Thrust 3: Localized Property Enhancement for Cast Magnesium Alloys

Thrust Lead: Vineet V. Joshi

Project Leads: Michael Brady,

Jiheon (Jay) Jun, Mageshwari Komarasamy

DOE-VTO AMR 2021

Project ID # MAT-234

LMCP Overview

Timeline

- Lab Call Award – September 2020
- Kickoff – November 2020
- End – September 2023
- 5% Percent complete

Budget

- Total project funding $15M/3 years
- Funding for FY 2021 - $5M

Lightweight Metals Core Program Overview			
	Title	**# of Projects**	**FY21**
Thrust 1	Selective Processing of Aluminum Sheet Materials	3	$1,300,000
Thrust 2	Selective Processing of Aluminum Castings	3	$1,450,000
Thrust 3	Selective Processing of Magnesium Castings	2	$1,100,000
Thrust 4	Crosscutting Thrust - Characterization, Modeling and Lifecycle	7	$1,150,000

Barriers and Technical Targets

- Materials Performance and Cost limit the penetration of lightweight Al and Mg alloys into the entire range of vehicle
- New Alloy development is slow and costly
- Recyclability is complex due to large number of different alloys

Partners

- Program Lead
  - Pacific Northwest National Laboratory
- Partner Laboratories
  - Oak Ridge National Laboratory
  - Argonne National Laboratory
- Industry Engagement
  - Informal support and guidance from OEMS and Tier 1 suppliers
  - CRADAs planned for future years

Thrust 3 Overview

Timeline and Budget

- Project start: Oct 2020
- Project end: Sep 2023
- Percent complete: 5%
- **Thrust 3 Budget**
  - **FY21: $1,100k**

Barriers and Technical Targets

- Magnesium cast parts offer excellent opportunities for vehicle lightweighting, reduced part and alloy count, and lowered assembly costs.
- Science and engineering challenges inherent to Mg cast materials: low ductility, low fatigue performance in stressed members, and corrosion

- **Technical Target: a suite of low-cost, advanced manufacturing processes that can improve the local properties of castings and allow higher performance, lighter weight and potentially enable lower cost and fewer alloys in the glider to simplify the supply chain and recycle path.**

Thrust 3. Localized Property Enhancements for Cast Structural Aluminum Applications

Project	Title	FY21
3A1	Cast magnesium alloy surface modifications to improve the corrosion performance- Reactive Processes (ORNL)	$450k*
3A2	Cast magnesium alloy surface modifications to improve the corrosion performance- Surface Alloying (PNNL)	$350k
3B	Local Thermomechanical Property Modification of Magnesium Castings via Solid-Phase Processing techniques (PNNL)	$300k
	Thrust Totals	$1,100k

*Funding received in Feb'21

Partners

- Program Lead Lab
  - Pacific Northwest National Lab (PNNL)

- Thrust 3 Participating Labs
  - Pacific Northwest National Lab (PNNL)
  - Oak Ridge National Laboratory (ORNL)
  - Argonne National Laboratory (ANL)

- Thrust 3 Collaborators
  - Applied Research Laboratory – Pennsylvania State University
  - Volunteer Aerospace

Relevance

Objective

- Perform selective processing to enhance corrosion resistance and improve the local mechanical properties to address shortcomings of typical commercial magnesium alloy castings
- This thrust will bring together PNNL, ORNL, and ANL to develop scalable and cost-effective processing methods to locally enhance the properties of cast magnesium to enable broader implementation of lightweight alloys in vehicles.

Impact

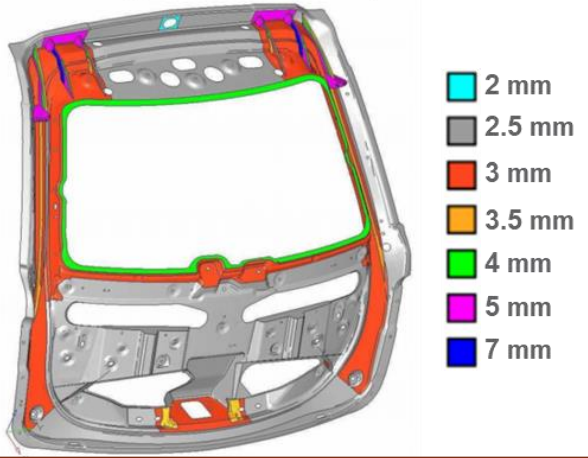
- Improved corrosion resistance and mechanical properties will aid in the more widespread adoption of Mg components to achieve vehicle light weighting goals

Thrust 3 Motivation: Localized Property Enhancements for Cast Magnesium

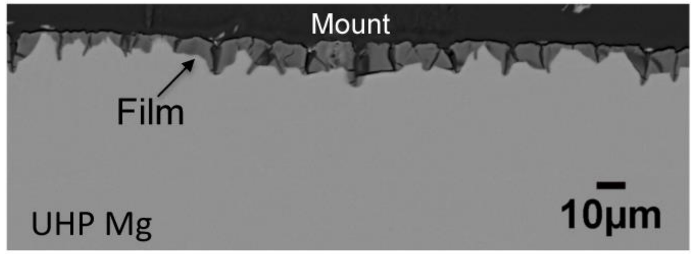
- Large magnesium cast parts offer excellent opportunities for vehicle lightweighting, reduced part counts and lowered assembly costs
- Over 90% of Mg cast components are manufactured via high-pressure die casting process.
- Fast, economical, and produces complex Mg components

- **Scientific and Engineering Challenges of integrating Mg castings into the BIW :**
  - Corrosion (general, macro and micro-galvanic)
  - Low ductility
  - Porosity
  - Fatigue in stressed members

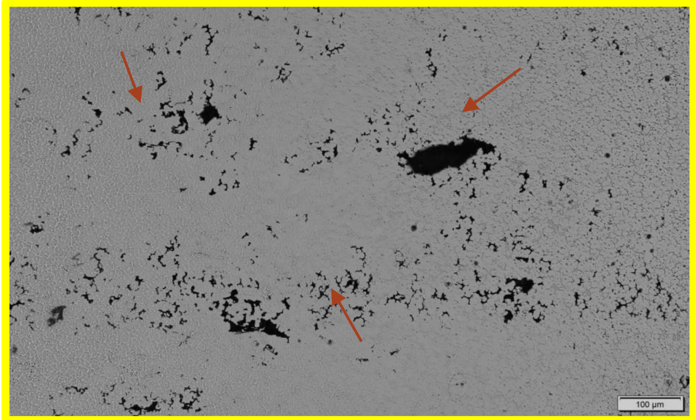
Cast magnesium inner panel-Meridian[1]



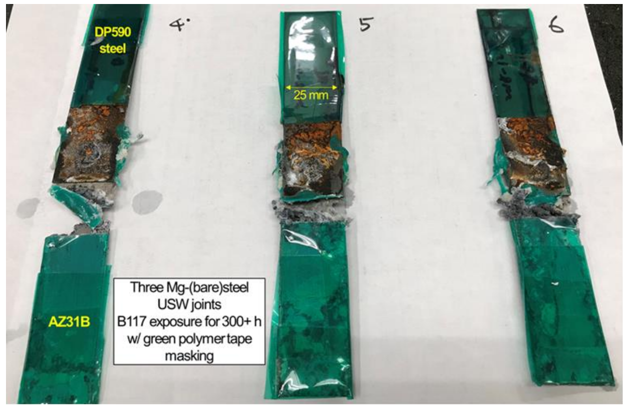
Cross-Section Showing Non-Protective Mg-O-H Scale Formed in Water



Porosity in Mg Castings



Galvanic Corrosion in Mg-Steel Joints



Overcoming the key issues in Mg high-pressure die castings (HPDC) via localized property modifications to enable the increased use of Mg cast components in high strength and durable applications to meet the weight reduction goal.

