Development of Metallic Slurry Coatings

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Outline

- **Background: Advanced materials for fossil energy applications**
- **Problem: Limitations of materials in aggressive environments**
- **Objective: Develop & fabricate low-cost protective systems**
- **Slurry processing of protective coating materials**
  - **Why coat metal systems?**
  - **Progress**
- **Research Highlights**
- **Future Research**
- **Acknowledgements**

Advanced Materials for Fossil Energy Applications

- **Temperatures up to 1550 ^{o}C**
- **Aggressive species include:**
  - **Sulfur**
  - **Nitrogen**
  - **Trace heavy metals**
  - **Alkali salts**
  - **Steam**
  - **Molten slag**
- **Protection systems will be necessary to extend lifetimes of materials in these environments**
- **The efforts in this project are aimed at developing a cost effective process for applying potentially protective coating systems**

Objectives

- **The development of low cost coatings for protection of corrosion and/or environmentally sensitive metallic substrates.**
  - **Dip coating selected as process**
  - **Work will initially focus on ferritic martensitic alloys**
  - **Aluminum diffusion in T91 for demonstration**
    - **Commercial metal systems as substrate material**
    - **Aluminum slurries (iron aluminide) as coating material**

Key Issues

- **Apply basic colloid principles developed in ceramic systems to the metallic systems**
- **Collaboration with other FE-ARM projects to ensure property relationships are addressed**

Why Coat Metallic Systems

- **Coal-fired power plant efficiency improvements requires increase in steam temperature and pressure**
- **Extensive steam side oxidation an issue for 9%Cr ferritic/martensitic alloys**
- **Aluminide coatings can significantly reduce the oxidation rate of ferritic and austenitic steels in exhaust/steam environment**

Why Coat Metallic Systems (2)

- **Potential slurry coating advantages:**
  - **Substrate alloy can be customized for properties other than corrosion resistance**
  - **Reduced processing costs**
  - **Alternative substrate processing approaches possible, i.e., lower annealing temperatures, times, etc…**
- **Challenges:**
  - **Physical, chemical and mechanical differences between substrate and coating can lead to detrimental interaction thus limiting lifetimes**
  - **Others already "dip" coating but lag in understanding underlying principles affecting substrate/coating interface on resulting property lifetimes**

Historic Coating Perspectives

Samurai Sword (Hamon-refractory clay) 800 A.D.

Flemish Medallion (enameled) 1520-1530 A.D.

Niello Armor (metal sulfides) 1550 A.D.

Present Day Coating Perspectives

- **Pint, Haynes/ORNL**
  - **CVD of model coatings on Fe-9Cr-1Mo**
- **Zhang/Tennessee Technological University**
  - **Aluminide pack cementation and CVD coatings**
- **Agüero/INTA (Spain)**
  - **Al slurry/brush coatings (commercial source) on P92, P22, P23 alloys**
- **"Commercial Sources"**
  - **Sermatech (slurry aluminizing)**

Selection of Metallic System Based on Short Term and Long Term Benefits

- **Short term – ferritic martensitic alloys:**
  - **Development efforts have improved mechanical behavior while decreasing alloy's resistance to steam oxidation**
  - **Commercial coating systems with known HT oxidation resistance have been tested on these alloys and early results are promising**
  - **Al slurries will be developed using colloidal techniques, and slurries will be applied to T91 alloy substrates**
  - **Coatings will be heat treated at varying temperatures to determine processing parameters (potential joining metal forming and coating steps)**
  - **Environmental exposure/testing and creep testing will be completed on coated alloys**
- **Long term – Austenitic Alloys & Ni-based superalloys:**
  - **Knowledge gained from the development of coatings for ferritic martensitic alloys will be applied here**

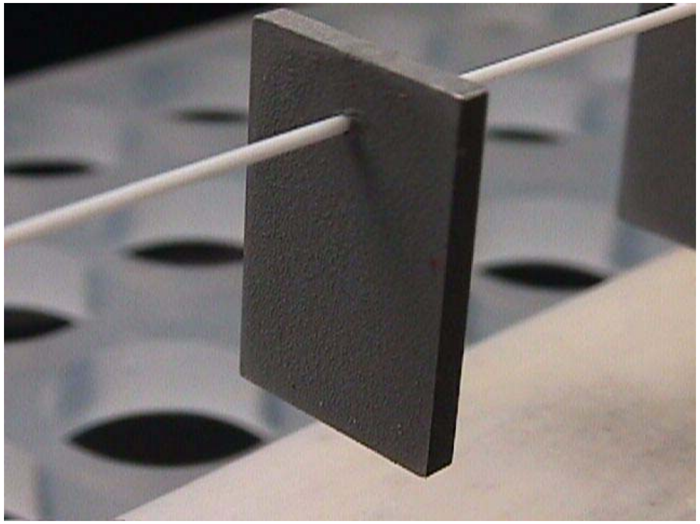
Putting Scientific Principles to Practice

- **Applied colloidal principles to develop slurry formulation**
  - **Surface Charge (stability and dispersant selection)**
  - **Rheology (flow behavior as a function of solids loadings, solvent selection and dispersant concentration)**
  - **Effect of interface wetting and interactions**
- **Evaluate processing-property relationships**
  - **Solids concentrations and processing temperatures effect upon Al diffusion or aluminide phase formation**

Where Did We Leave Off Last?

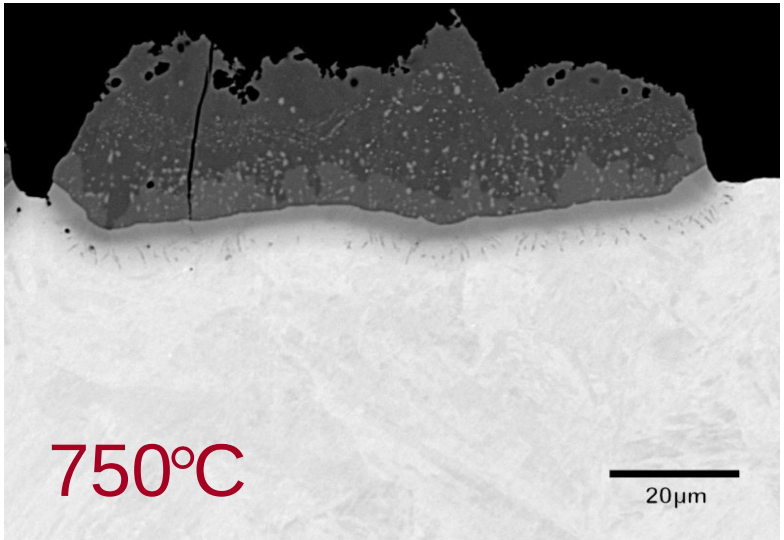
- **Aqueous coating approach was feasible**
  - **Dispersant identified**
  - **Al solids loadings identified (5 vol%)**
  - **Flow behavior established for effective dipping and coating**
  - **Wetting angle characterized as a function of processing conditions (water and solids)**
- **Sintering study completed**
  - **750°C/ 2 hours in argon formed “islands”**
  - **1050°C/ 2 hours in argon formed uniform infiltration across substrate**
  - **Large grains evident at surface of 1050°C condition**
  - **Formation of “unknown” material between diffusion zone and substrate**

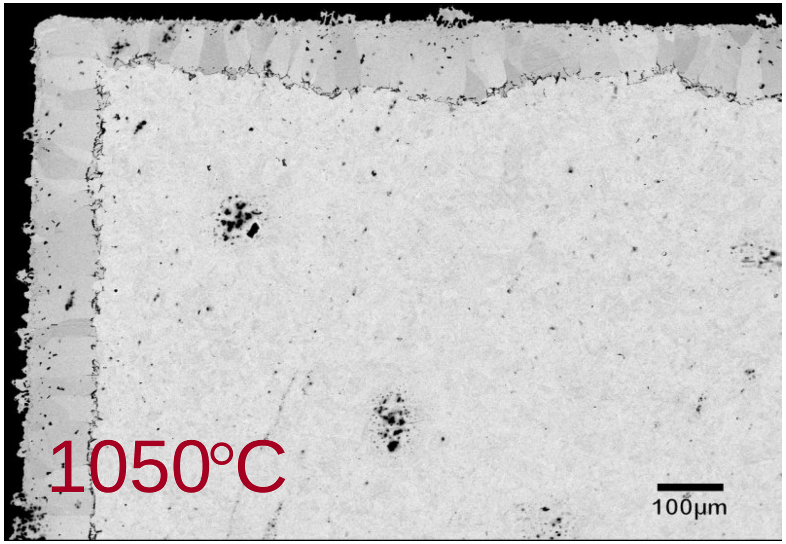
Formation of Coating is Dependent Upon Sintering Temperature



