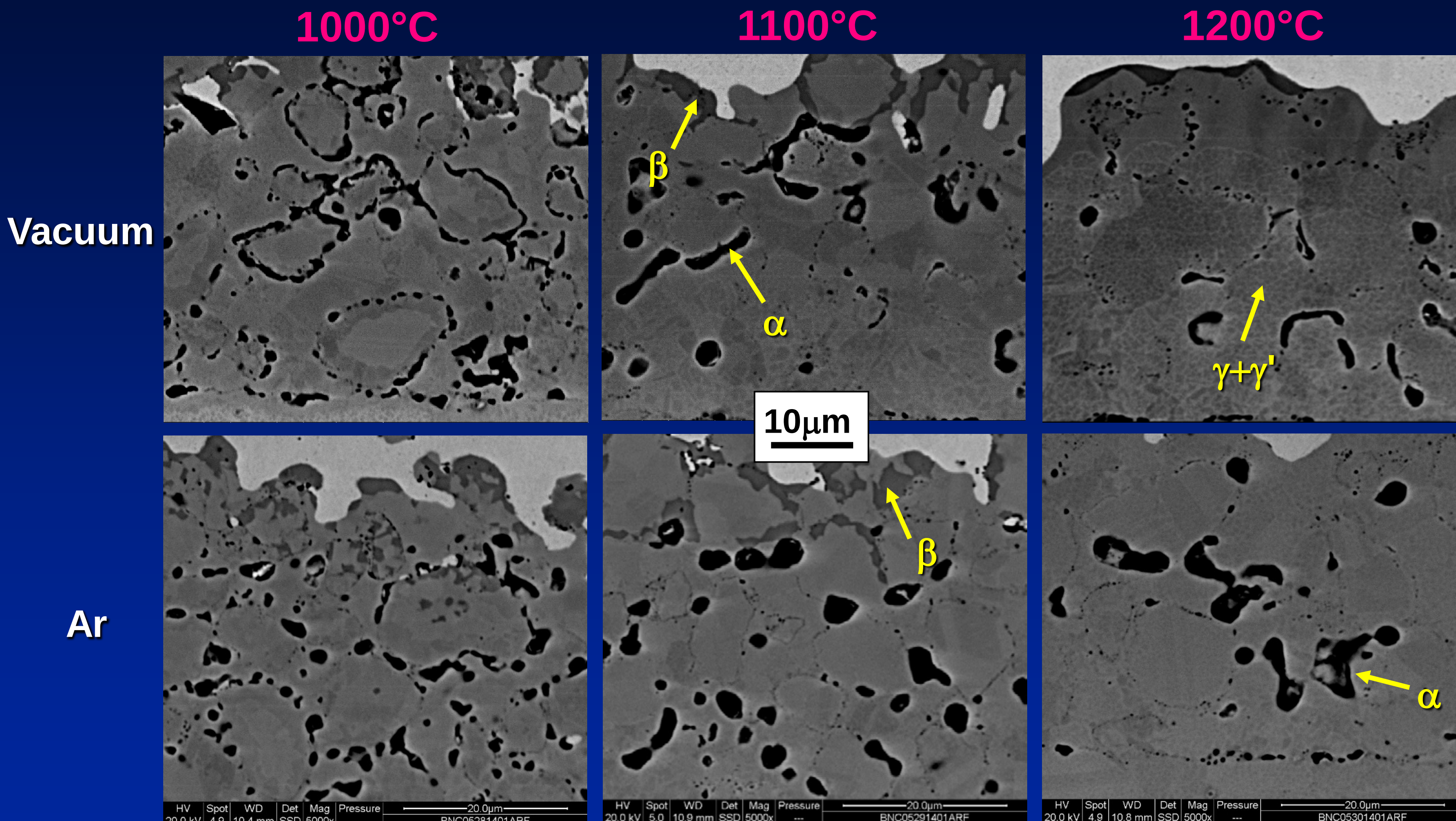
After Heat Treatment in Vacuum: β + γ’



After Heat Treatment in Ar: β + γ + γ’



