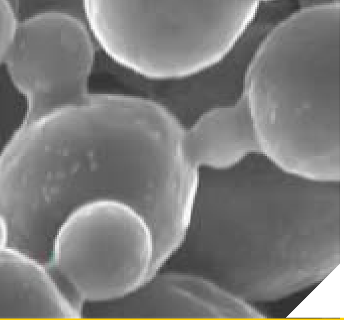

Surface Layer Characterization of Atomized Magnesium for use in Powder Metallurgy Products

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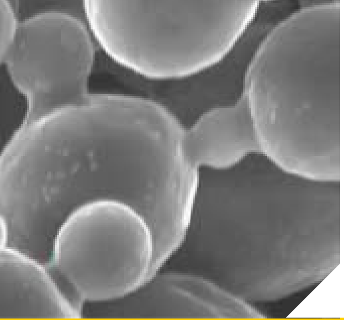
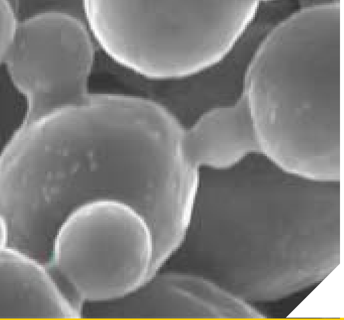


Outline

- Introduction
- Background
- Surface Contaminants
- Mg Surface Contaminants
- Mg Sintering Strategies
- Future Work
- Acknowledgments



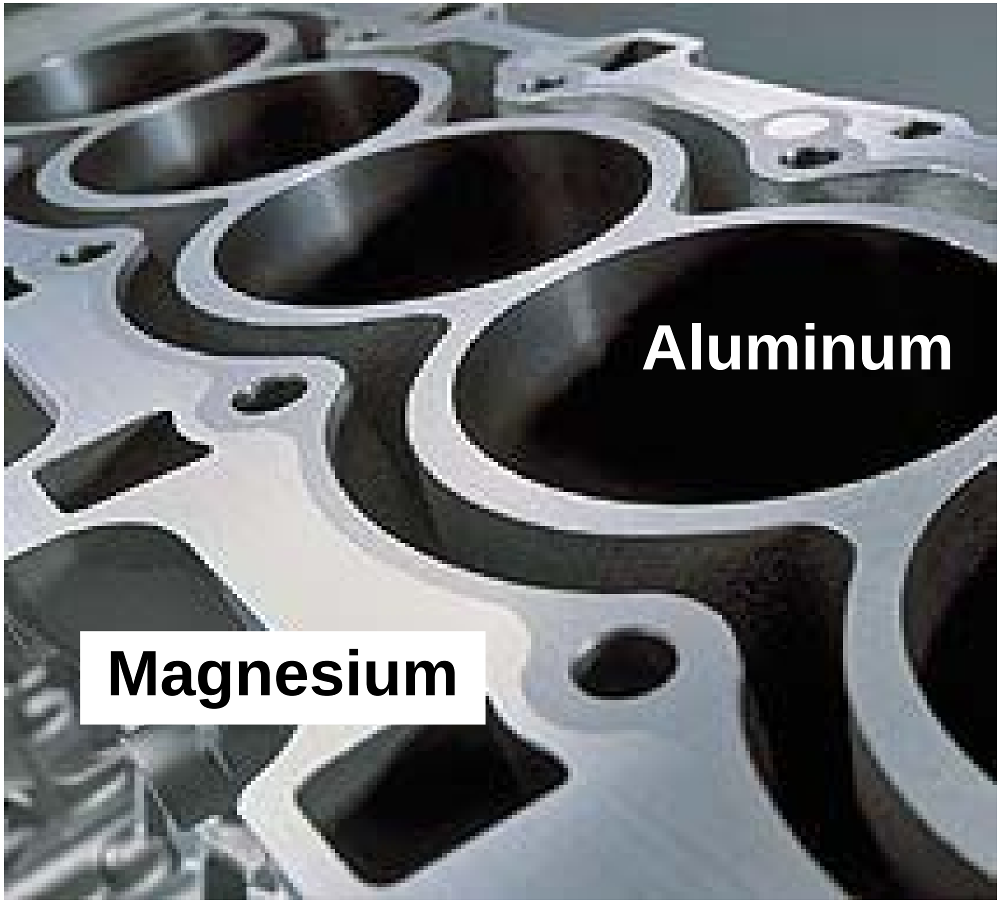
Introduction

Benefits of Magnesium

- High stiffness to weight ratio
- High damping capacity
- Recyclable

Issues with Magnesium

- Lack of developed alloys
- Difficult forming
- Corrosion



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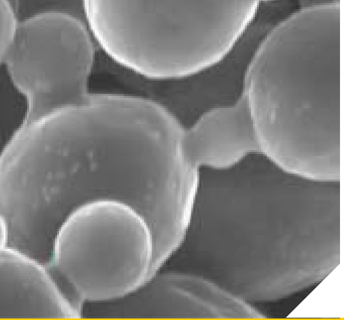


Introduction

Powder Metallurgy

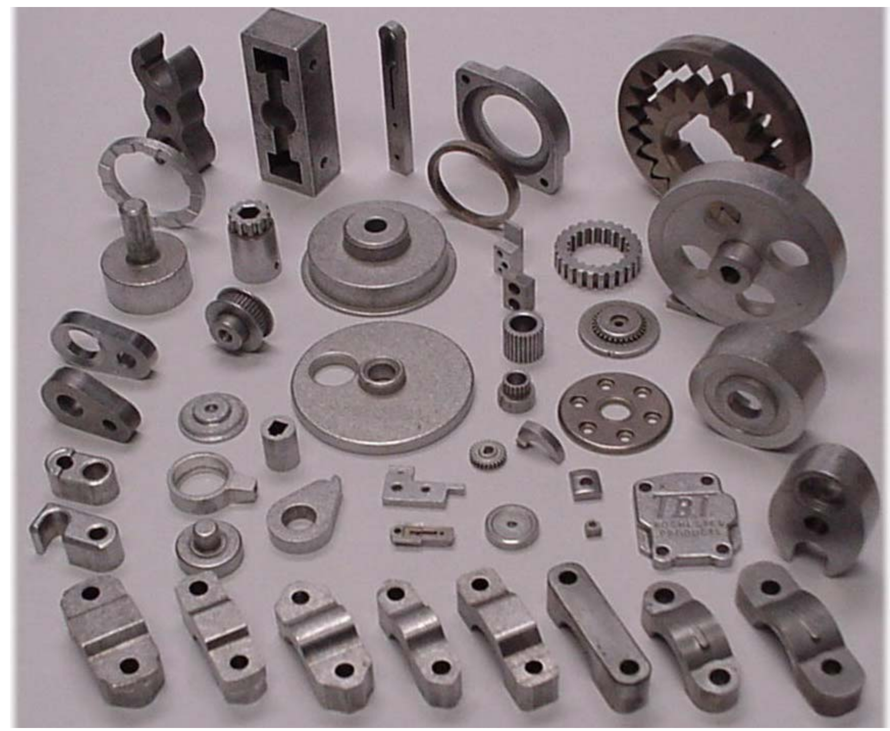
•Powder metal feedstock

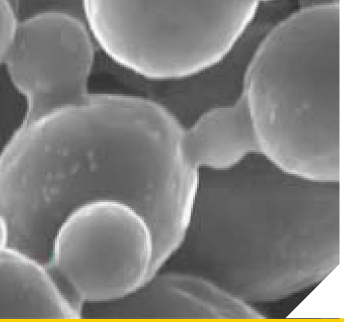
•Compacted at high pressure in specially shaped die