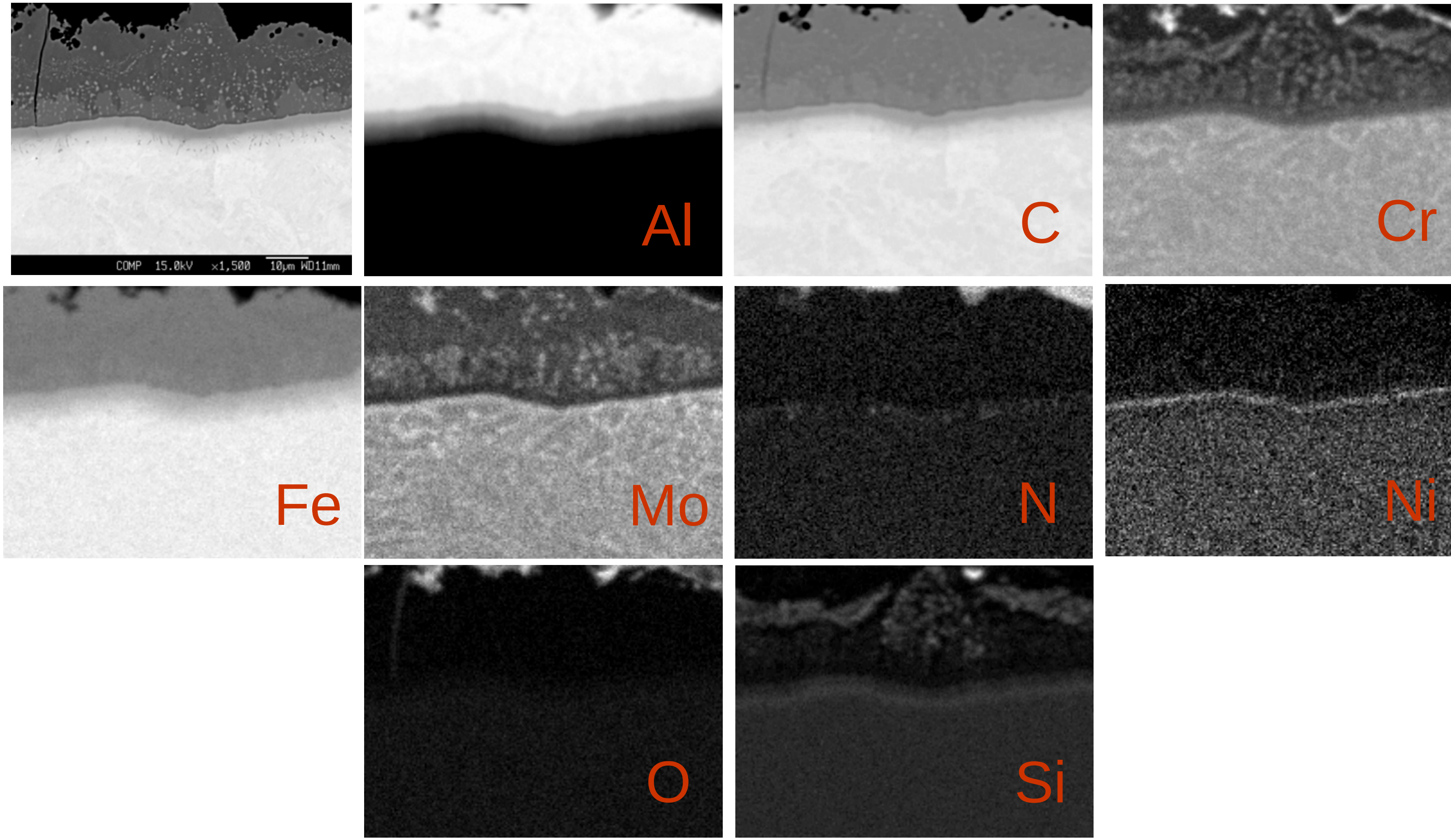
As Coated Surfaces "Uniform"

- 5% Al Aqueous Slurry on T 91 Substrate
- Sintered at temperature for 2 hours in argon



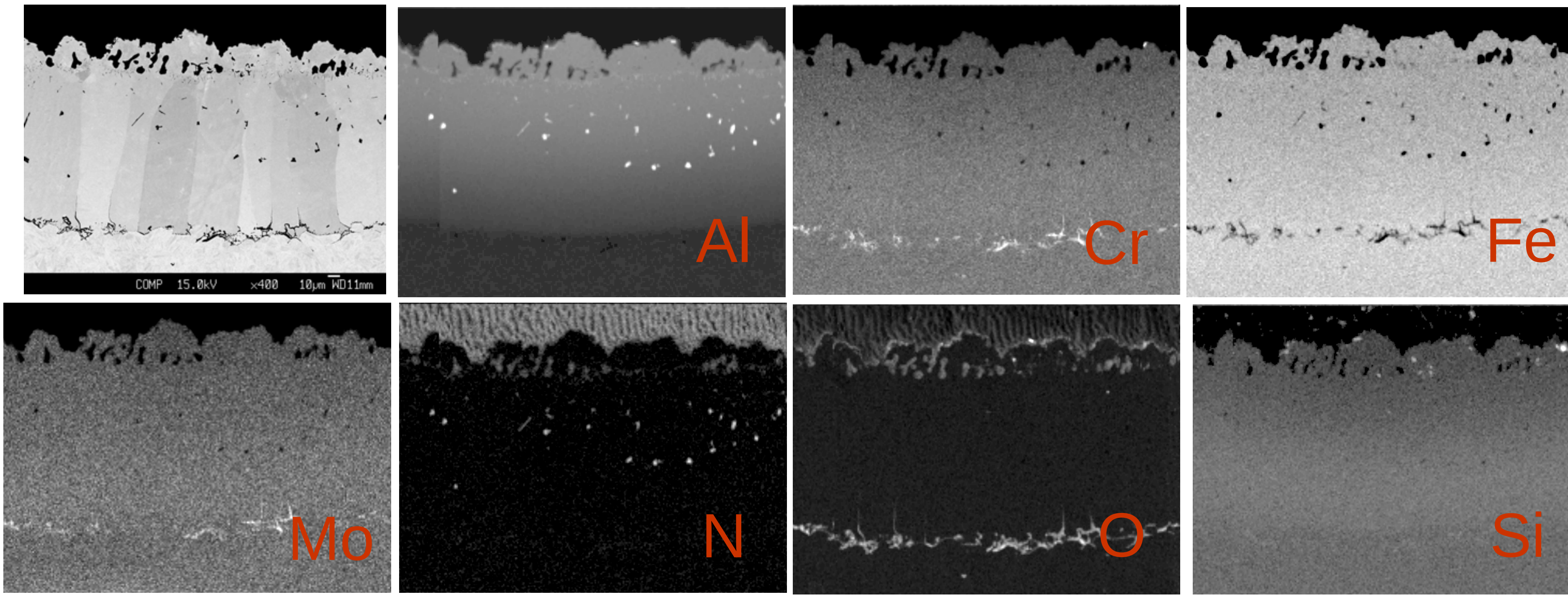


Initial Al Diffusion; Migration of Mo, N and Ni to Interface (750°C, 2 hrs/Argon)



Al Diffusion Zone More Uniform at 1050°C

(2 hrs/Argon)



- Oxygen at interface: Is it a result of an aqueous slurry or other processing variable (Al powder, contamination)?
- Should an organic slurry be evaluated?