NiCo-CrAlY Coatings after Diffusion Heat Treatment

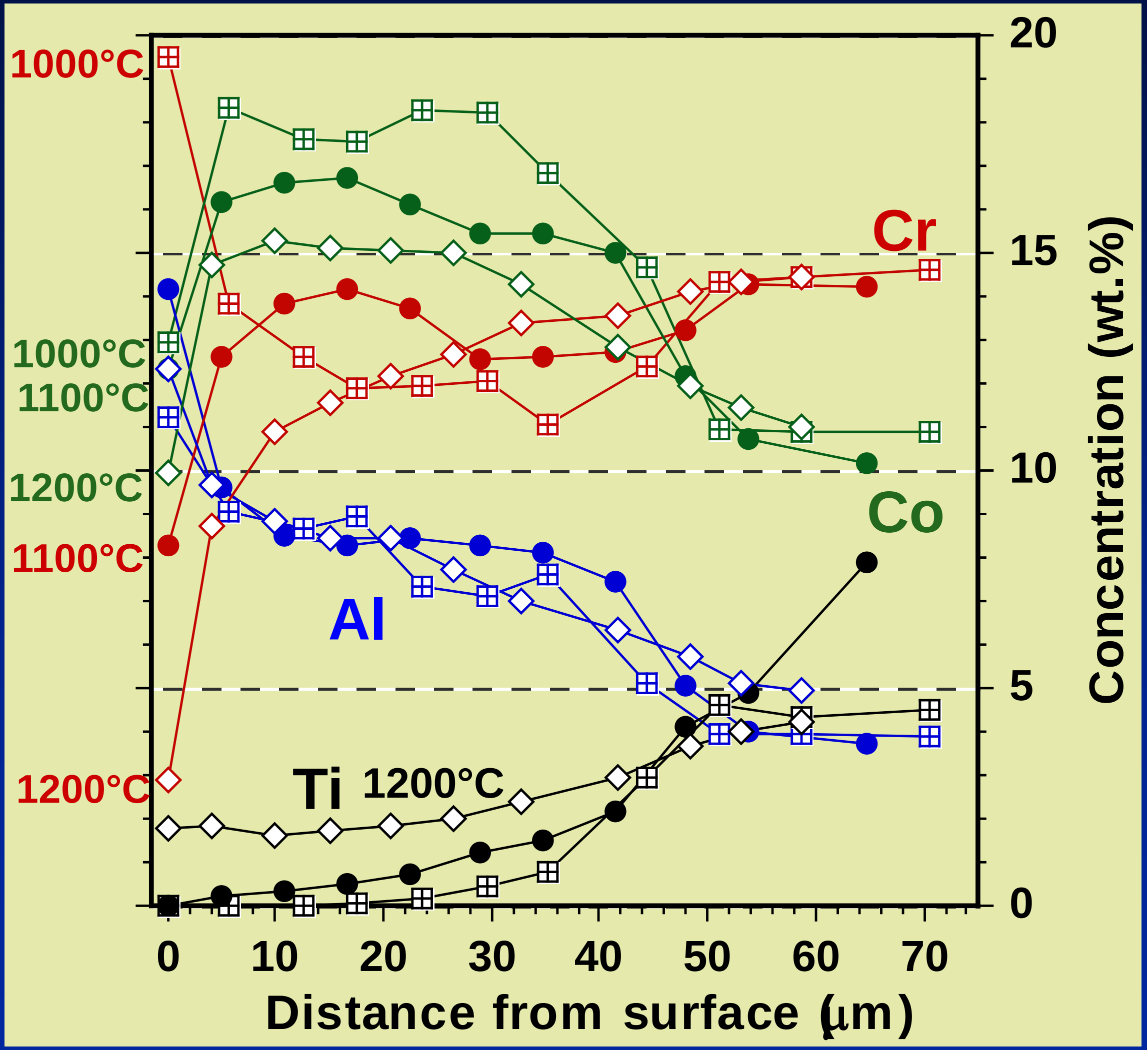


- **Phases such as β, γ’, and γ were observed**

Heat Treatment in Vacuum - NiCoCrAlY

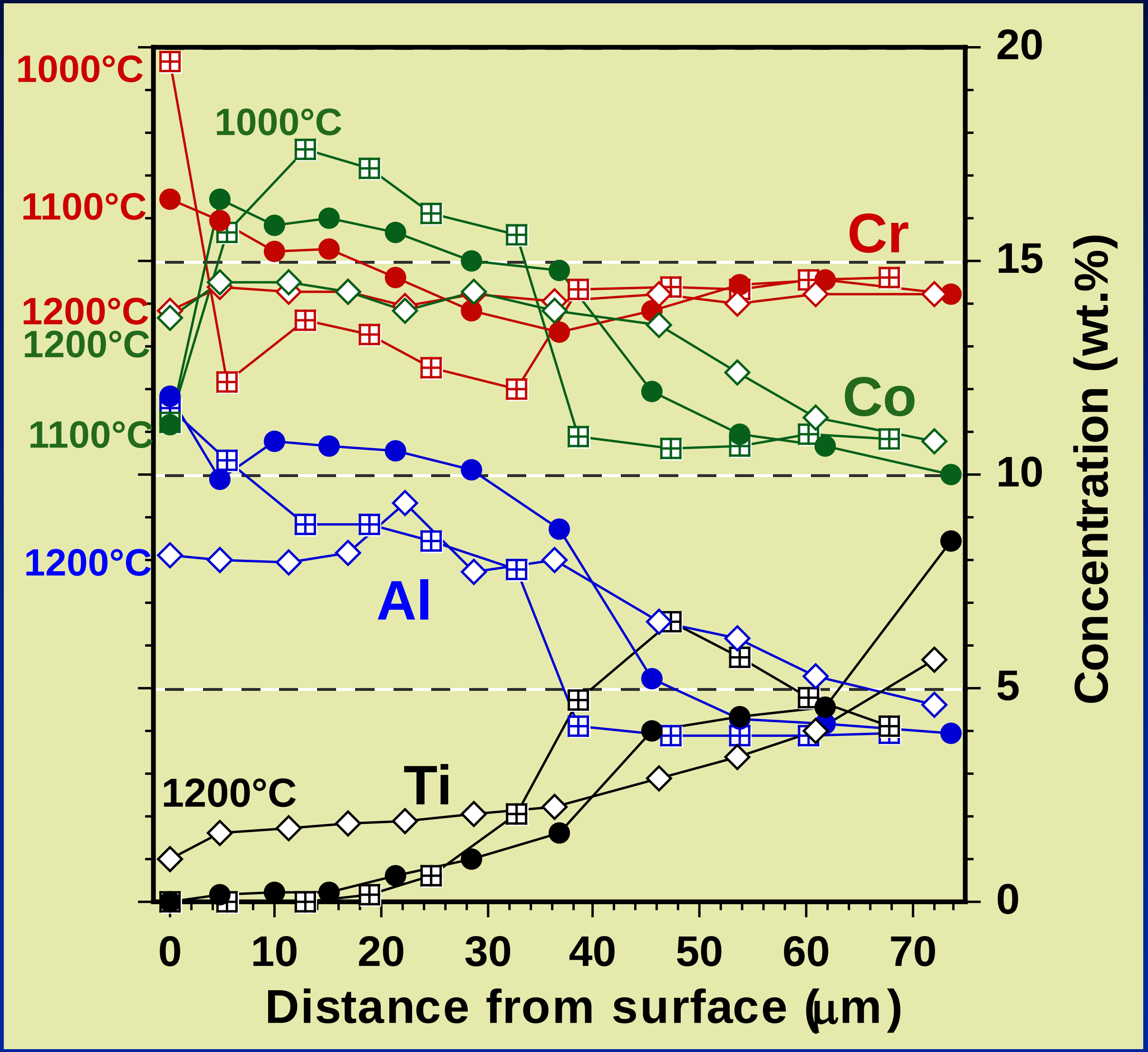
René 80: Ni-3.0Al-14.1Cr-9.3Co-4.0W-3.9Mo-5.1Ti-0.16C-0.016B-0.02Zr, wt.%

- **Coating: 8-9 Al, 11-14Cr, 15-18Co (wt.%)**
- **Cr evaporation at 1100-1200°C**
- **3% Cr and 2% Ti at surface 2h at 1200°C**