•Sintered at temperature below melting

•Near-net shape parts

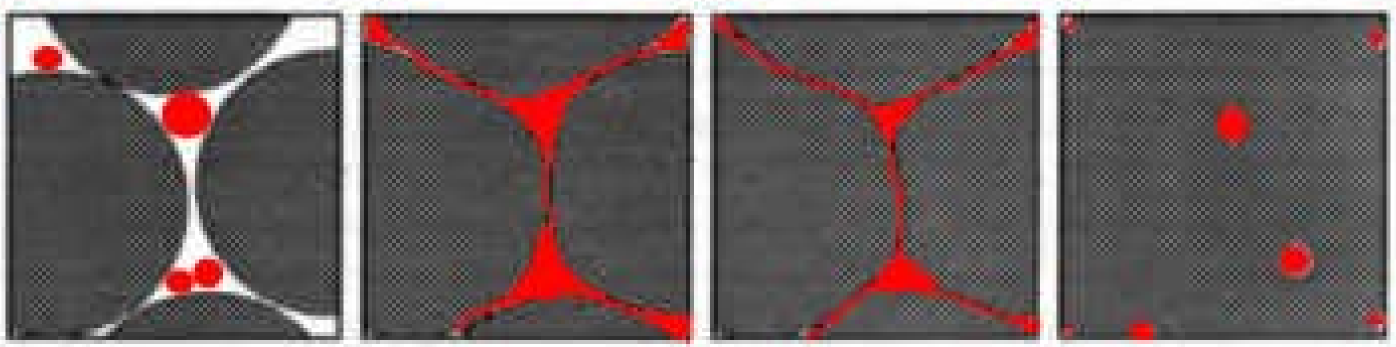
•Mg P/M largely unexplored





Sintering of Metal Powders

- Stages of sintering
  - » Point contact (A)
  - » Initial stage (B)
  - » Intermediate stage (C)
  - » Final stage (D)



A B C D

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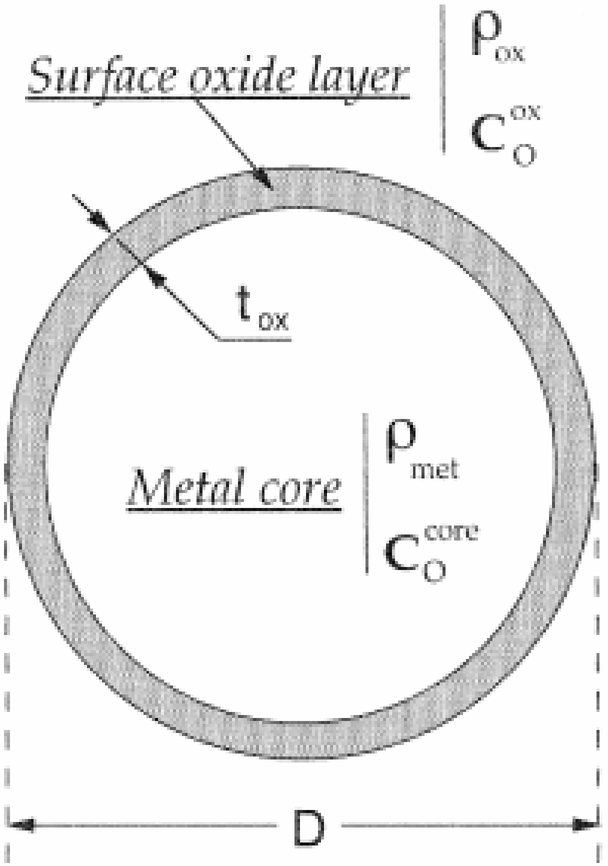
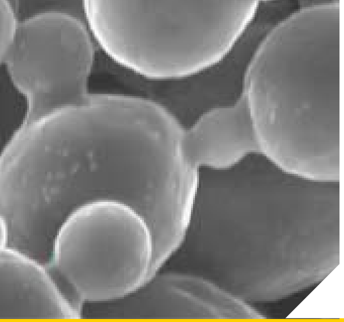
Surface Contaminants on Metal Powders

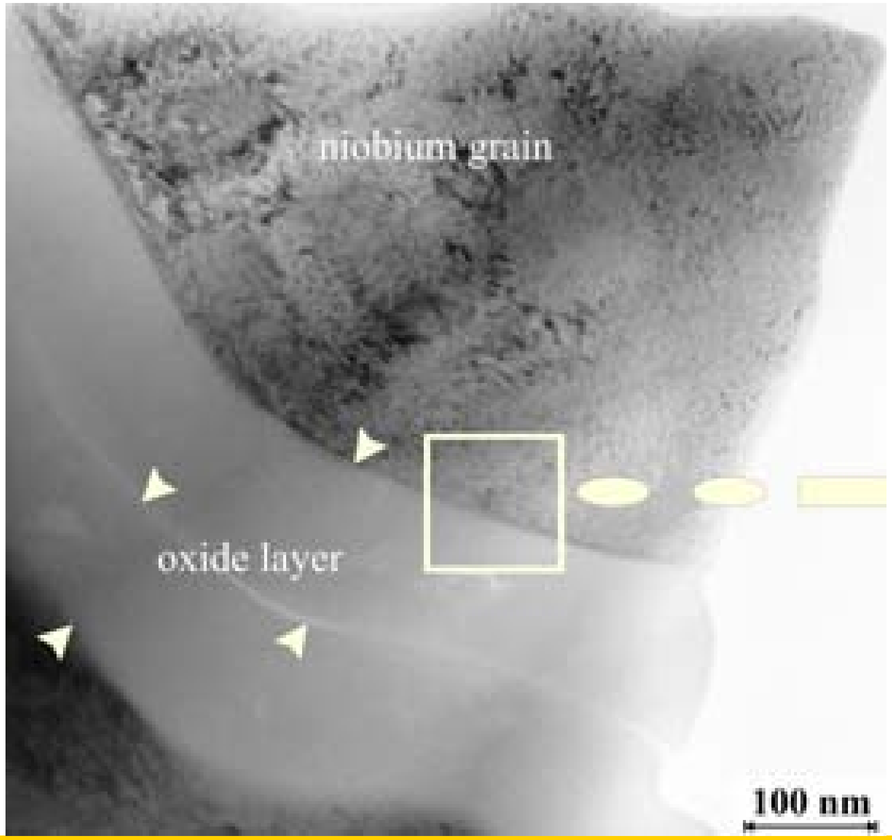


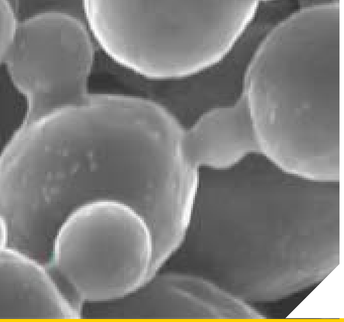
- Metal core
- Surface layer
  - Oxide?
  - Hydroxide?
  - Carbonate?
  - Thickness?