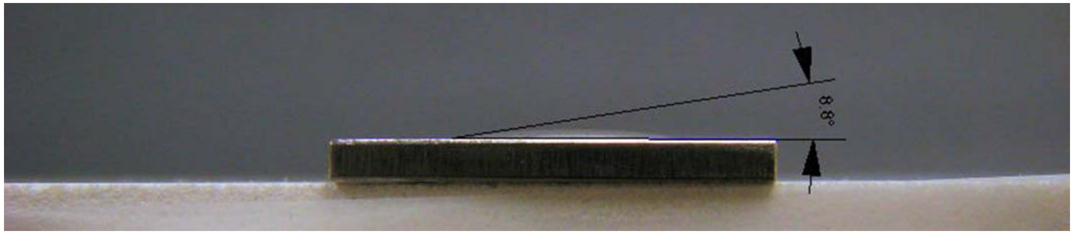
Going Green: why organic

- **No hydroxide formation at Al/alumina surfaces in solution**
  - **Potential source of oxygen at interface**
- **Higher solids loadings possible = more material/less “islands”**
  - **Al solids loadings experiments (5, 10, 20 and 25 vol%)**
  - **Flow behavior established for effective dipping and coating**
  - **Wetting angle characterized**
- **Sintering study repeated**
  - **350°C/ 2 hours in argon formed “discrete particles”**
  - **750°C/ 2 hours in argon formed more uniform infiltration across substrate; cracking evident**
  - **1050°C/ 2 hours in argon formed large grains; more defected than aqueous counterpart**

Wetting Behavior: Aqueous Vs. Organic

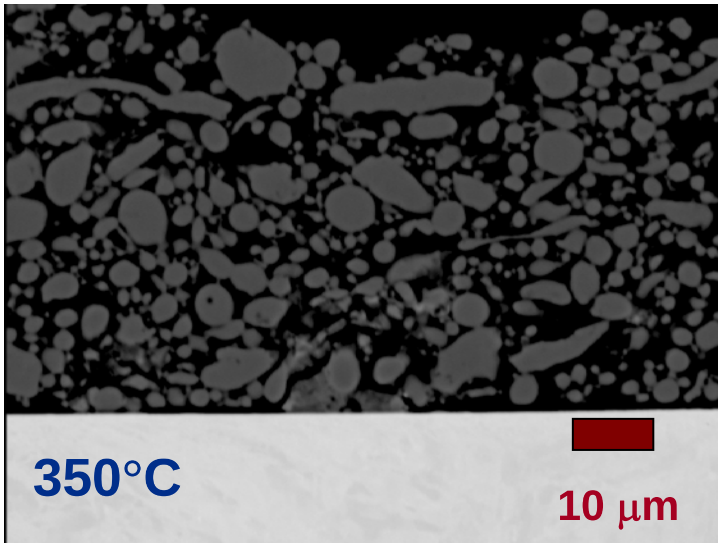
Slurry (%Al)	Contact Angle
5% – DI H_2O	33.91
5% - Organic	0
10% - Organic	~ 2-5
20% - Organic	8.8
25% - Organic	39.3

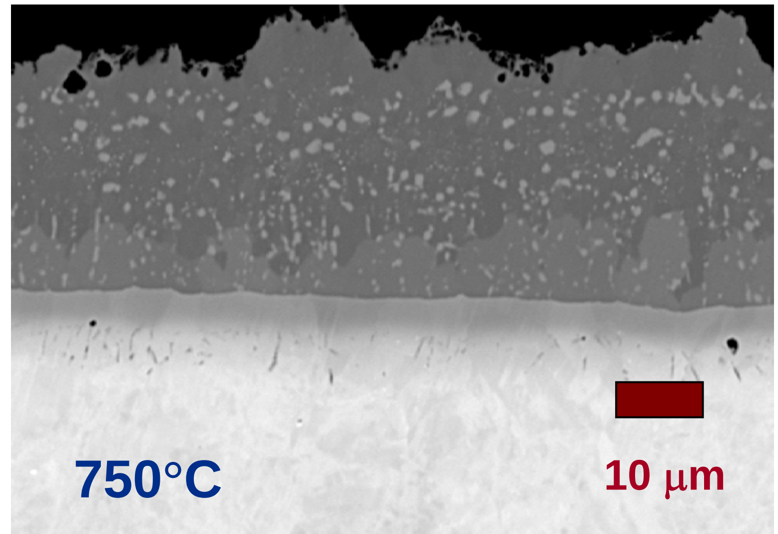
5% – DI H_2O

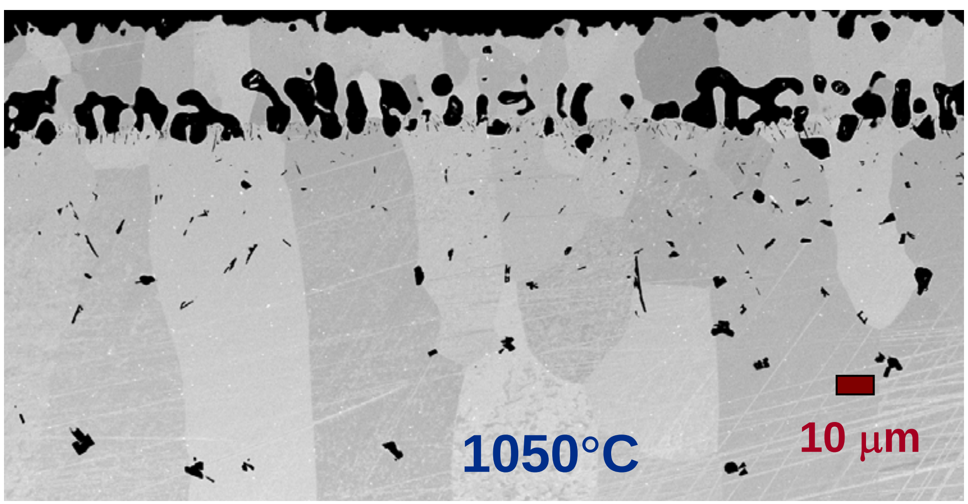


20% - Organic

Organic Al Slurry Microstructure Formation as a Function of Temperature "Similar" to Aqueous Systems at High Solids Loadings (> 20 vol% Al)