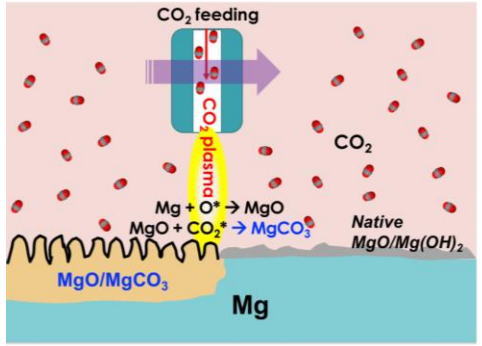
[1]https://www.amm.com/events/download.ashx/document/speaker/7981/a0ID000000X0kJUMAZ/Presentation
[2]https://icme.hpc.msstate.edu/mediawiki/index.php/Failure_Analysis_of_an_AZ91_Automotive_Shock_Tower.html

Approach: Improving the Local Corrosion and Mechanical Properties of Cast Magnesium Alloys

Project 3A

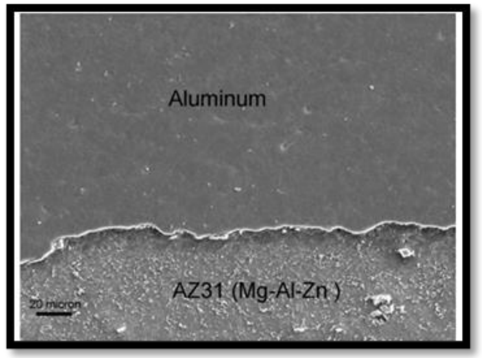
Cast magnesium alloy surface modifications to improve the corrosion performance

Reactive Processes (ORNL)



- Leverage CO_2 affinity of Mg-O to form Mg-C-O
- Leverage greater stability of AlN vs Mg_3N_2 or higher vapor pressure of Mg vs Al to enrich surface in Al
- Laser, atmospheric plasma, wet/dry thermal process

Surface Alloying (PNNL)



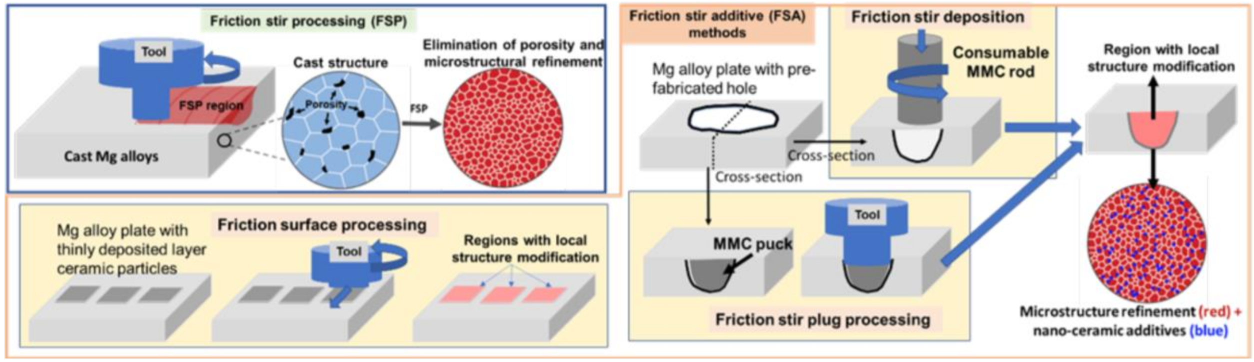
- **Cold spray:** Al, Cr, Ti, Zn, ceramics to electrically isolate
- **Additive Manufact.:** Al, Zn, low Tm glass to electrically isolate
- **Surface Alloying:** To enhance Al/Zn coating adherence for better compatibility with Al/steel coating processing

Surface and Coatings Technology Volume 309, 15 January 2017, Pages 423-435

Project Integration

Project 3B

Local Thermomechanical Property Modification of Magnesium Castings via Solid-Phase Processing techniques (PNNL)



- **Friction stir processing:** Surface and volumetric modification of AZ and AM alloys
- **Friction stir additive:** Local alloying with high strength non-RE Mg cast alloys
- **Friction stir additive:** Addition of nanometer and micrometer-sized non-metallic reinforcements

Supported by Ab-Initio Calculations and Advanced Characterization (Supported by Thrust 4)

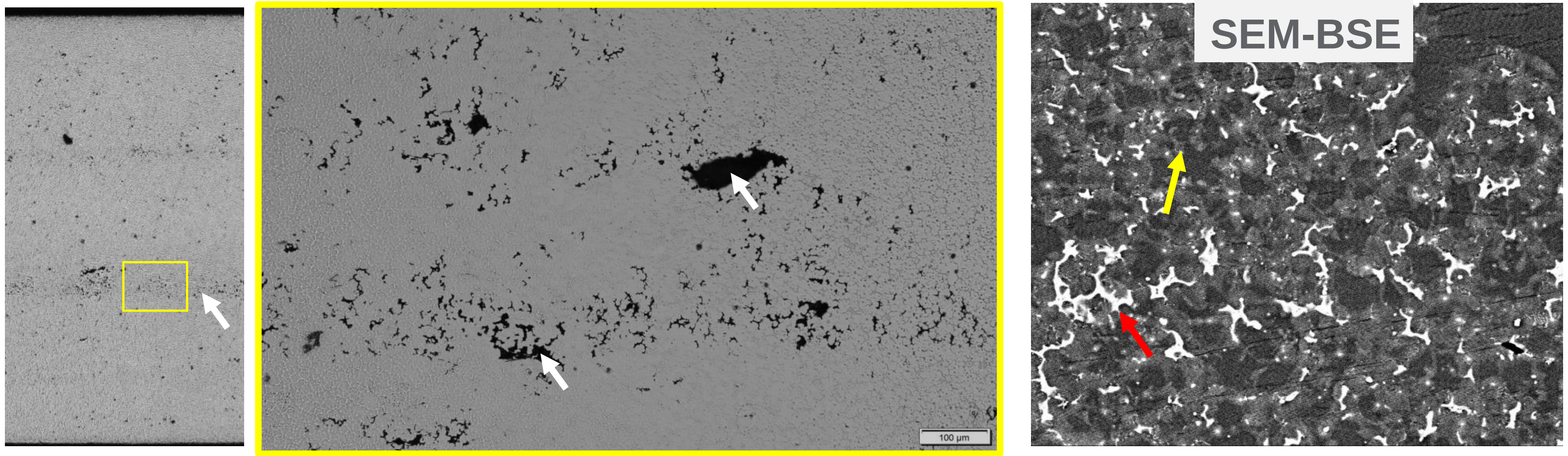
Milestones

Due Date	Project	Milestone	Status
Dec 2020	3	Thrust 3 Planning and Kickoff: PNNL will host a planning and kickoff meeting between all members of the LMCP and VTO stakeholders, to review scope, schedule, budget, management structure, and expectations.	☑
		Procure HPDC AZ91 and AM60 alloys	☑
Mar 2020	3A1	Complete first iteration of at least one reactive surface process and/or one surface alloying process for at least one cast Mg alloy	*
	3A2	Cast magnesium alloy surface modifications to improve the corrosion Performance: Complete one surface alloying process on as-cast magnesium surface	☑
Jun 2021	3A1	Complete corrosion characterization of at least one iteration of reactive surface process and one surface alloying process for at least one cast Mg alloy	*
	3A2	Cast magnesium alloy surface modifications to improve the corrosion Performance: Characterize and electrochemical properties measurement of the surface modified magnesium casting	
Sept 2021	3A	Complete surface and corrosion characterization for at least two reactive surface and/or surface alloying approaches	
	3B	Effect of FSP on fatigue: PNNL will demonstrate that FSP can refine microstructure (breaking-up of particles, reduced particles aspect ratio, and grain refinement) and can lead to improvement in fatigue lifetime. Stress-controlled fatigue tests will be carried out in the as-cast and friction stir processed conditions.	