Surface Contaminants

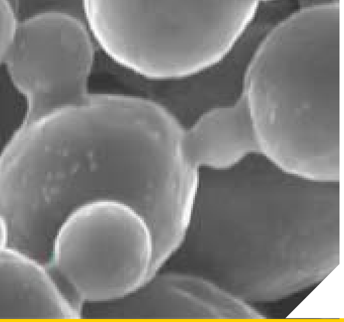
- Characterizing surface layer
  - Auger electron spectroscopy (AES)
  - X-ray photoelectron spectroscopy (XPS)
  - Secondary ion mass spectroscopy (SIMS)
  - Transmission electron microscopy (TEM)





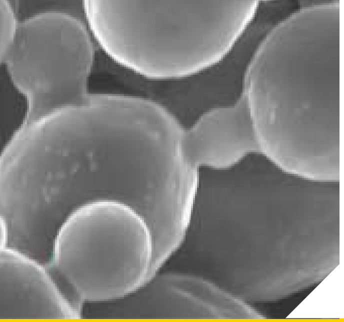
Surface Contaminants and Sintering

- Dealing with the surface layer
  - Dissolve layer into metal
  - Diffuse metal through layer
  - Thermo-chemical reduction



Surface Contaminants and Sintering

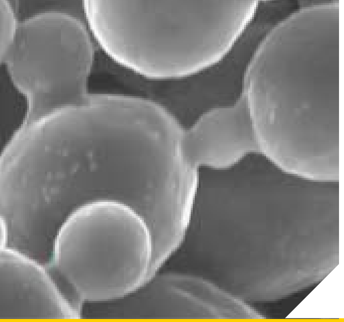
- **Dissolve layer into metal**
  - Depends on oxygen solubility in metal
  - Sintering preceded by incubation period
    - Fe ~10 seconds
    - Al ~ 100+ days (Estimate)
    - Mg ~100+ days (Estimate)



Surface Contaminants and Sintering

- **Diffuse metal through layer**
  - Depends on diffusion rates and layer thickness

	D_M $m^2\ sec^{-1}$	D_{Ox} $m^2\ sec^{-1}$
Cu	5.65×10^{-13}	6.65×10^{-12}
Al	1.84×10^{-12}	5.51×10^{-30}
Mg	3.01×10^{-12}	5.25×10^{-24}

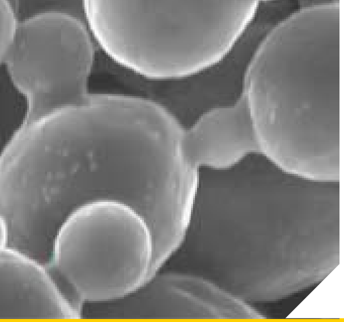


Surface Contaminants and Sintering

- **Thermo-chemical reduction**
    - Free energy diagram

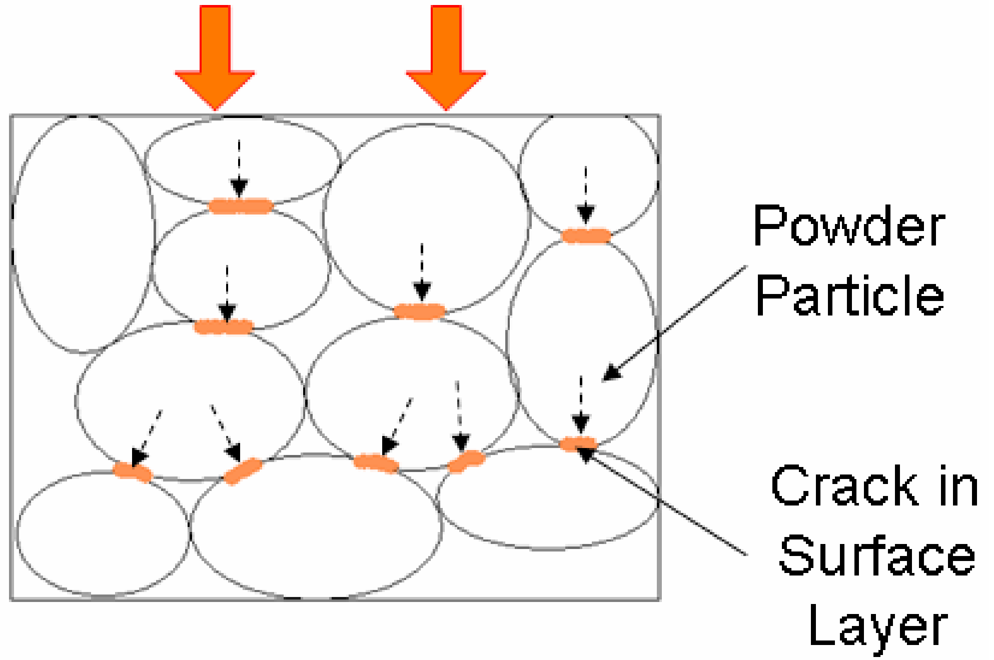
– Appropriate temperature, pressure and atmosphere

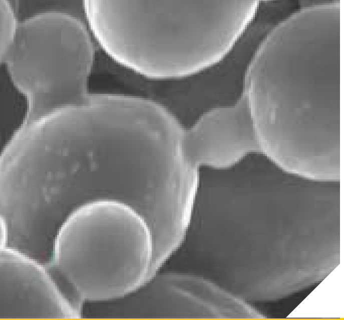
– Addition of more reactive metal (Mg in Al)



Surface Contaminants and Sintering

- **Break layer**
  - Create short-circuit pathway for diffusion through cracks in layer
  - Accomplished mechanically or chemically