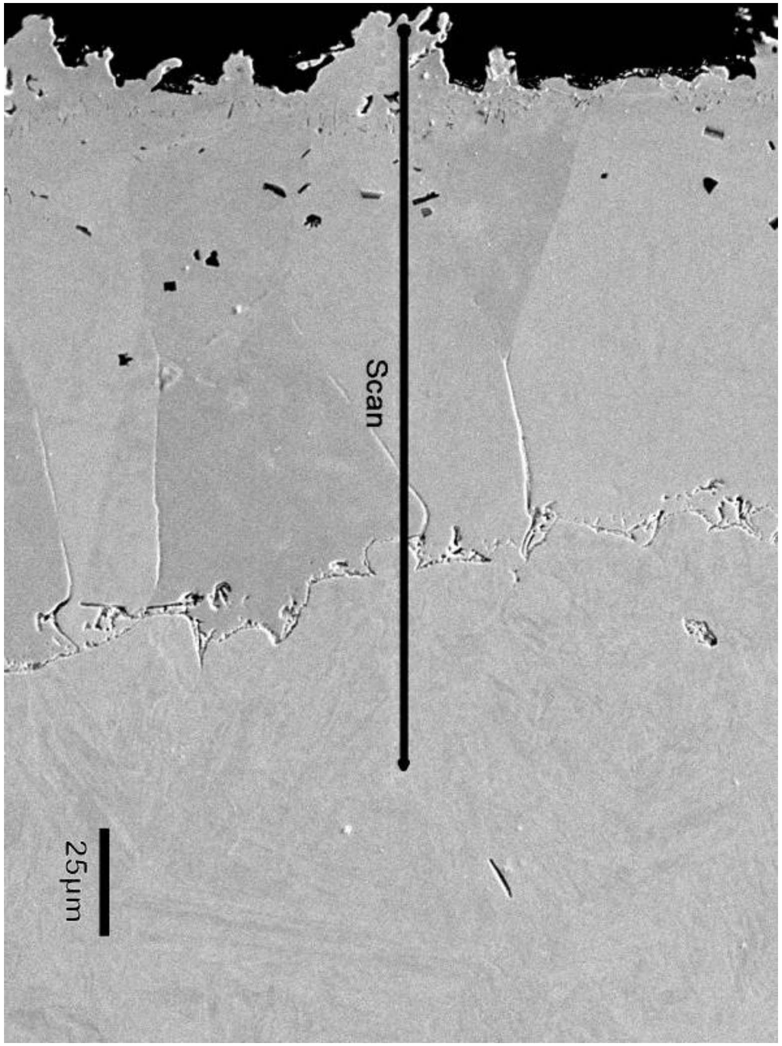


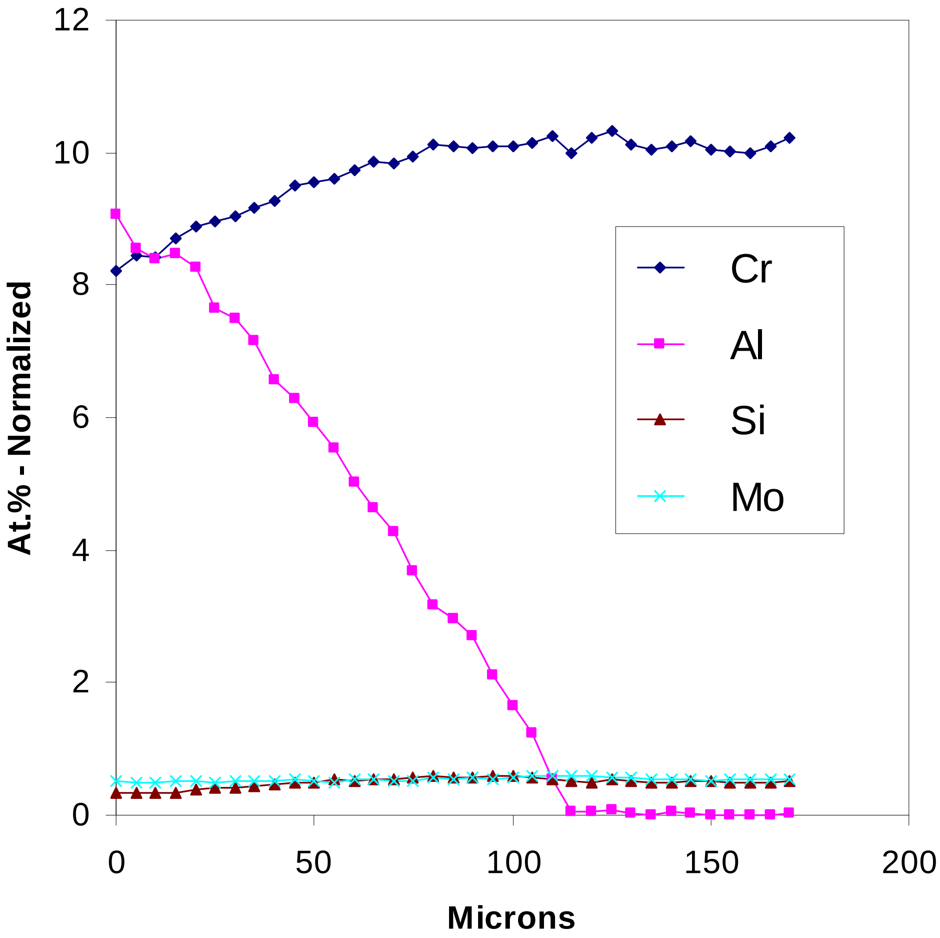




- 750°C: wetting behavior uniform at 20 vol% Al loading (ie., no islands), some cracking evident
- 1050°C: formation of porosity

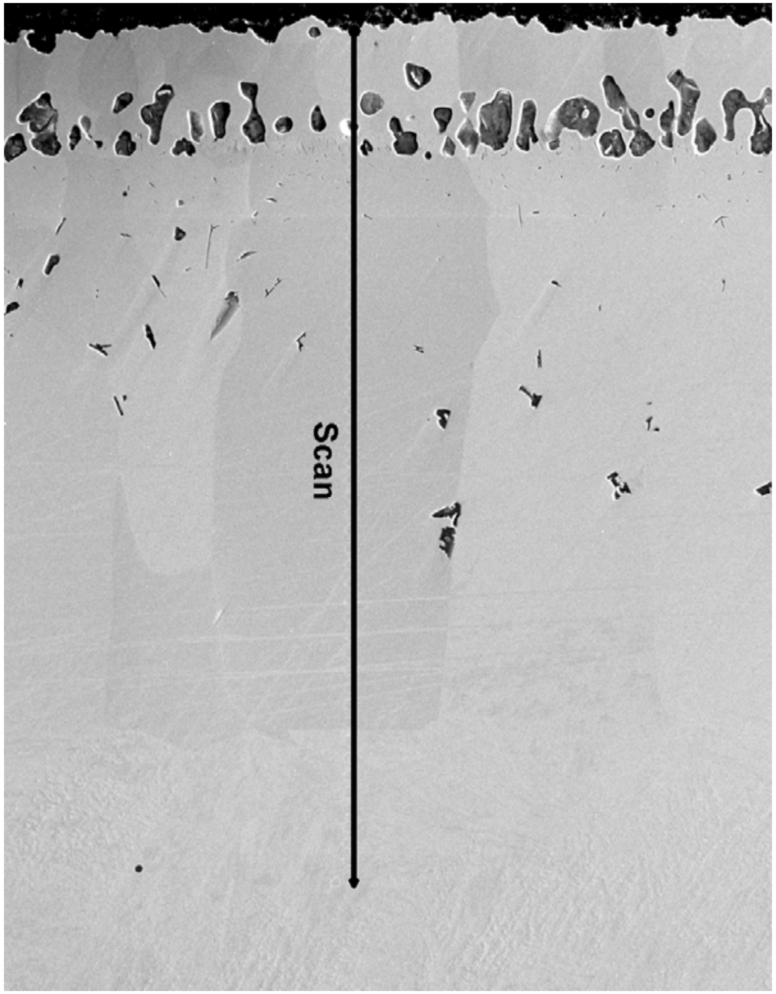
Is Adequate Al Diffusion Occurring?