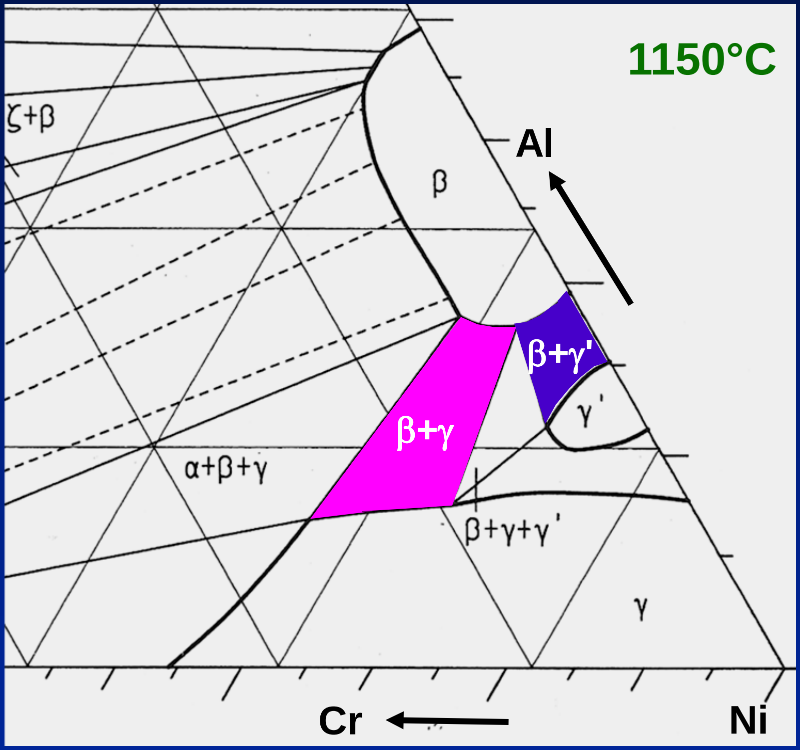
Heat Treatment in Ar - NiCoCrAlY

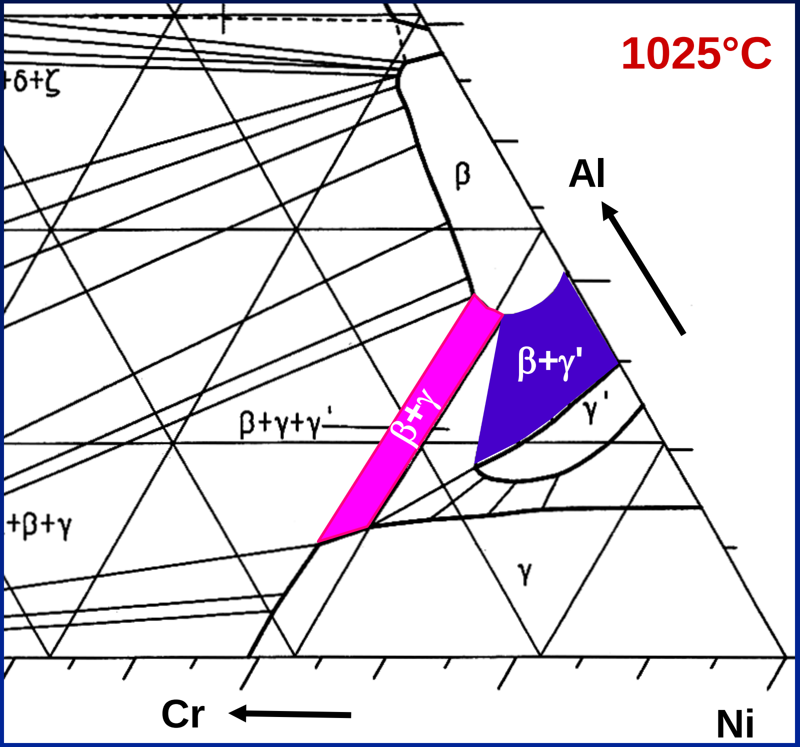
- Coating: 8-10 Al, 13-15Cr, 14-18Co (wt.%)
- Less Cr evaporation; 14-17 at 1100-1200°C
- 1-2% Ti at surface after 2h at 1200°C



Coating Phase Constituents

Typical MCrAlY composition: 16-22 Al, 18-22 Cr, 0.3Y, at.%
(8-12 Al, 18-22 Cr, 0.5Y, wt.%)