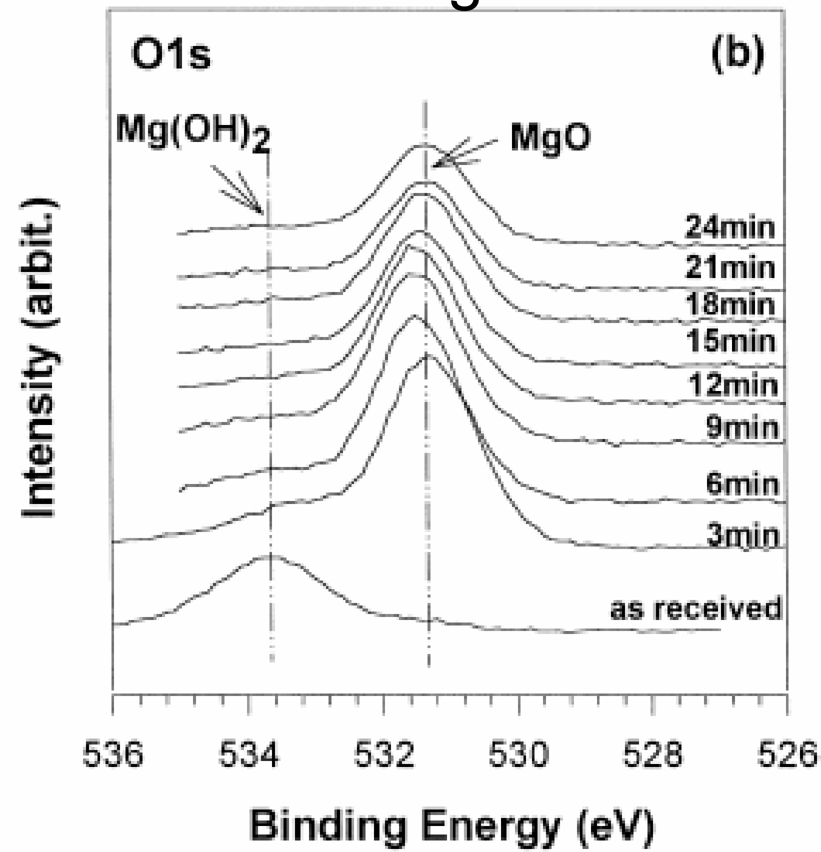




Mg Surface Contaminants

- When exposed to air, MgO forms with $Mg(OH)_2$ on the surface
- Thickness depends on exposure time
  - 1 min, 2.65 nm
  - 7 days, 5.31 nm
  - 7 years, 5.67 nm

XPS of Mg Surface



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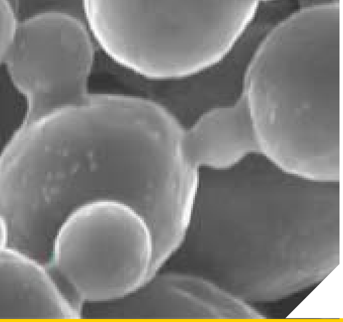
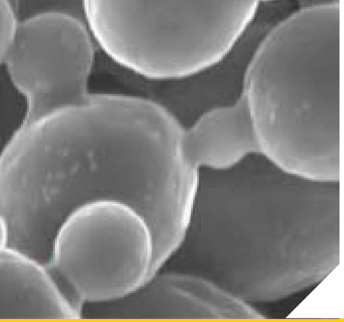


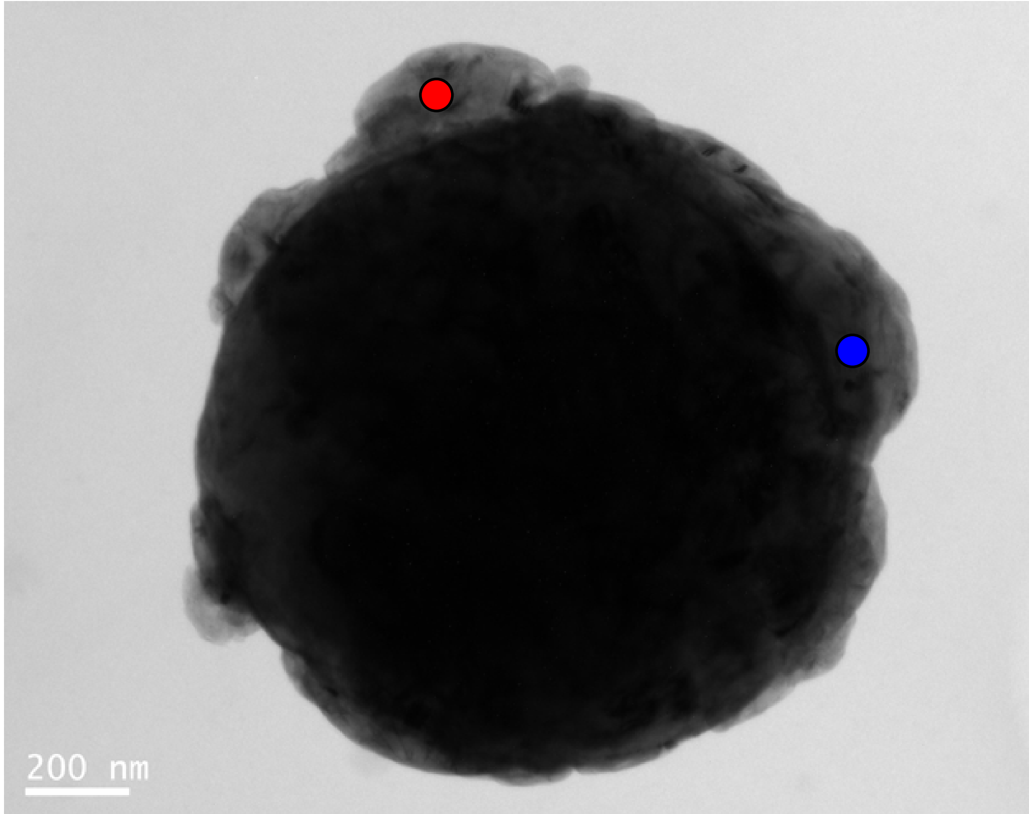
Research Objective

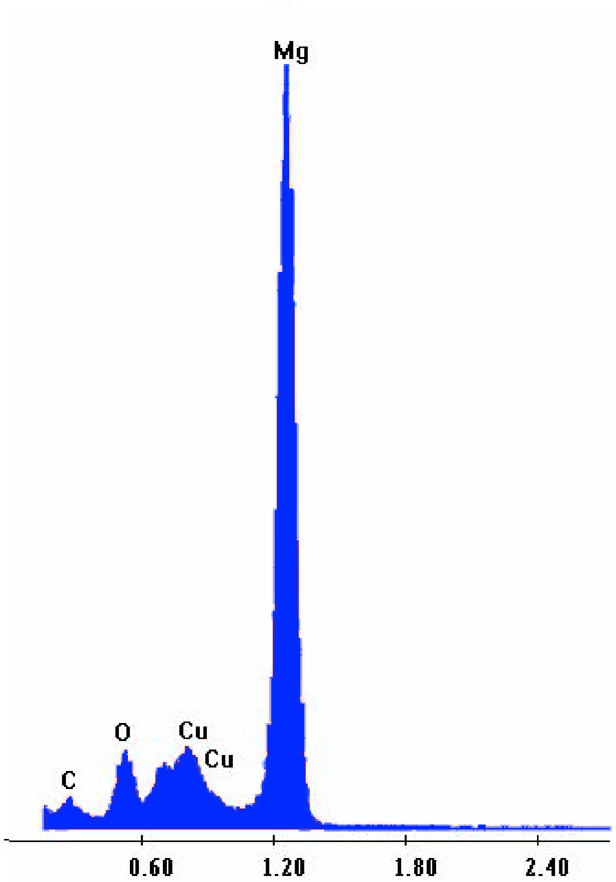
- Fundamentals of magnesium sintering
  - Composition and thickness of surface layer by AES, XPS, SIMS, FIB/TEM
  - Decomposition reactions during sintering by DSC, DTA, TGA

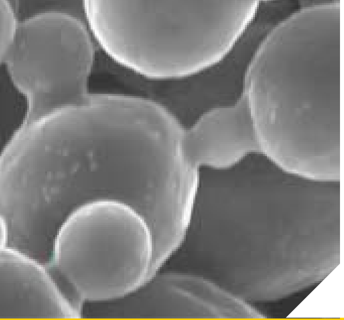
- Practical strategies to aid sintering and mechanical properties