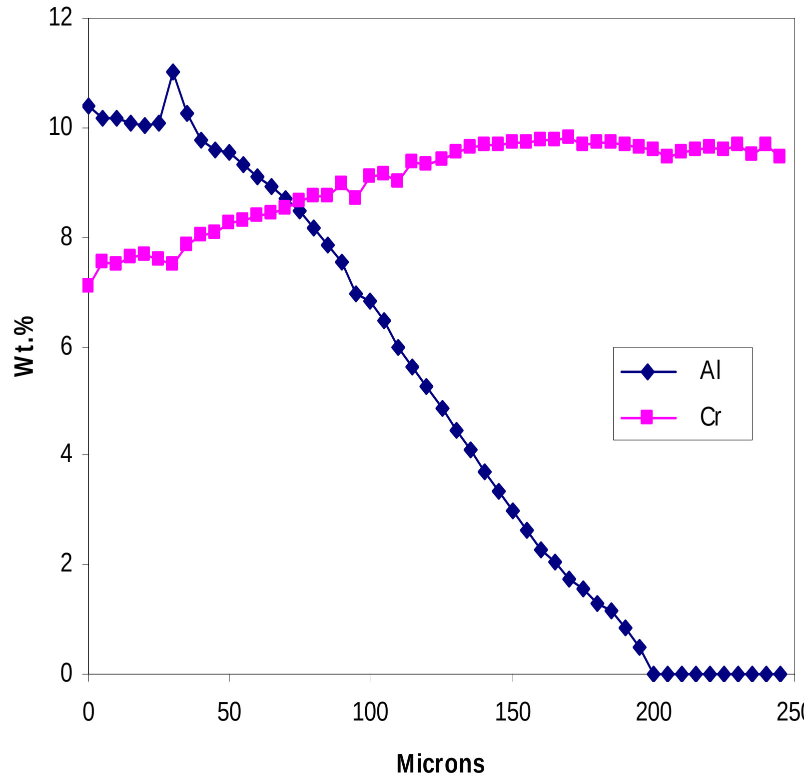




5 vol% Al solids, 1050°C/2 hr in Argon

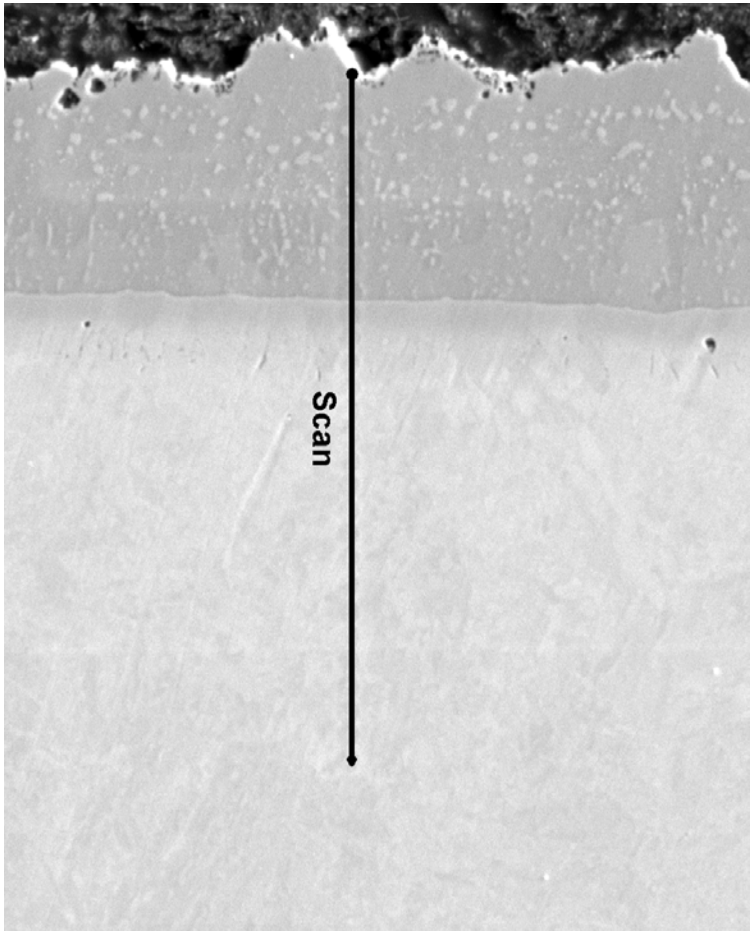
Al Diffusion Profiles Similar at 1050°C

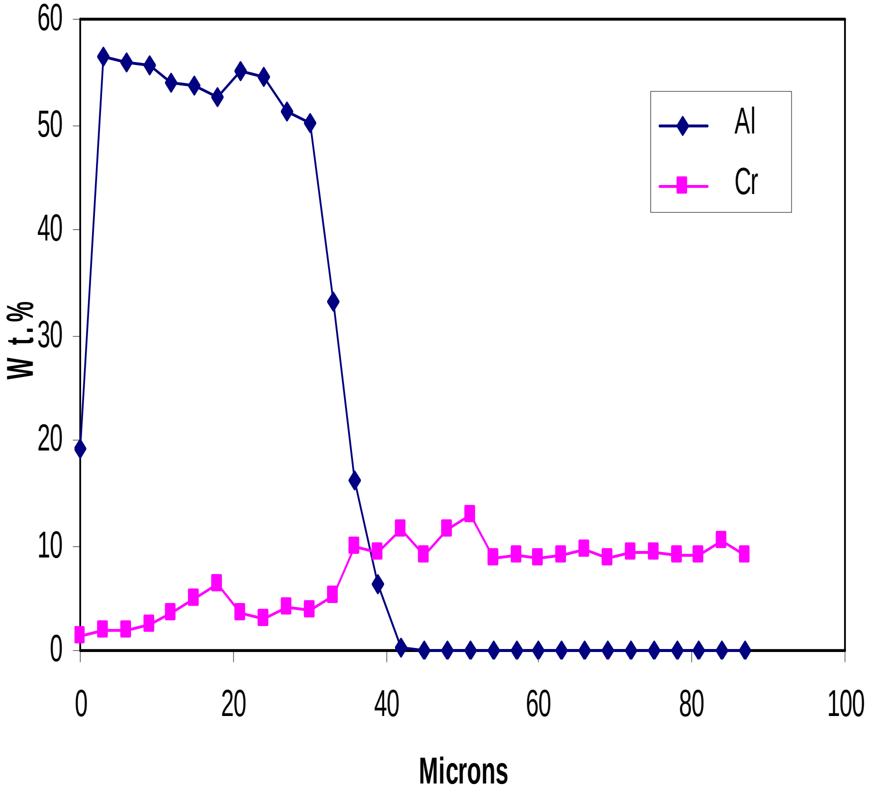




20 organic vol% Al solids, 1050°C/2 hr in Argon

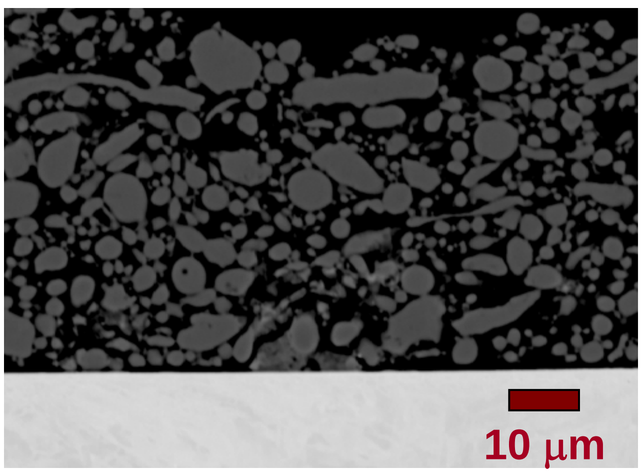
Al Concentration Higher at Lower Temp for Organic System