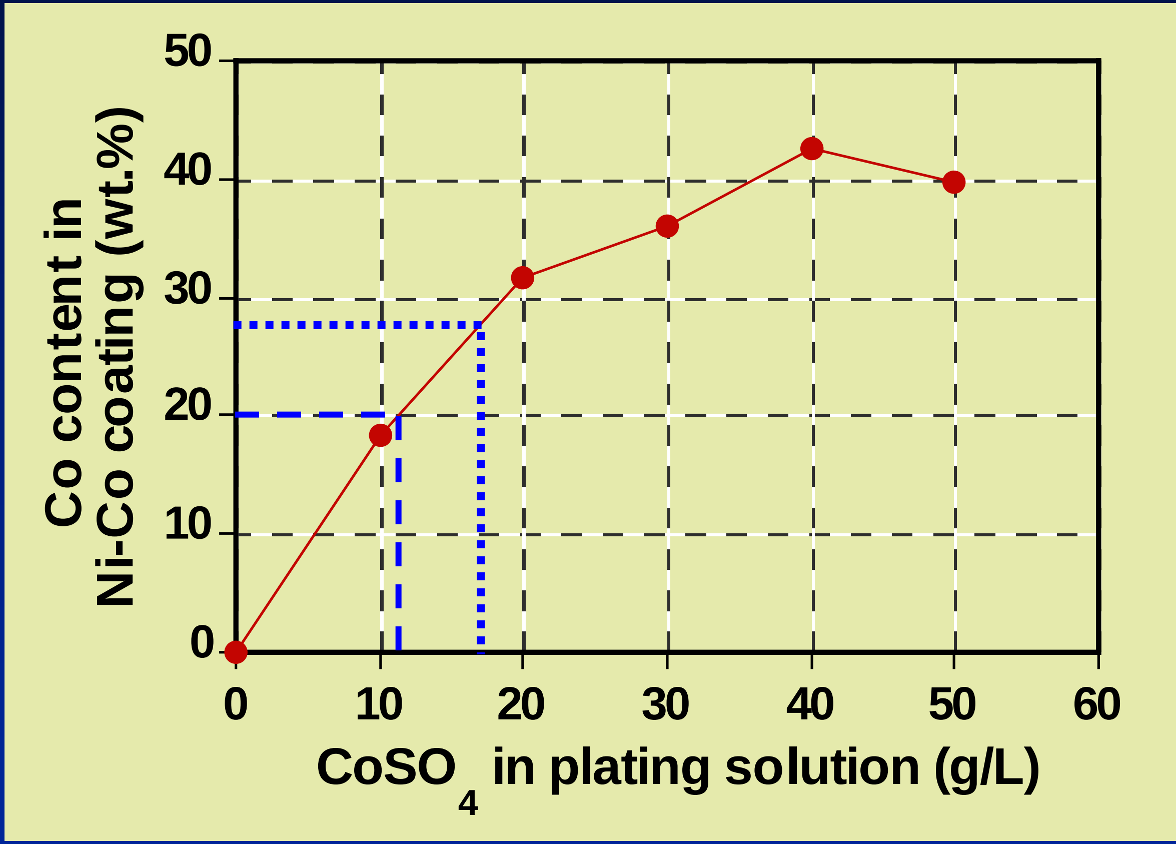




- **Co destabilizes γ' phase and also improves ductility (>20 wt.% Co)**
- **Need to increase Cr and Co contents**

Approaches to Increase Co and Cr Contents in Electrodeposited NiCoCrAlY Coatings

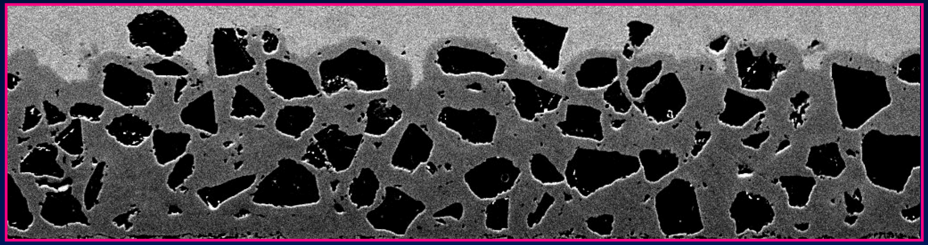
- **Co: increase $CoSO_4$ in the plating solution**