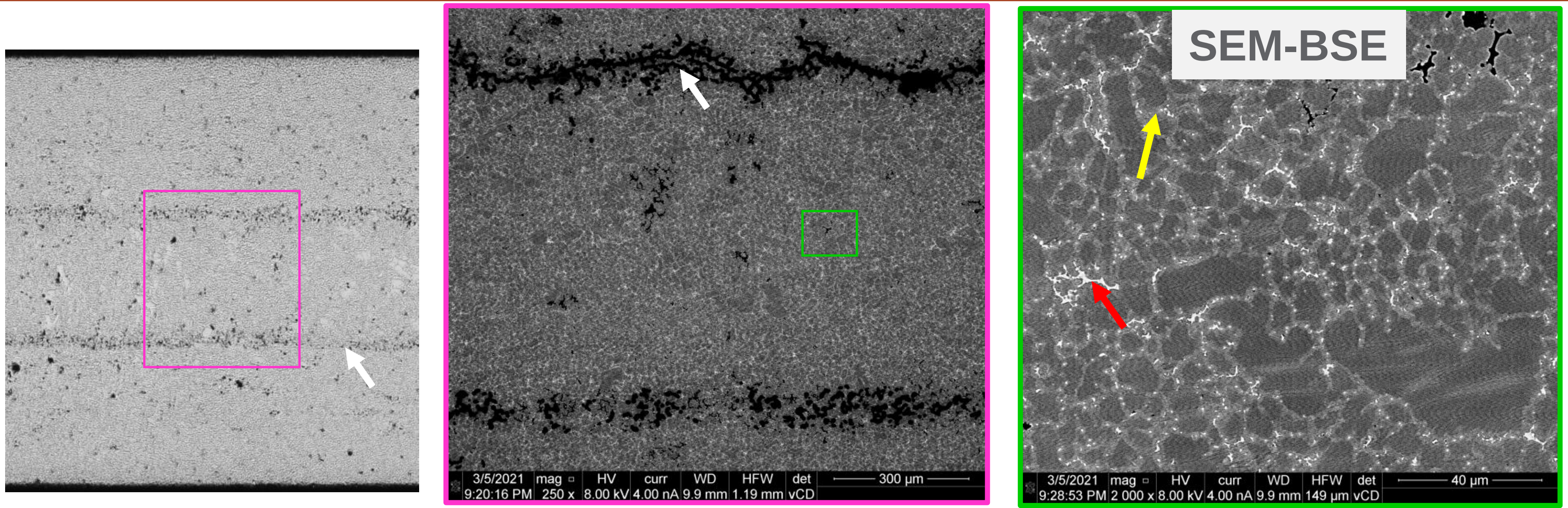
* Activity delayed as the funding was received in Feb’21

Accomplishments: Baseline Casting Microstructure and Hardness analysis

AZ91



AM60



- Porosity is observed in both AZ91 and AM60 high pressure die cast plates (marked by white arrows).
- AM60 exhibited significantly larger porosity fraction as compared to AZ91.
- Furthermore, both $Mg_{17}Al_{12}$ (β phase, marked by red arrows) and Al-Zn solute segregation (marked by yellow arrows) were noted in the Mg-Al matrix.

Hardness mapping of the HPDC plates resulted in acceptable variation.

	Microhardness(HV0.2)
AZ91	74±5
AM60	59±6

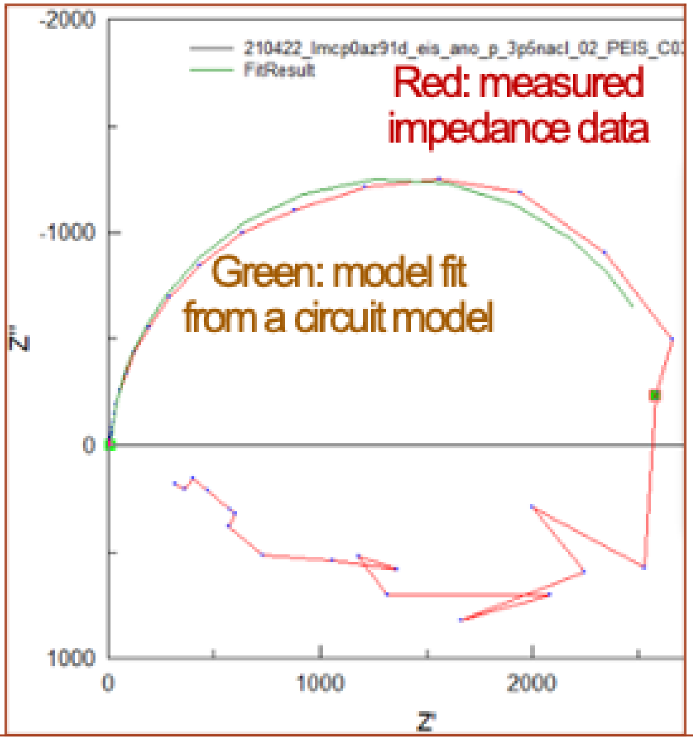
Accomplishments: (Project 3A1): Completed electrochemical Property Measurements of untreated AZ91D- Baseline Studies

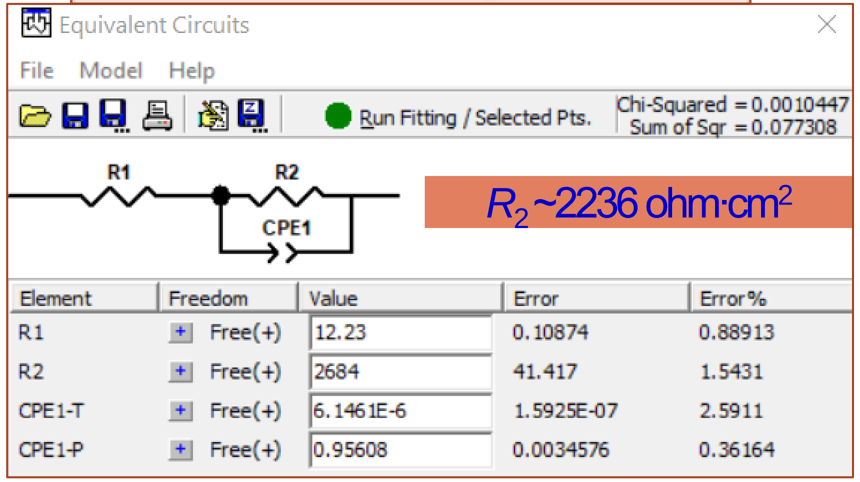
EIS measurement details

- 600-grit finished Al7075-T6 w/ 0.83 cm^2 surface area
- 3.5 wt.% NaCl at RT, open to air
- Open circuit potential (OCP) delay for 40 min
- Amplitude ±10 mV with respect to OCP
- Frequency range: 200kHz to 15 mHz
- Pt wire counter electrode & reference saturated calomel electrode (SCE)