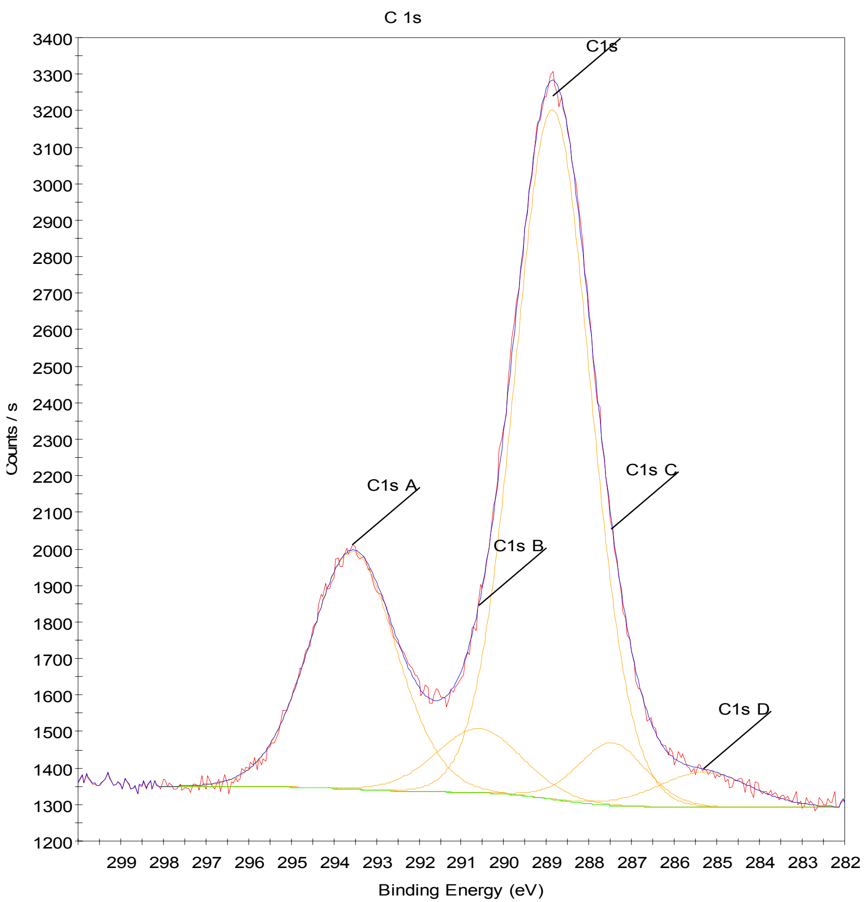
Mg Atomized Powder Surface Contaminants (TEM)





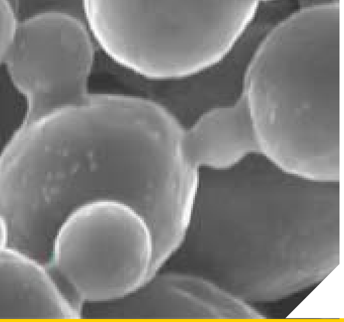


Mg Atomized Powder Surface Contaminants (XPS)

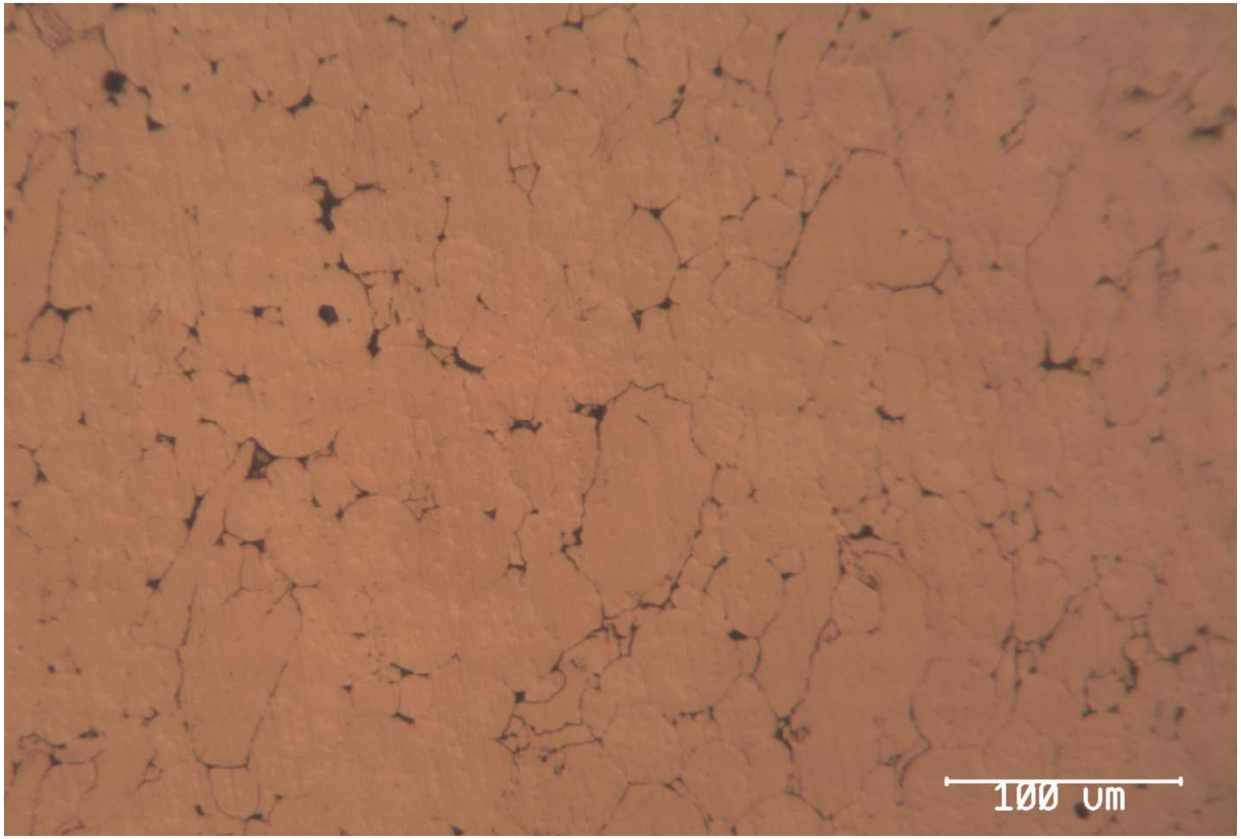


XPS identified that the surface contained:

- Magnesium
- Oxygen
- Carbon

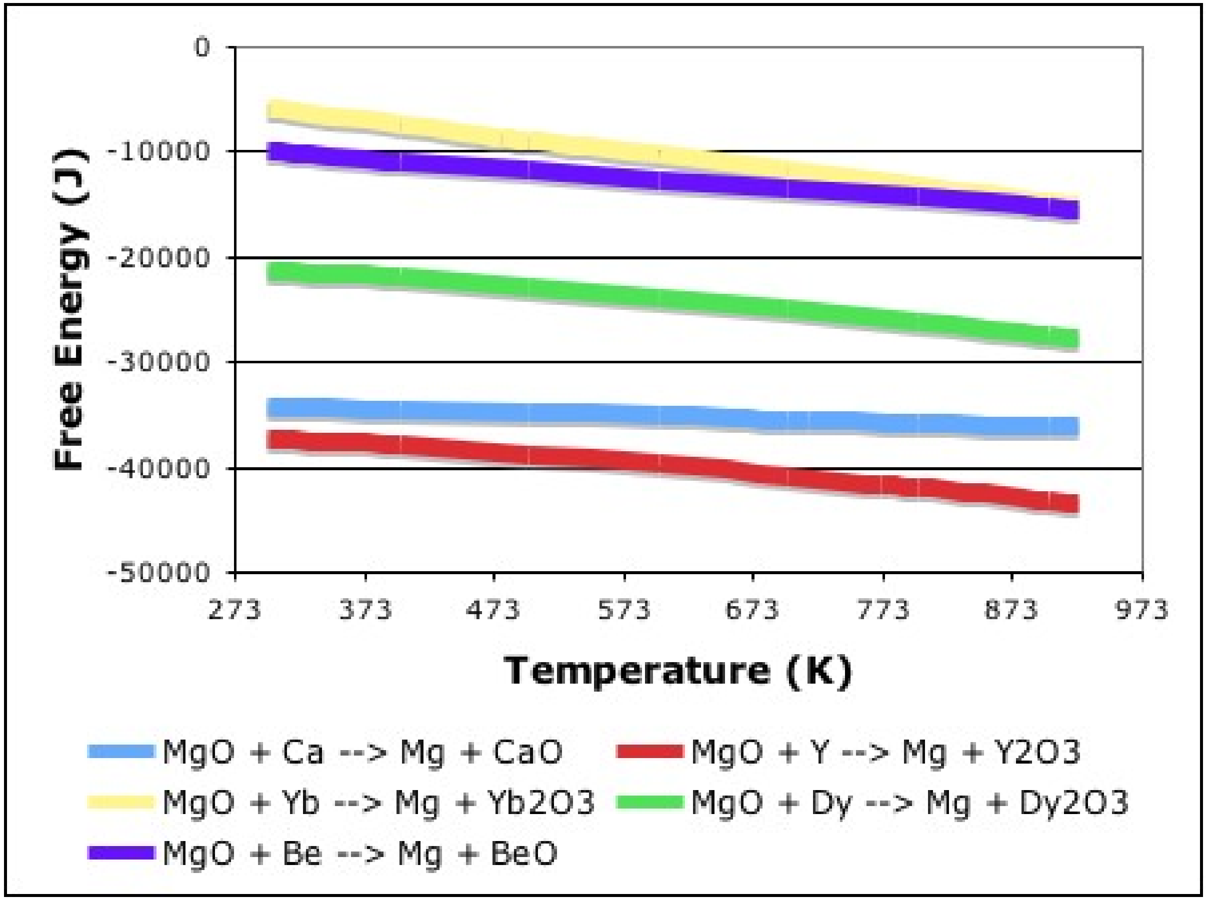


Mg Sintering Strategies (Increased sintering time)



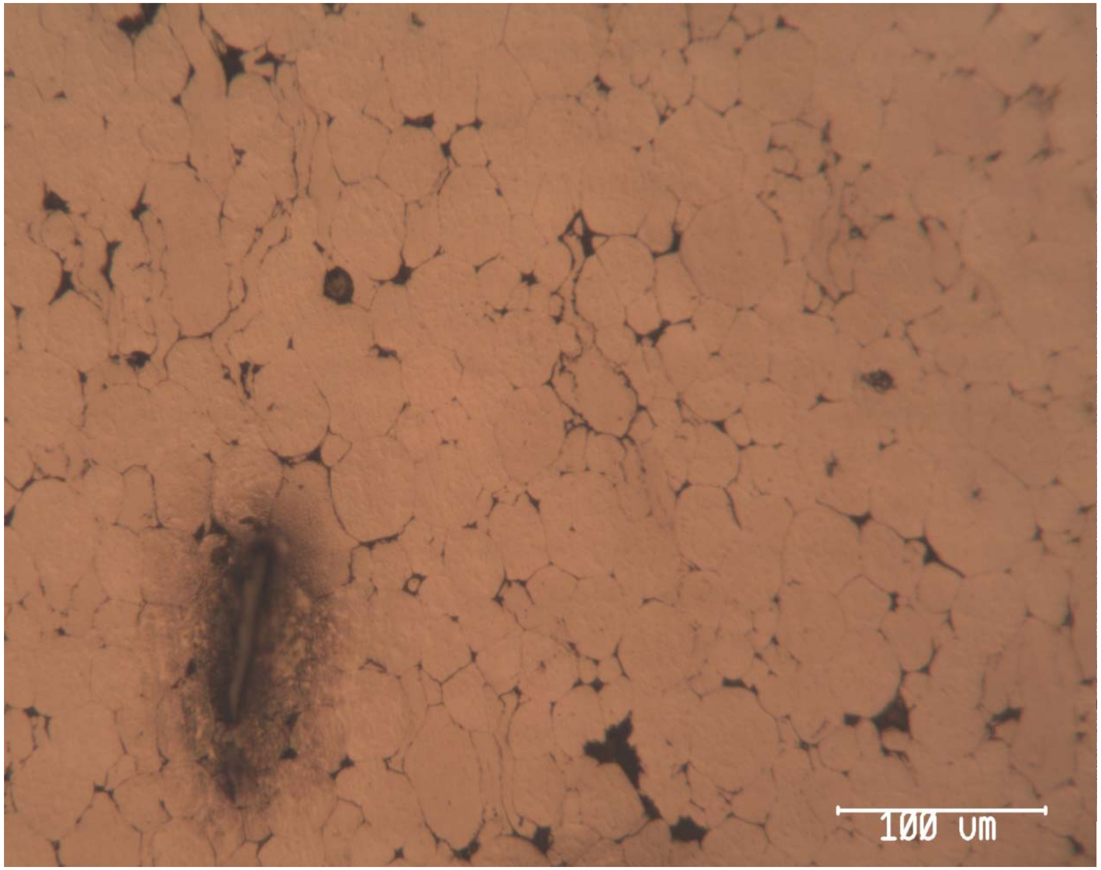
- Pure Mg
- 600ºC
- 6 hours
- 40 min

Mg Sintering Strategies (Thermo-chemical reduction)