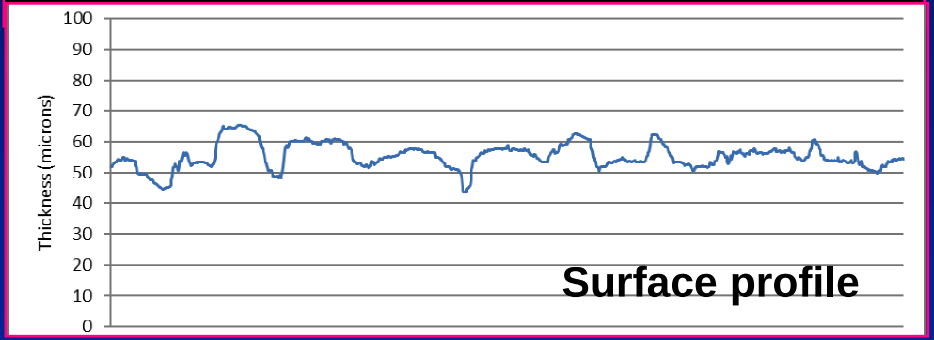


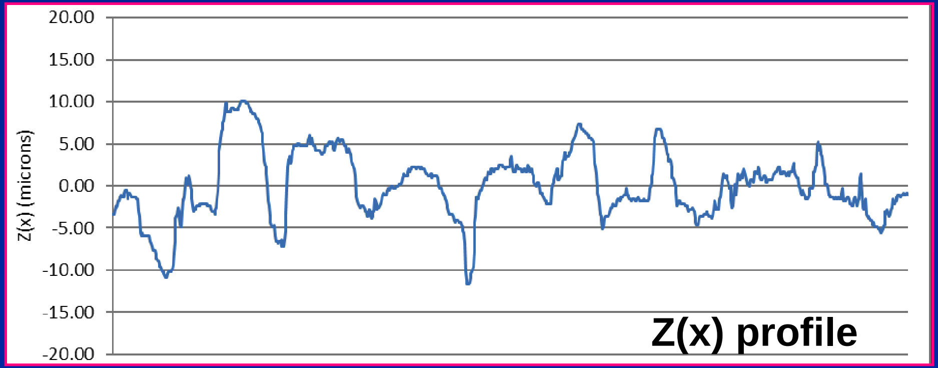
- **Cr: (1) increase the Cr level in Cr-Al-Y powder;**

  (2) reduce Cr evaporation during heat treatment

Characterization of Coating Surface Roughness







- **In order to provide optimum adherence for an APS TBC top coat, a surface roughness of >10 μm Ra is desirable.**

$$Z(x) = y(x) - \bar{y}$$

$$Ra = \frac{1}{n}\sum_{i=1}^{n}\left|Z_i\right|$$

Roughness of As-deposited Coatings

- Horizontal setup (TTU powder, particle loading: 10 g/L)

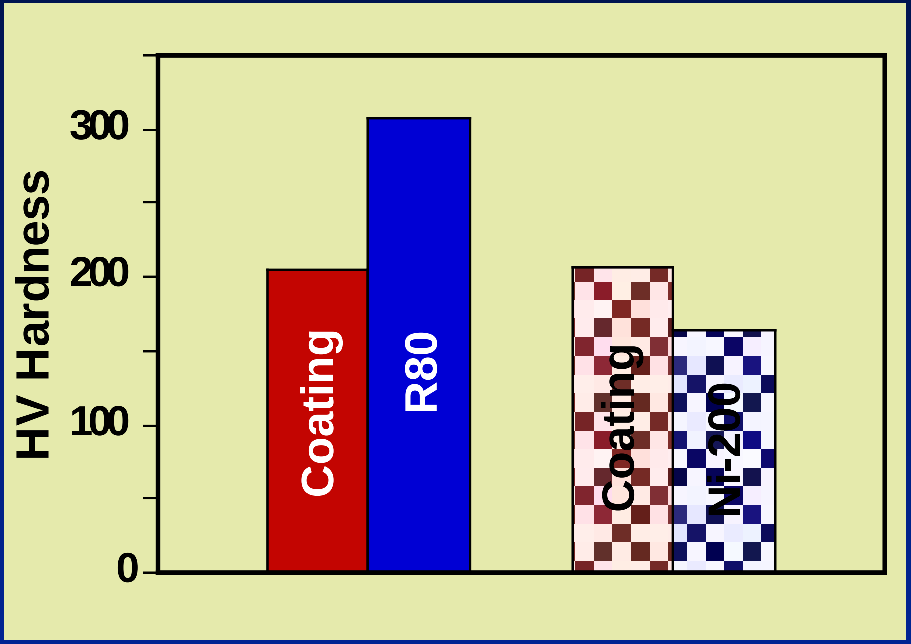
Current density (mA/cm^2)	Stirring (rpm)	Particle (vol.%)	Ra (μm)
20	80	26	6.3±0.6
60	80	20	10.3±3.9
20	300	21	3.4±1.6
60	300	32	7.4±0.6