Impedance data fitting to determine R_2

AZ91D (0.833 cm^2) Nyquist plots



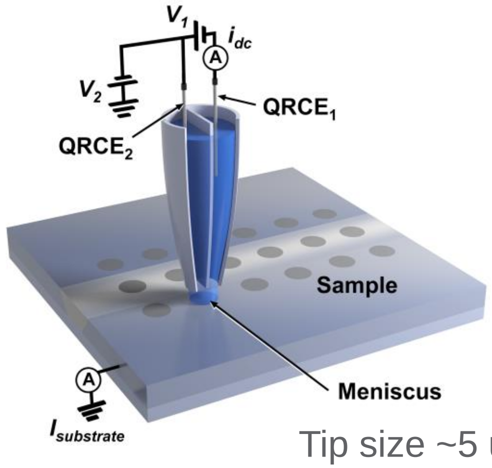


3 individual R_2 (ohm·cm^2) & Avg. from uncoated AZ91D in 3.5 wt.%	
ORNL data	2640
	2995
	2236
	(Avg.) 2624

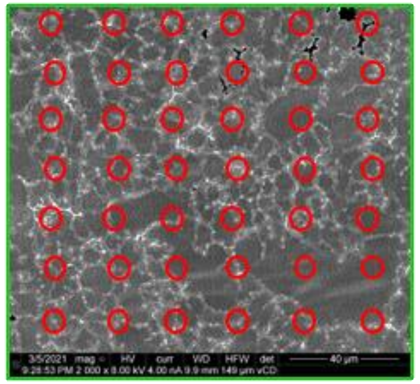
Baseline corrosion data is consistent with AZ91D literature

Accomplishment (Project 3A2): Determining the Local Electrochemical Properties of AM60 and AZ91- Baseline Studies

Scanning Electrochemical Cell Microscopy (SECCM)

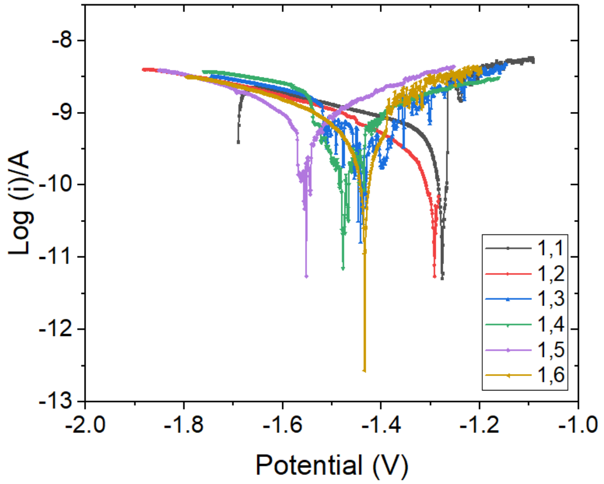


Tip size ~5 um
Electrolyte: 0.01 M NaCl
Electrode: Ag/AgCl

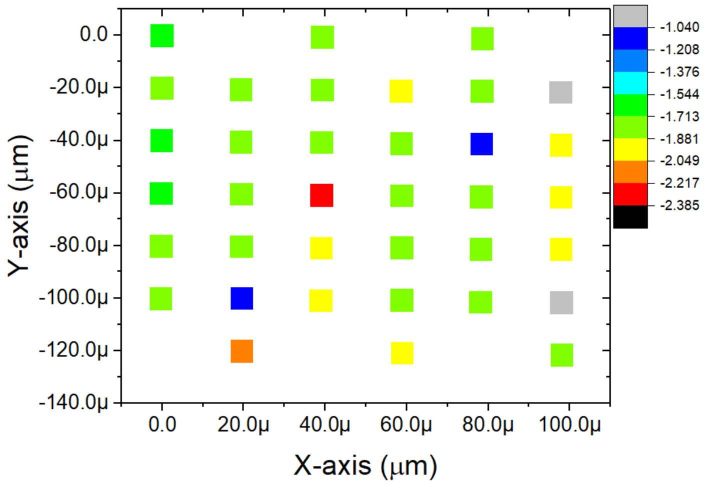


Areas for electrochemical mapping using SECCM

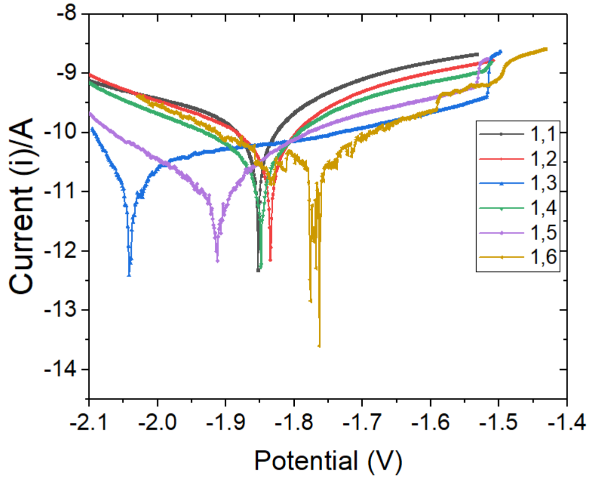
AZ91- Surface Electrochemical Properties