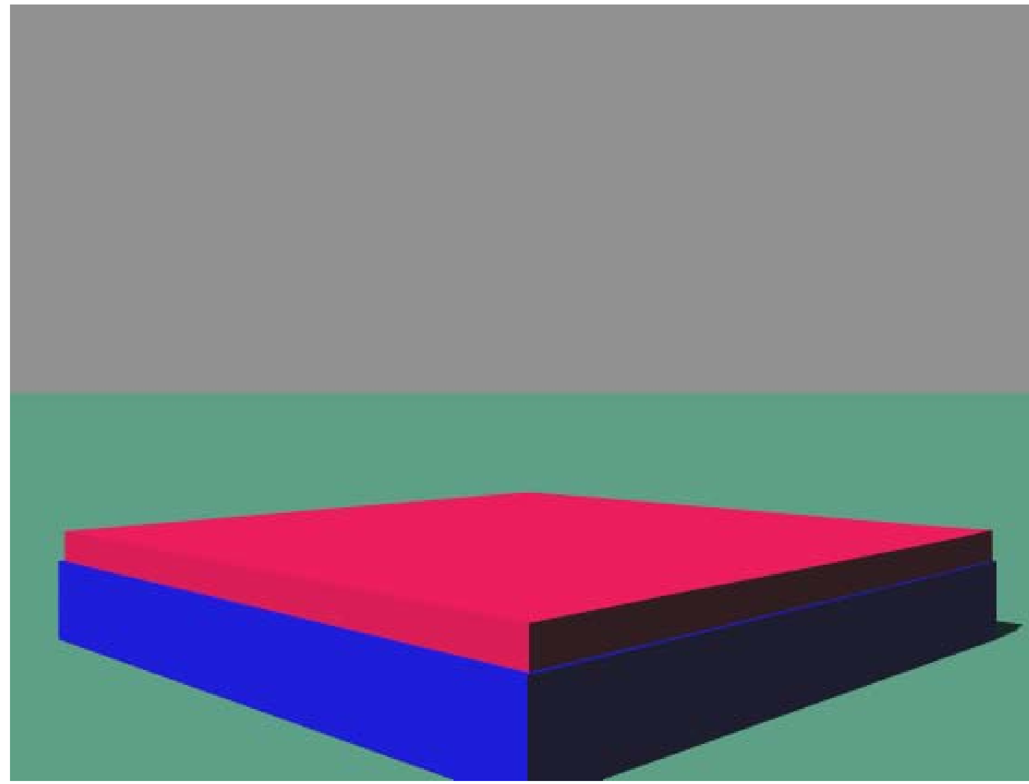


20 organic vol% Al solids, 750°C/2 hr in Argon

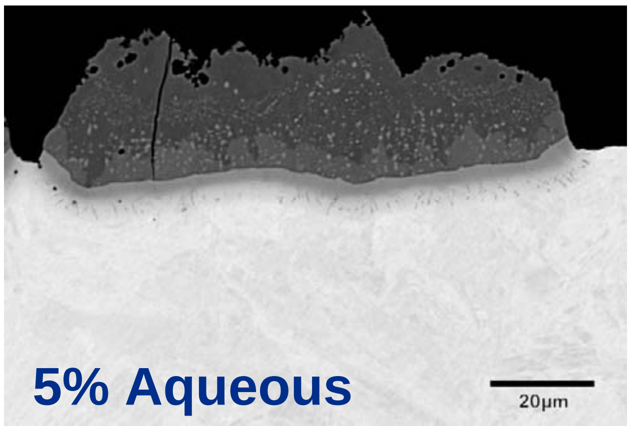
Removal of Organic Species Occurs Below Al Melt Temperature



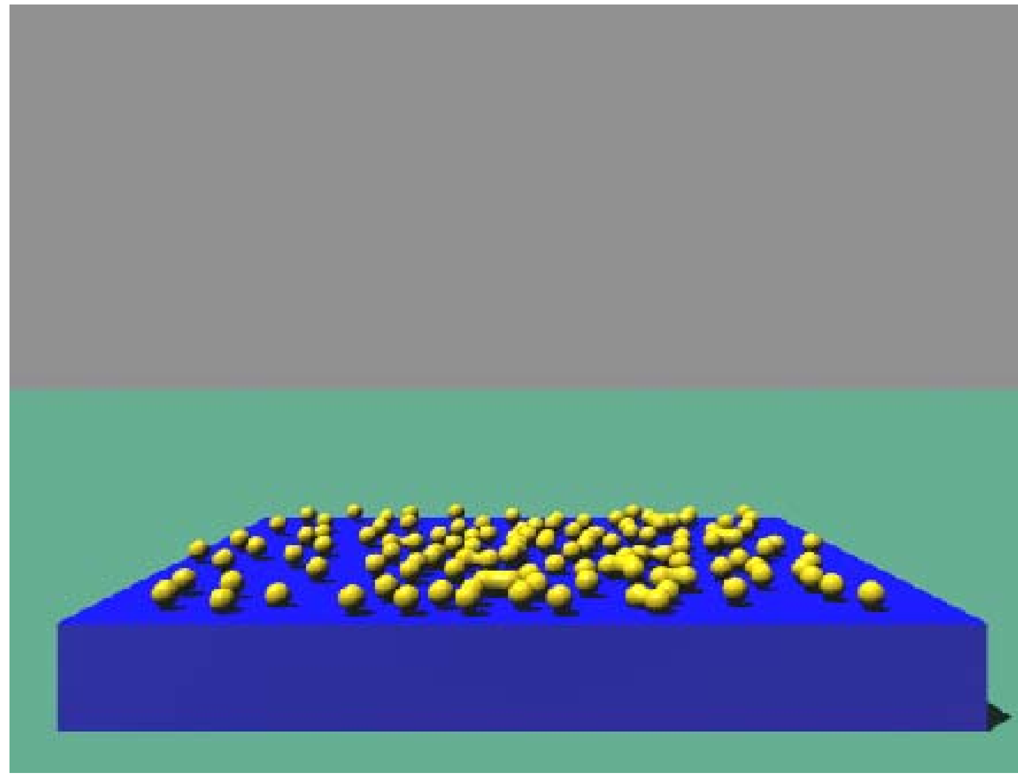
350°C/2 hours in argon



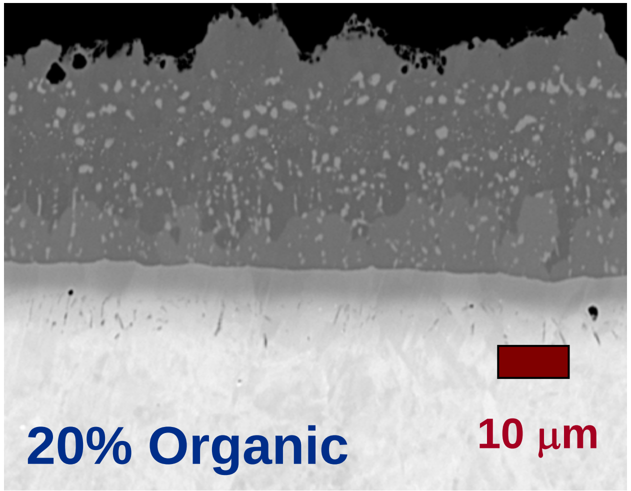
Island Formation Resulting from Wetting of Al melt at Temperature



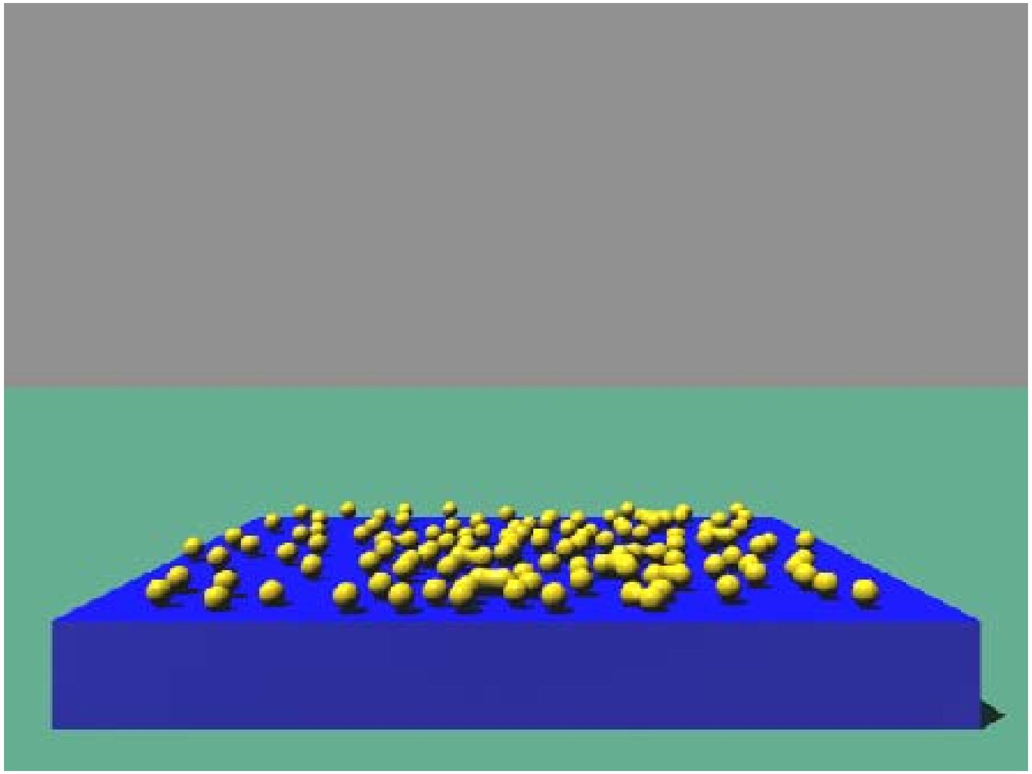
750°C/2 hours in argon



Desired Wetting Behavior Will Enable Uniform Al Diffusion



750°C/2 hours in argon



Summary of Results

- **Al slurry microstructures are dependent upon**
  - **Slurry variables (solvent, solids loading, wetting)**
  - **Sintering conditions (temperature)**
- **Organic Al slurries optimized for higher solids loadings and improved wetting at room temperature**
- **Improved Al diffusion is feasible with processing controls**

Future Work

- **Evaluation of slurry coating and process efficacy of metallic-based systems**
  - **Refine Al diffusion profiles in slurry systems to meet model predictions and CVD results**
  - **Test in simulated fossil environments**
- **Environmental and mechanical testing to obtain confirmation of performance and feedback**
- **Coordinate effort with metals/corrosion/oxidation projects to maintain relevancy**

Acknowledgements

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Questions?