- Barrel setup (particle loading: 20 g/L, current density: 20 mA/cm^2)

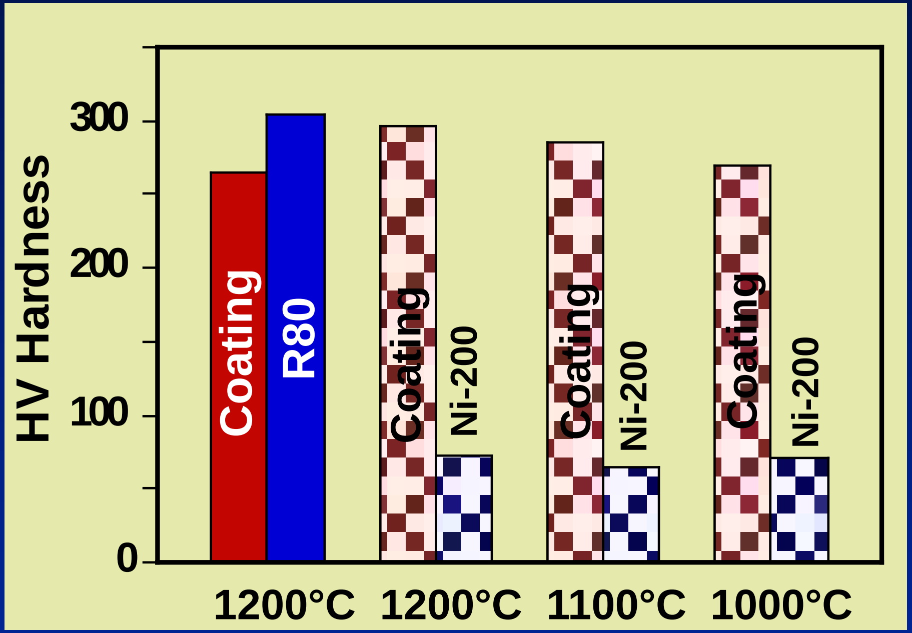
Powder	Rotating (rpm)	Particle (vol.%)	Ra (μm)
Commercial	4	54	3.6±0.4
Commercial	7	47	4.5±0.7
Commercial	10	30	3.6±0.6
TTU	4	33	6.0±1.0
TTU	7	35	4.1±0.7
TTU	10	30	2.9±0.2

Characterization of NiCrAlY Coating Hardness

- **As-deposited specimens (35-40 vol.% CrAlY in Ni)**



- **After heat treatment (2h in vacuum at 1000-1200°C)**



- **Hardness of as-deposited coating was measured in the Ni matrix**
- **Hardness is lower than thermal sprayed Ni-22Cr-10Al-1Y coating (380-530 HV).** ***(Mishra, et al., J. Tribol., 2006;)***

Future Work

- **Evaluation of Coating Performance**
  - Oxidation testing in water vapor at ORNL
  - Understanding of failure mechanism
- **Coatings for oxidation testing (1100°C, air + 10% H_2O)**

– Pack cementation NiAl
– HVOF MCrAlY
– Electro-codeposited NiCrAlY
– Electro-codeposited NiCoCrAlY (current composition)
– Electro-codeposited NiCoCrAlY (increased Cr & Co)

Summary

- A rotating barrel system was established and utilized to synthesize Ni-CrAlY & NiCo-CrAlY composite coatings with uniform particle incorporation.
  - Particle incorporation was affected by particle shape and density
  - Decreasing current density led to increased particle incorporation
  - 25-40 vol.% CrAlY particles were incorporated
- Post-deposition heat treatments were conducted in vacuum and Ar at 1000-1200°C.
  - High Cr evaporation in vacuum at ≥1100°C
  - Co and Cr contents need to be further increased
- Coating hardness and surface roughness were evaluated.
  - Electro-deposited coatings showed Ra <10μm
  - Hardness was lower than thermal sprayed coatings

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