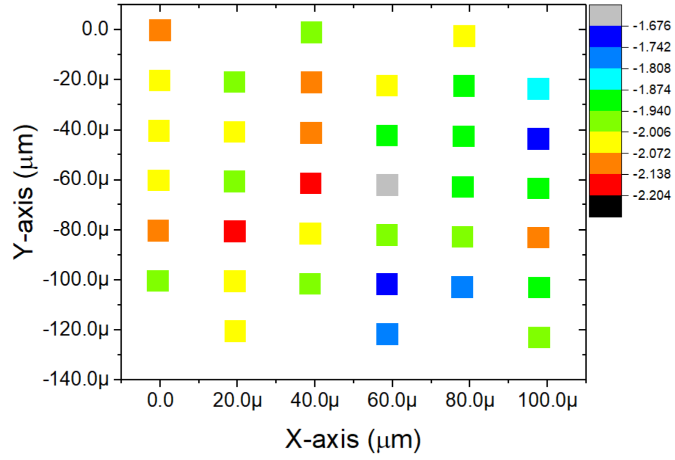
E_{corr}: Area map



AM60- Surface Electrochemical Properties



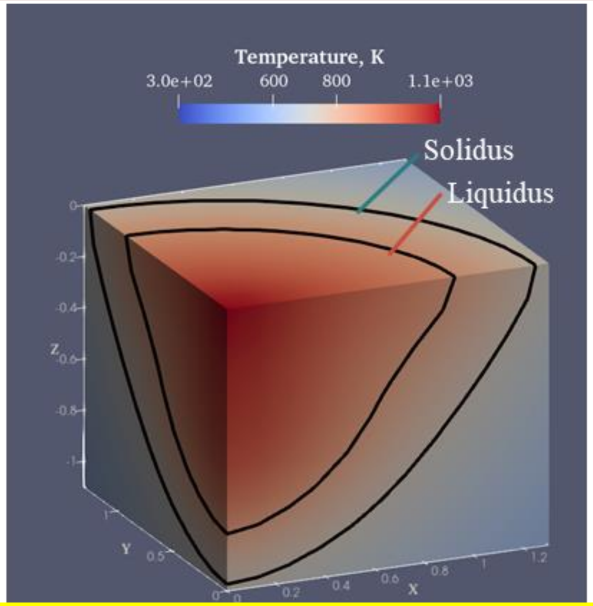
E_{corr}: Area map



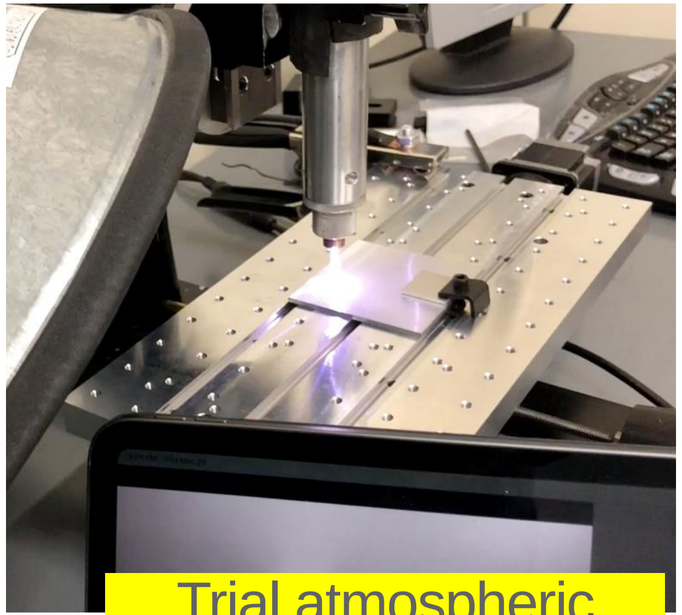
- Micro-segregation and presence of precipitates leads to varied electrochemical properties on the surface of both AZ91 and AM60 which results in micro-galvanic corrosion
- The surface modification techniques will attempt to alleviate this electrochemical variation

Accomplishments: (Project 3A): Reactive surface modification efforts- Processing Parameter Development

	Laser (thermal effects)	Atmospheric plasma (chemical effects)
Goal	Modify near-surface 2nd phase microstructure to enhance corrosion resistance (solutionize or melt + fast cool) Locally volatilize Mg to effectively enrich Al at surface to enhance corrosion-resistance	Alloy surface reaction(s) by chemical plasma to form Mg-Al-O, Mg-Al-O-C , or Mg-Al-N rich surfaces -Air, N_2, CO_2 plasma
Progress	▪ Initial modeling of AZ91D near-surface temperature during laser treatment to guide experiments ▪ Laser parameter experiment matrix in progress	▪ Atmospheric plasma equipment installed (cover gas enclosure designed and in progress)



Simulated laser-melted AZ91D cross-section

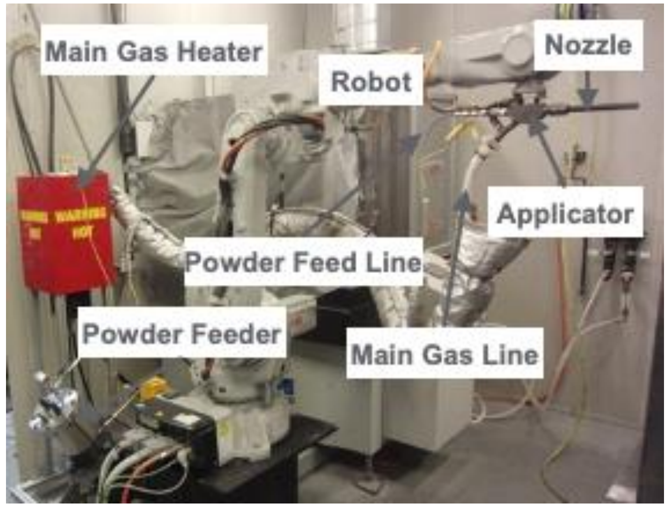


Trial atmospheric plasma operation

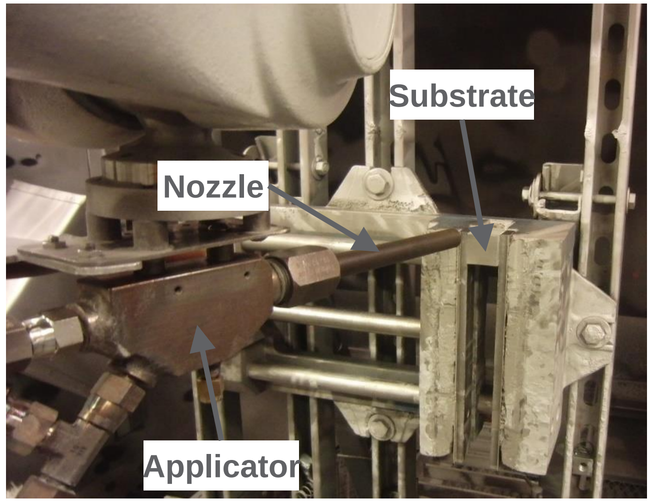
Accomplishments: (Project 3A) Cold Spray of Al6061 on AM60 and AZ91- Processing Parameter Development