Previous Ceramic Accomplishments

• **Demonstrated feasibility and flexibility of process**
• **Established "generic" process parameters**
• **Reduced sintering temperatures to minimize damage to substrate**

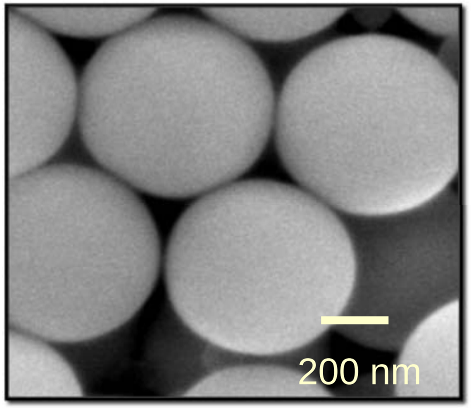
Rare earth silicate coating on a complex-shaped component (NT154 Si_3N_4 Blade)

- **The process is flexible, i.e., it can be modified to incorporate a wide range of ceramic particles (e.g., mullite, BSAS, zirconia, rare-earth silicates and disilicates, aluminates, and aluminosilicates) and solvents (e.g., aqueous and organic)**
  - **Complex-shaped components to be coated are dipped into a slurry (ceramic particles suspended in a solvent medium).**
  - **As-dipped coatings are dried and heat treated at elevated temperatures to promote densification**
  - **Can be used as a patch for damaged coatings**
  - **Resultant coating quality depends upon slurry rheology and wetting behavior**

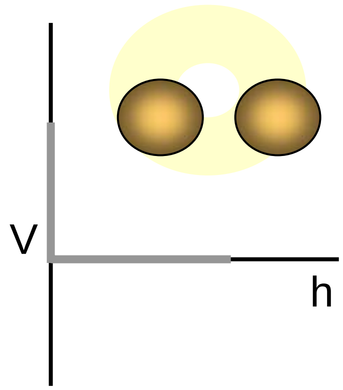
Tailoring Interactions Between Colloidal Building Blocks

Colloidal particles --> basic "building blocks"

- **must control interparticle forces to tailor structure, rheological properties, and drying**

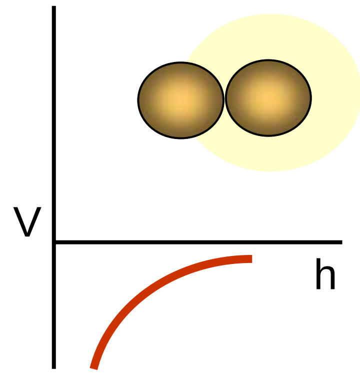


Hard sphere



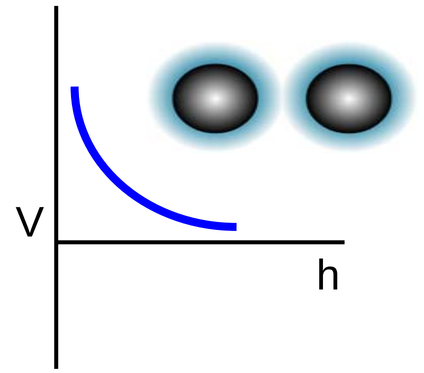
indexed matched
highly screened

Attractive



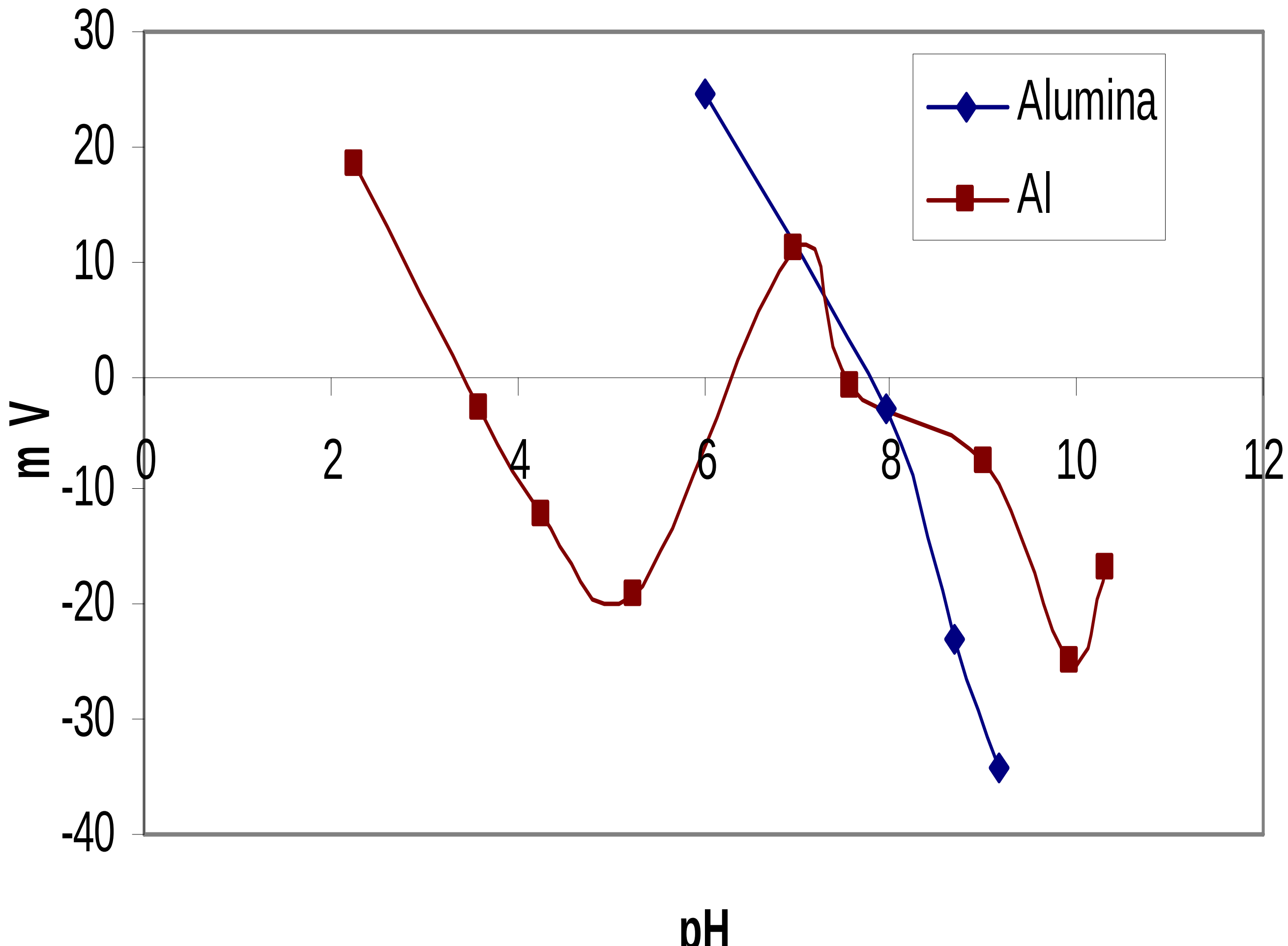
VdW forces
depletion forces

Soft Sphere



steric-stabilized
charge-stabilized

Can An Aqueous Solvent Be Utilized?