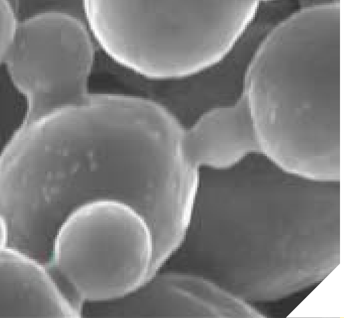


Elements with more stable oxides:
- Yb
- Be
- Dy
- Ca
- Y

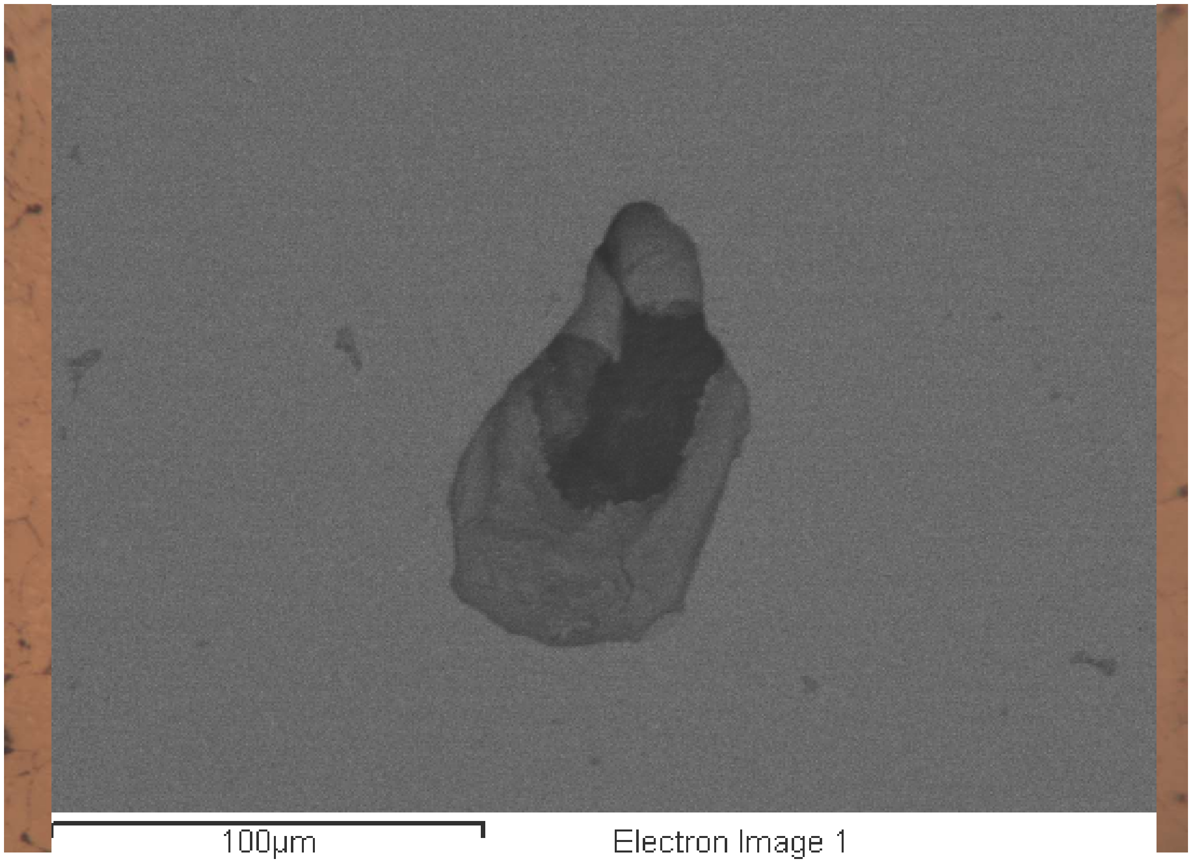
Mg Sintering Strategies (Thermo-chemical reduction)



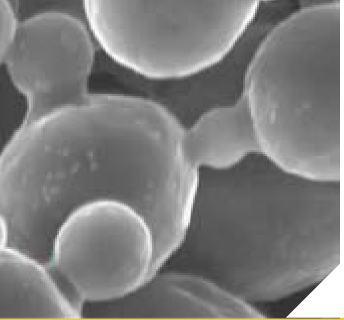
- 1 wt% Y
- 600ºC
- 40 min



Mg Sintering Strategies (Thermo-chemical reduction)

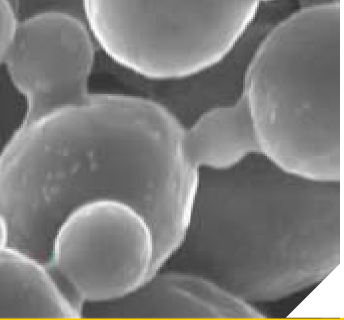


- 1 wt% Ca
- 600ºC
- 40 min



Mg Sintering Strategies (Post Sintering Forging)

- Samples of 95% or greater density will withstand hot or cold rolling to further increase density
  - 50% cold reduction, 150% hot reduction
  - Density increases near theoretical
  - Large increase in hardness



Mg Sintering Strategies (Sintering Atmosphere)

- Compacts can be sintered in argon or nitrogen
- During sintering, gas can become trapped as porosity closes
  - Argon completely inert, pressure inside pore prevents densification
  - Nitrogen may react, reducing pressure inside pore

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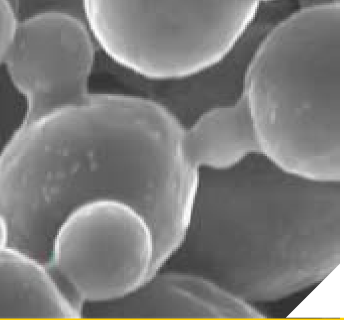
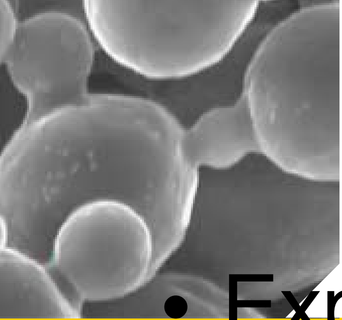


Mg Sintering Strategies (Powder Pre-Treatment)

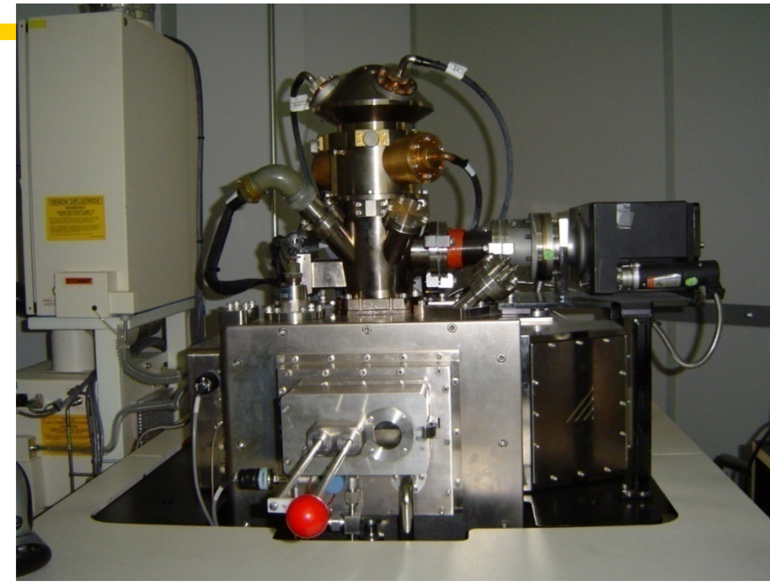
- Before processing, Mg powder can be dipped with a solution designed to dissolve the surface layer
  - Acids, bases, organic compounds possible
  - Difficulty arises when solution comes into contact with fresh Mg surface



Experiment for FIB/TEM

- Expose Mg powder (~ 50 μm) to air:
  - One day
  - Two days
  - Five days
  - Seven days
- Examination by FIB/TEM/EDS.
  Avoid:
  - Water, oxygen
  - Organic solvent
  - Destruction of film

A Micrion-2500 Single Beam FIB System



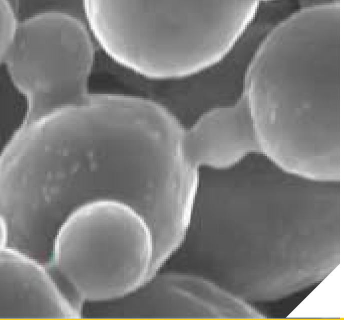
- 5 nm imaging resolution using a focused Ga ion beam.