Experimental Setup

Cold Spray System



Substrate in Vise

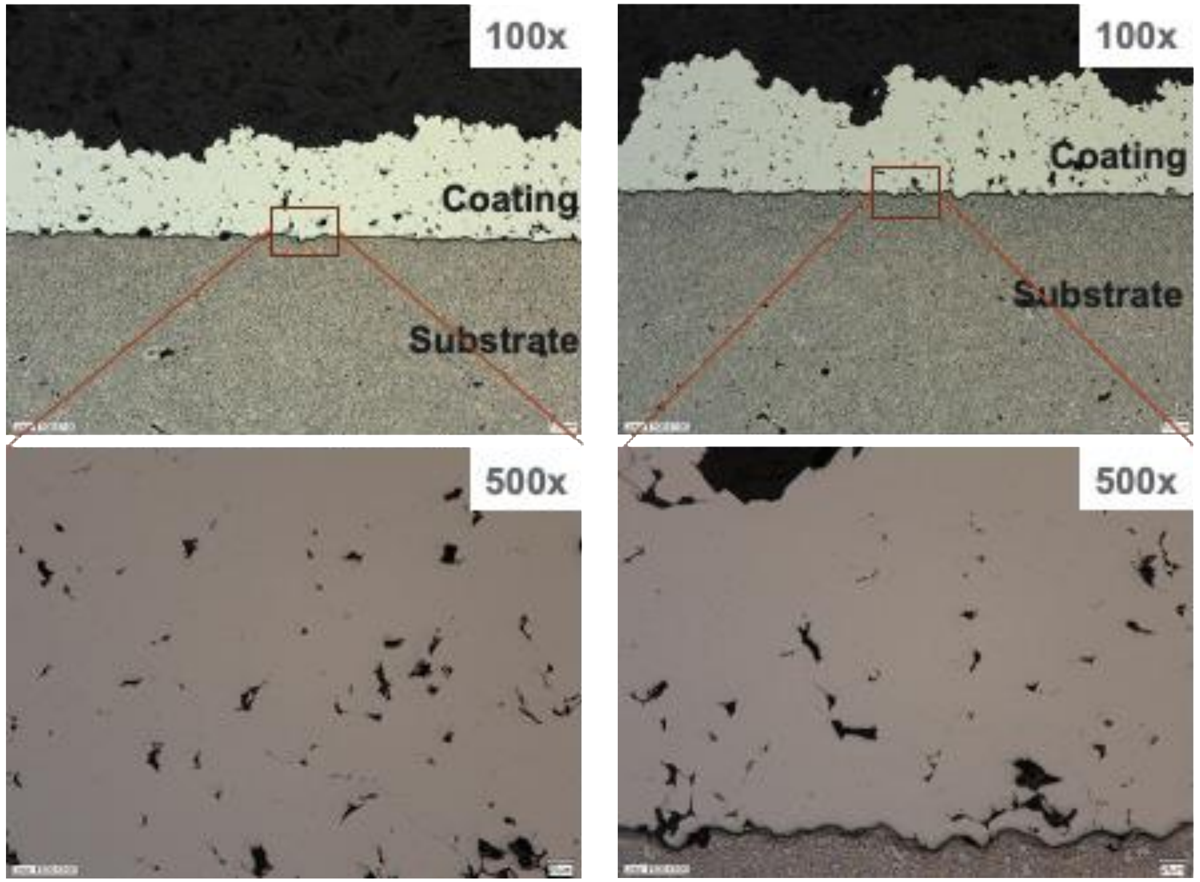


- 1"x1" coupons cut from AZ91 and AM60 samples
- Sprayed with surface preparation pass to promote adhesion
  - The first 1-2 passes are sprayed at an angle relative to the substrate
- Subsequent build-up passes sprayed with nozzle perpendicular to substrate

*Applied Research Laboratory, Pennsylvania State University

Cross-Sectional Analysis

AZ91 AM60



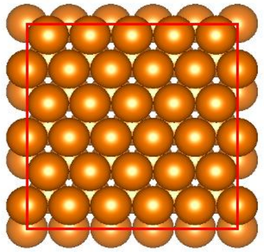
- Sprayed both AZ91 and AM60 with "standard" nitrogen parameters for **Al6061**
- Evaluating samples from initial sprays to determine the necessary process parameter changes required to produce higher-quality coatings

Accomplishments: (Project 3A) Ab-initio Modeling: Completed Baseline Analysis of Water Dissociation and Stabilization on Pure Mg and with Zn

Technical Approach

- Using Ab initio simulations/ Density functional theory (DFT), investigate effect of isolated dopants on the adsorption of isolated water molecules on Mg surface, their decomposition and behavior of the decomposition products
  - Adsorption of water molecules on the ideal and doped Mg surfaces: configurations and binding energies of adsorbed H_2O
  - Dissociation of H_2O molecules: stability of the decomposition products
    - OH and H
    - O^2 and 2H
  - Energetics of post-dissociation processes:
    - H_2 evolution
    - Diffusion of oxygen
- Determine the effect of alloying elements, oxide, carbonates, and crystal structure on the oxidation and decomposition behavior

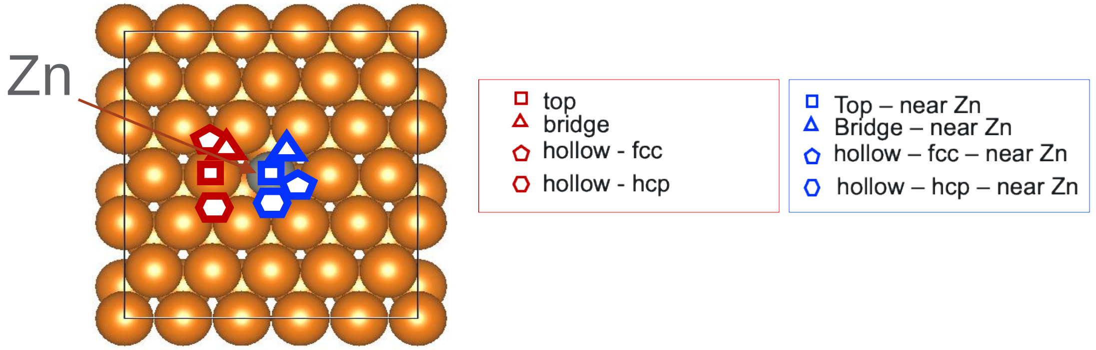
Mg (0001) surface; lateral cell



Thickness: 6 atomic planes

Additional Support obtained from Thrust 4

Water Dissociation and Stability of Dissociated Species on pure Mg and with Zn doping

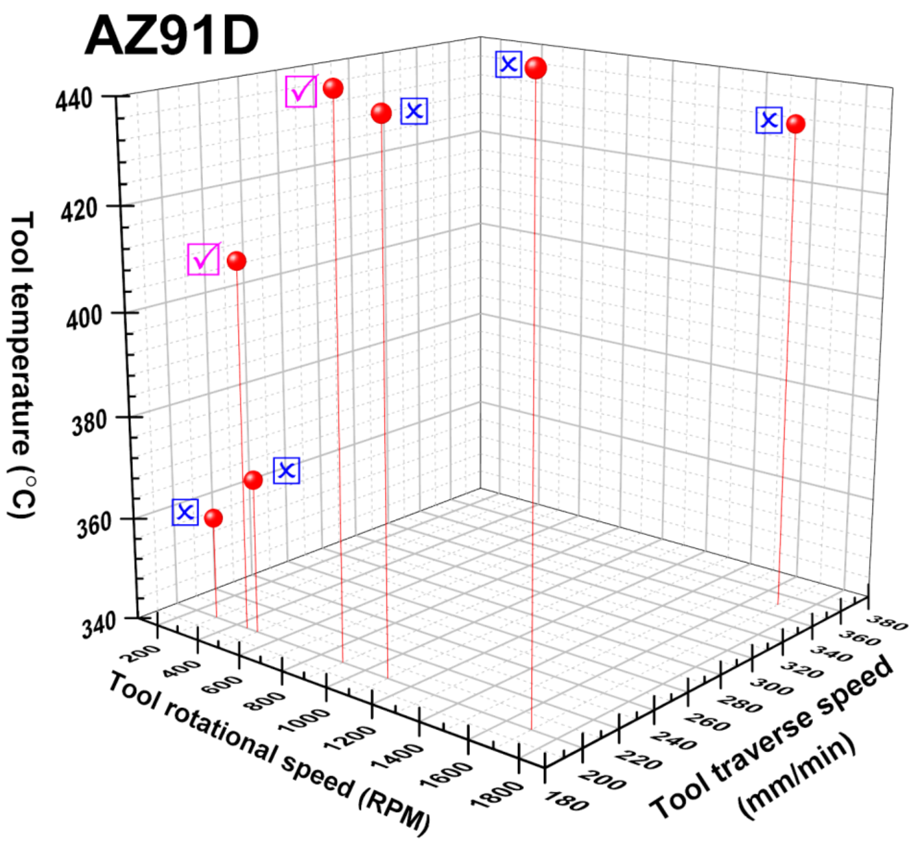


- Unlike water molecule, the dissociated water is more stable on Zn doped Mg surface.
- The dissociated water (OH+H) is more stable on the surface for both surfaces, suggesting exothermic reaction

Surface	E_{ads} (eV)	
	H_2O	O+2H (E_O+2E_H = E_{H2O}) (infinite distance)
Mg	-0.40	-1.70
Mg- Zn	-0.45	-2.25

Accomplishments (Project 3B)
Friction stir for AZ91D and AM60B: Processing parameter development