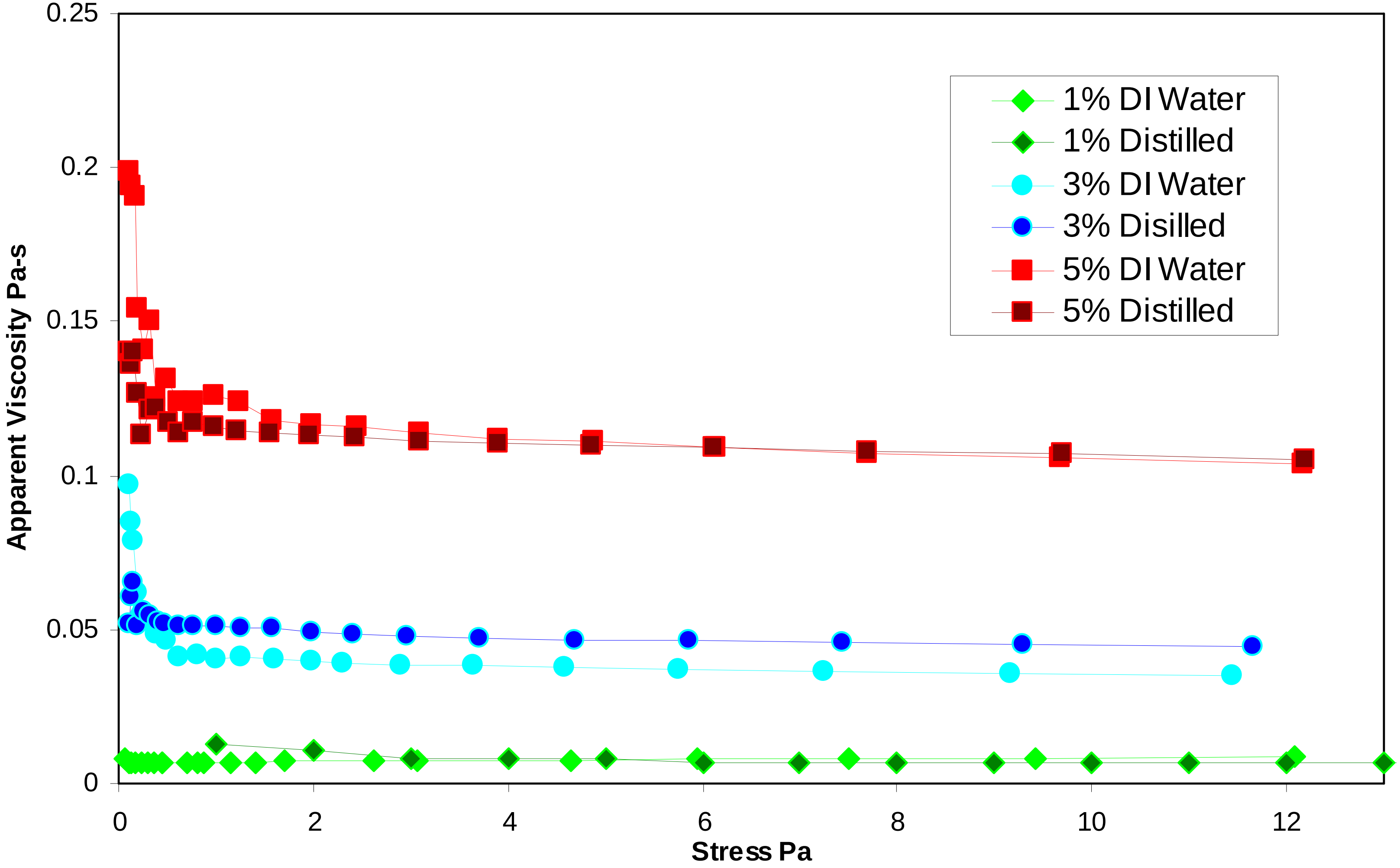
$Al + 2H_2O =$
$AlO_2^- + 4H^+ + 3e^-$

$Al_2O_3 + H_2O =$
$2AlO_2^- + 2H^+$

$M^{x+} \rightarrow M(OH)_{x\ (s)}$
$M2(CO3)_{x\ (s)}$

Polyacrylic acid is a potential dispersant

Viscosity Increases With Increasing Al Content

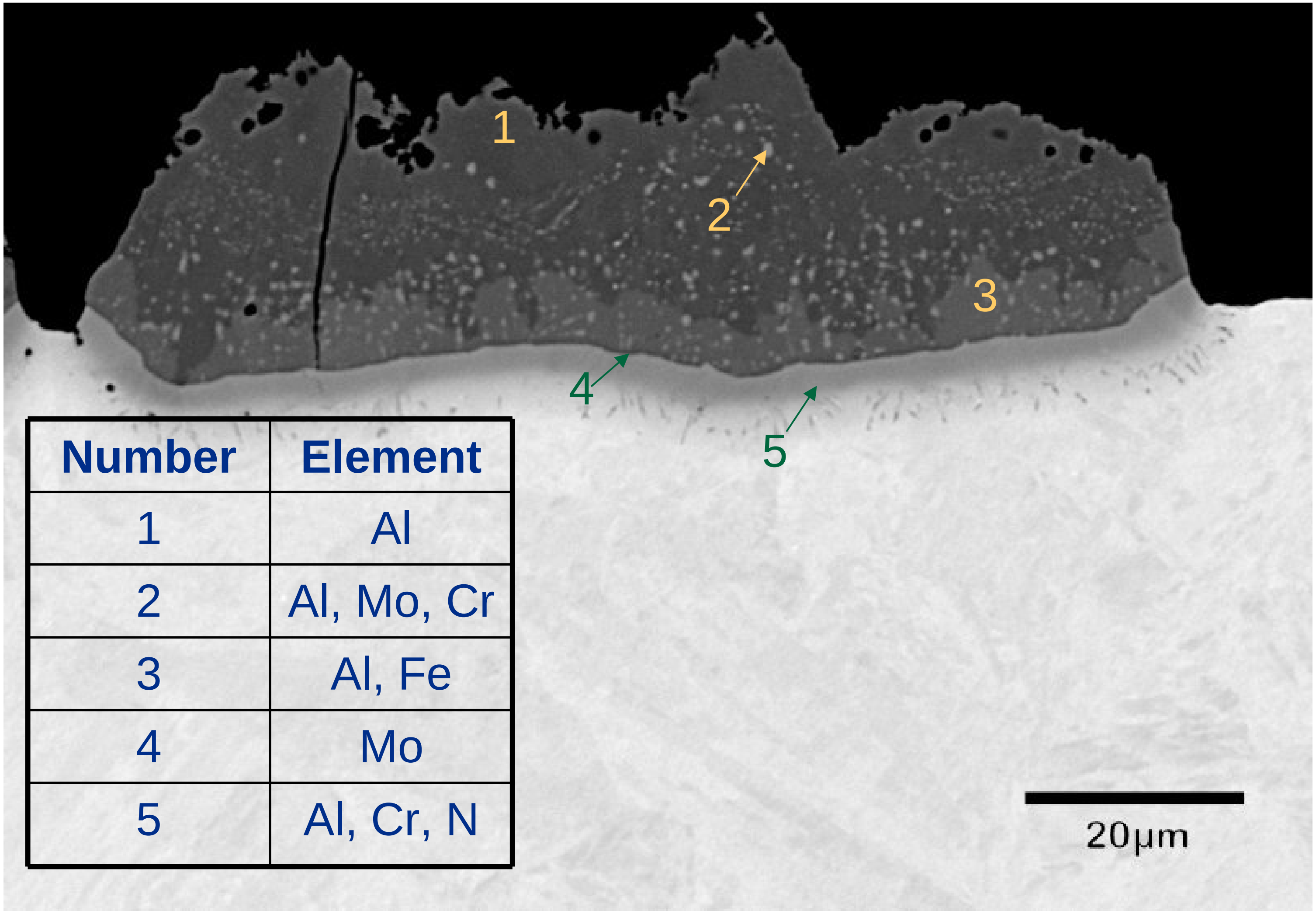


Al Solids and Contamination Can Alter Wetting Behavior of Slurry

Slurry (%Al)	Contact Angle
1% – DI H_2O	25.21
1% – Dist H_2O	41.52
5% – DI H_2O	33.91
5% – Dist H_2O	57.39

Al slurry droplet on T91 substrate

Elemental Diffusion Occurring at 750°C (2 hrs/Argon)



Number	Element
1	Al
2	Al, Mo, Cr
3	Al, Fe
4	Mo
5	Al, Cr, N