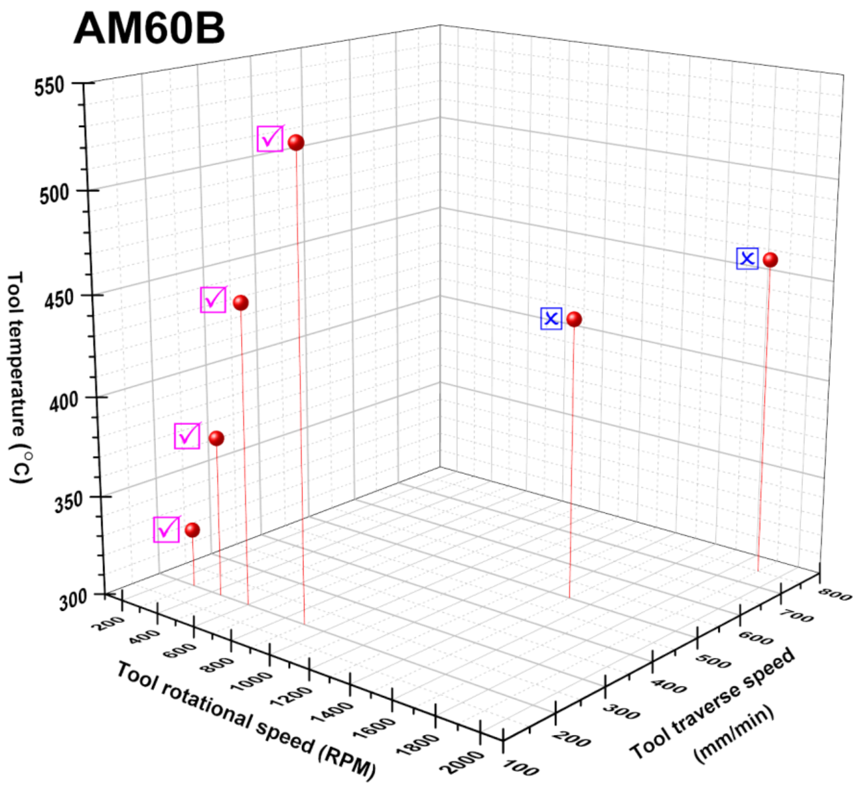
Tool temperature is plotted with tool rotation speed (RPM) and tool traverse speed (mm/min)



☒: Surface processing defects

☑: Surface defect-free

Initial processing parameter development varied both tool rotational speed and traverse rate to obtain defect-free processing surface.

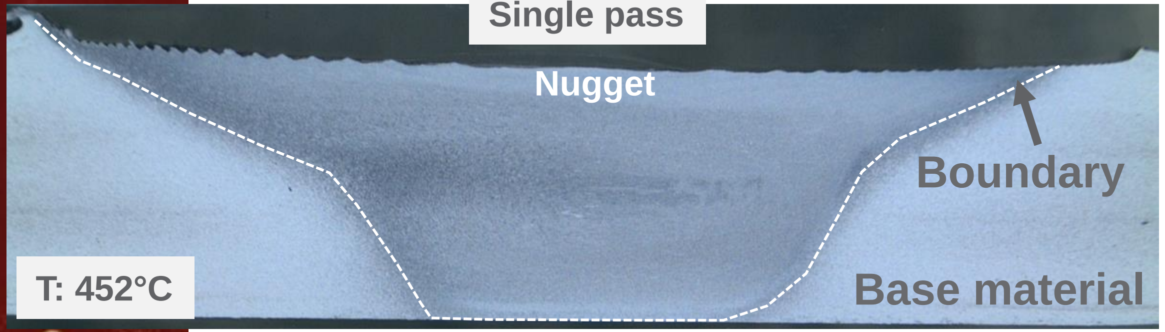


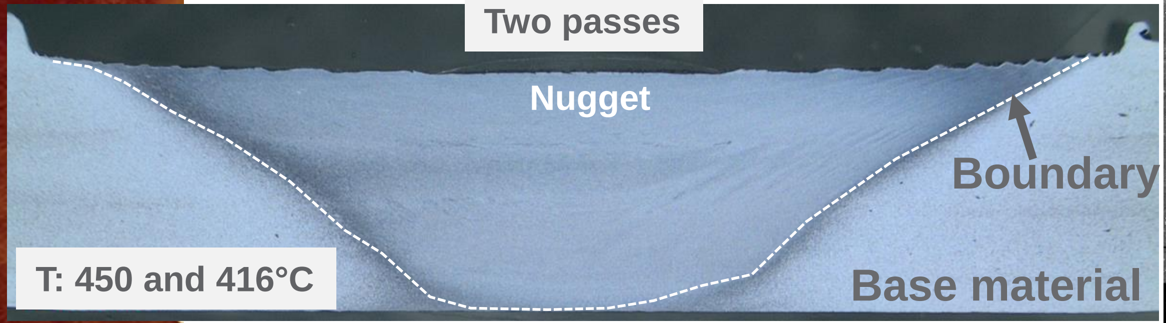
The work being performed here closely monitors the forces experienced during the processing. This will enable surface processing of thin and complex sections without the anvil support.

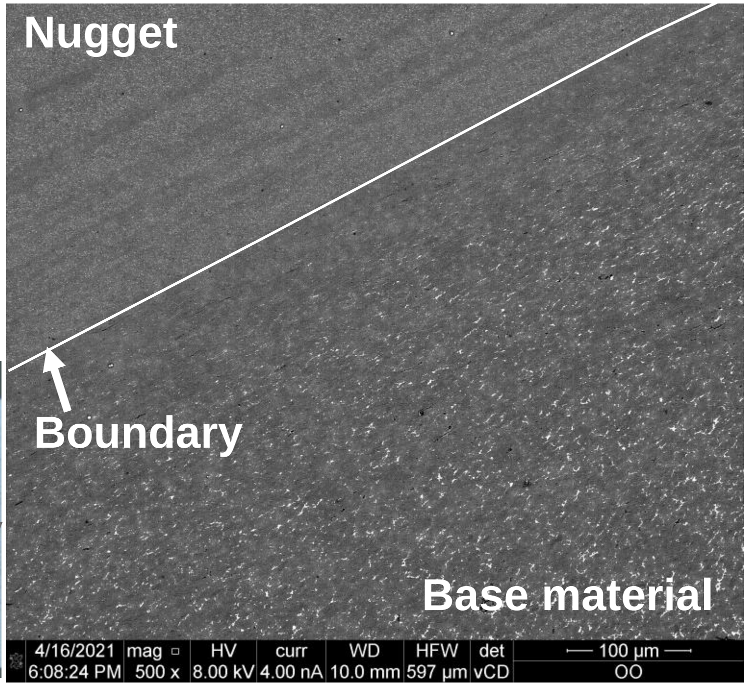
Pacific Northwest
NATIONAL LABORATORY

Accomplishments (Project 3B) Microstructural analysis of the friction stir processed cross-sections

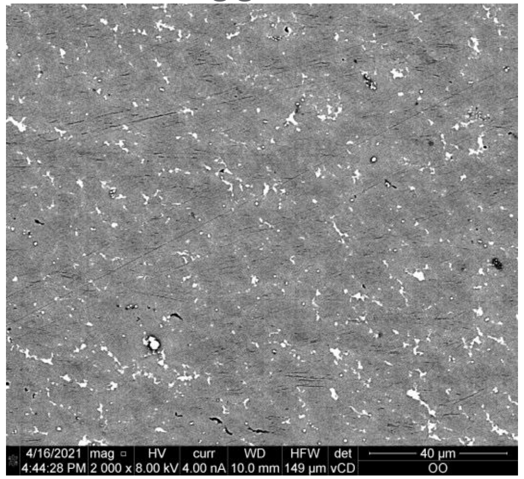
AZ91



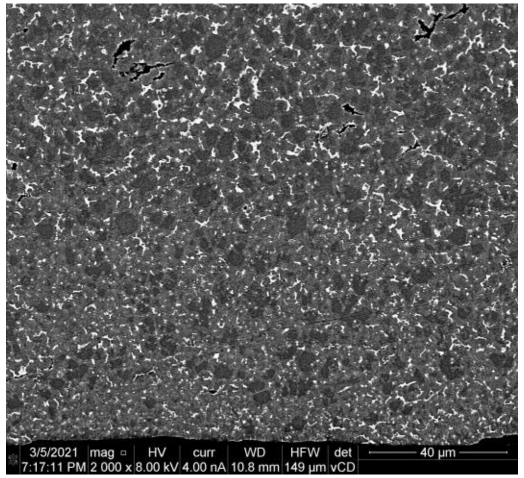




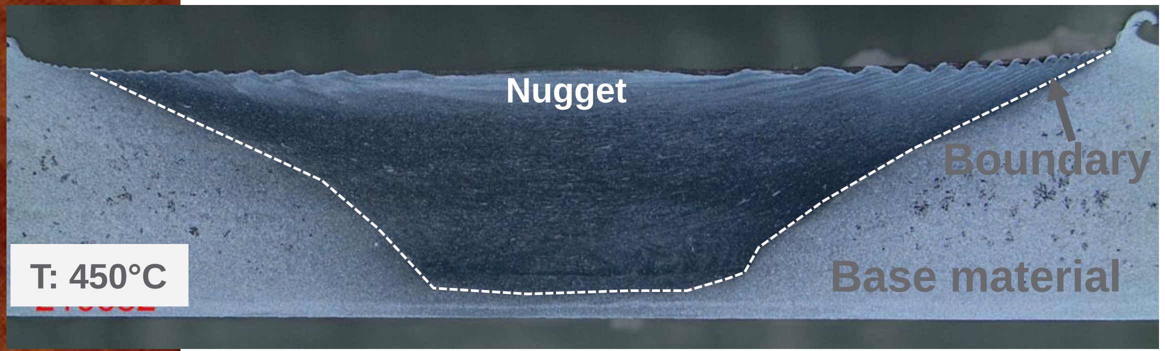
Nugget

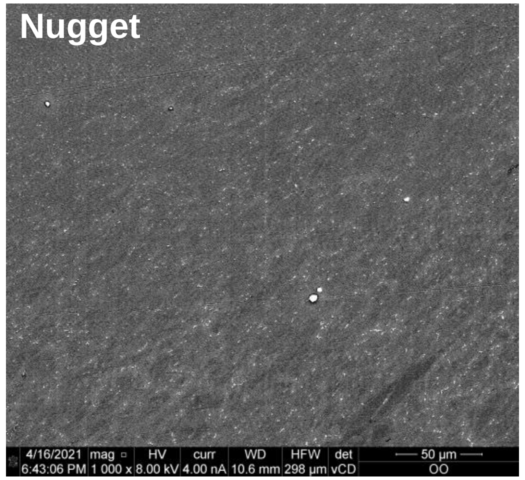


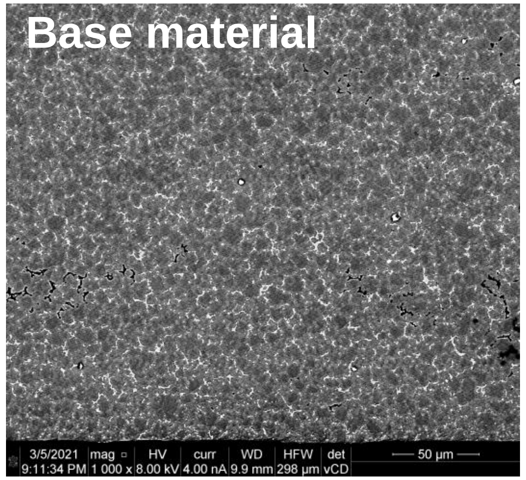
Base material



AM60







Macroscopic processing defects were not observed.

Refinement of the microstructure was observed.

Further investigation on the residual stresses are planned

Responses to Previous Years Reviewers' Comments

- This Project hasn't been reviewed before

Collaboration and coordination

- This thrust brings together PNNL, ORNL, and ANL teams to develop scalable and cost-effective processing methods to locally enhance the properties of cast magnesium by integrating projects and leverages each national lab expertise and capabilities
- 3A and 3B projects meet monthly to discuss results and progress
- The exact same batches of AZ91 and AM60 materials are being used by all the projects
- The tri-lab team formed supports surface modification, modeling, processing and characterization tasks
  - Task 3A1 provides additional support for bulk corrosion and electrochemical properties measurement across all Thrust 3 projects
  - Task 3A2 provides additional support for modeling and local electrochemical properties across all Thrust 3 projects
  - Task 3B provides additional support for characterization across all Thrust 3 projects
- Additional support is also provided by Thrust 4 for Ab-Initio Modeling Studies
- External Collaborators:
  - Applied Research Laboratory, Pennsylvania State University – Initial Cold Spray Trials
  - Volunteer Aerospace

Remaining challenges and barriers

- Replacement of the native-formed mixed oxide/hydroxide layer(s) on Mg with reactive surface modification to enhance the formation of aluminum and carbonate rich surface to form a more protective surface
- Produce a high-quality surface alloying commercial scale processing technique that causes sufficient adherence and protects Mg
- Solid Phase Processing of thin components without anvil support might bend the component and induce residual stresses and strains by the downward processing forces
- Solid Phase Processing processing of curved surfaces will be challenging and requires designing an appropriate processing tool

Proposed future work

- Define the processing window for the laser, plasma, cold spray, additive and surface alloying techniques on AZ91 and AM60
  - Perform characterization and electrochemical properties measurements on these surface modified samples
  - Predict the stability of water on these surfaces
- Demonstrate property improvements of friction stir processed Mg alloys
  - Perform microstructural characterization, hardness and tensile properties of friction stir processed AZ91 and AM60
  - Perform fatigue testing of of base and friction stir processed materials
  - Evaluate the corrosion performance of the friction stir processed region

*Any proposed future work is subject to change based on funding levels

Summary

- Project 3A utilizes reactive and alloying processes to modify the surface to demonstrate improved corrosion resistance in typical commercial magnesium alloy castings
  - The methodologies utilized are plasma, laser, cold spray, additive manufacturing
- Project 3B utilizes high shear solid phase processing to modify the surface to improve the mechanical properties along with the fatigue properties in typical commercial magnesium alloy castings
- HPDC AZ91D and AM60B exhibited porosity and micro-segregation and varied electrochemical properties in the as-cast condition
  - The surface modification techniques will attempt to alleviate these features and significantly improve the properties
- Along with this the processing windows for Atmosphere plasma, laser and cold spray techniques are being developed with commercial scalability in sight
- Initial high shear solid phase processing parameter development has led to defect-free processing in both AZ91D and AM60B HPDC plates and will enable surface processing on the thin as well as complex sections

Pacific Northwest
NATIONAL LABORATORY

Thank you