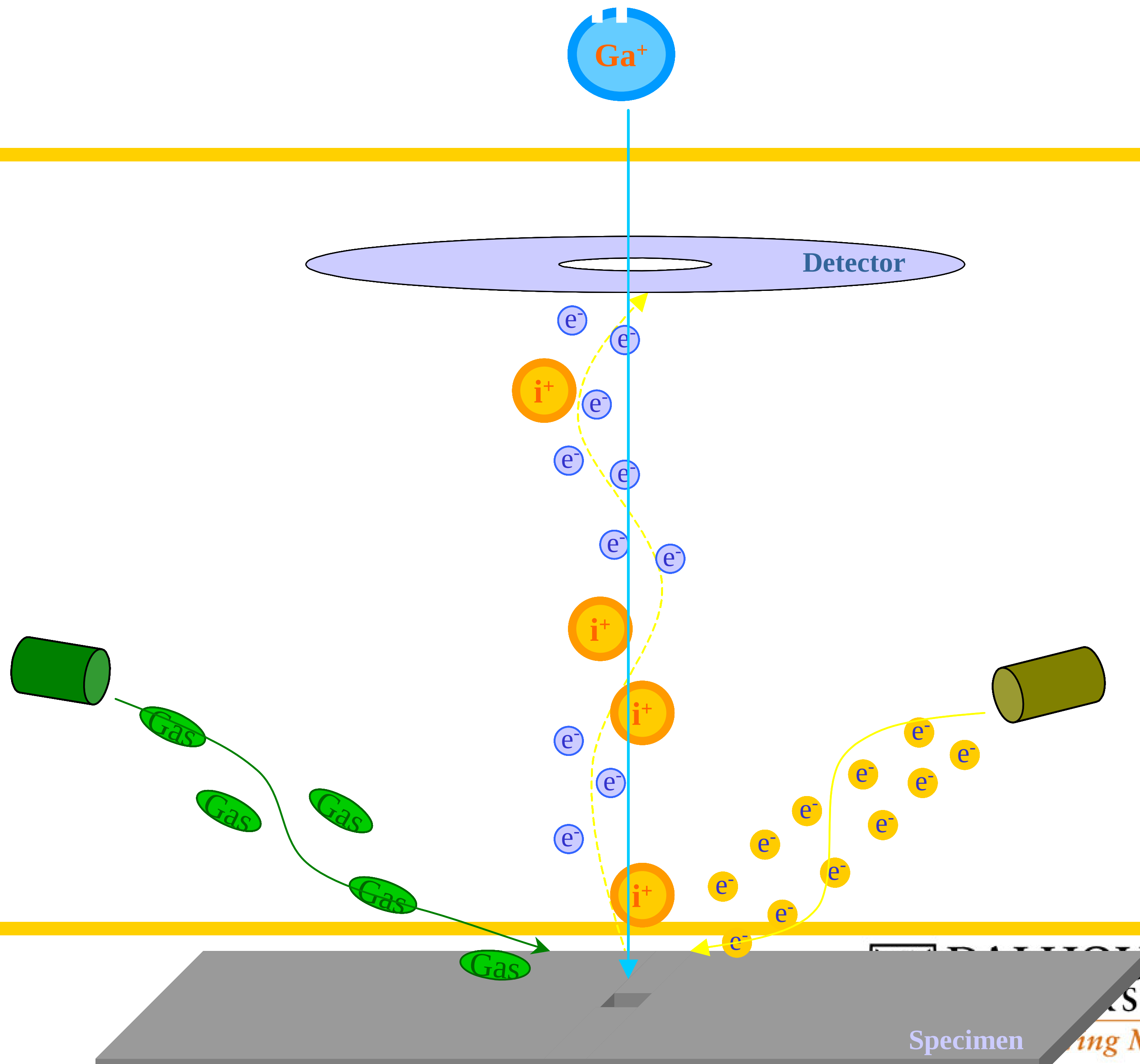
- Beam current ranges from 1 pA to 40 nA.

- “Stress free” site specific cross-sectioning and imaging.

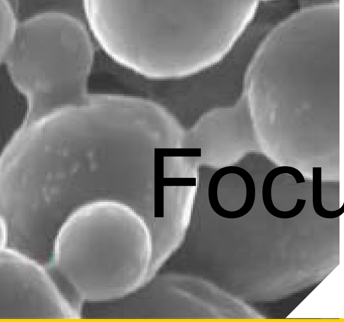
- Gas assisted etching and precise metal and oxide deposition.

-Secondary electron (SE) and secondary iron imaging.





Ga^+
Detector
e^-
i^+
Gas
Specimen



Focused Ion Beam (FIB) Microscopy

- The FIB microscopes were developed in the early 1980s. It has been widely implemented in the semiconductor industry as semiconductor device modification, device failure analysis.

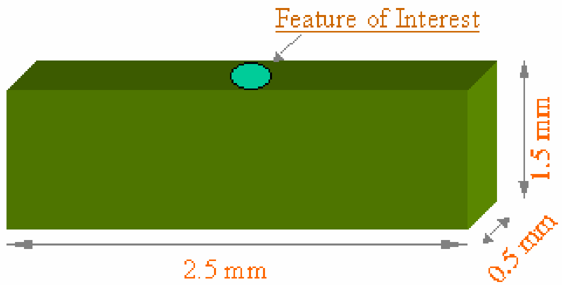
- In recent years, FIB found many applications in materials studies.

- Typical materials science applications include: **Stress-free ion beam cross-sectioning and high-resolution ion beam imaging, site-specific TEM specimen preparation, micro-machining and micro-deposition.**

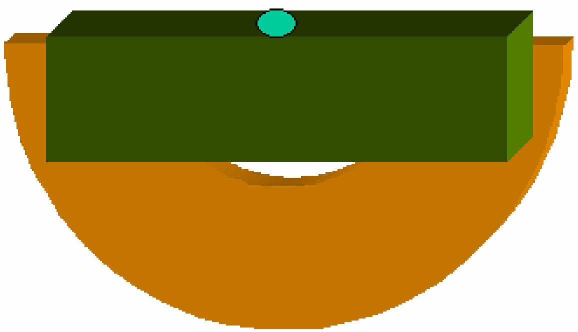
FIB TEM Sample Preparation Techniques

Traditional H-bar technique

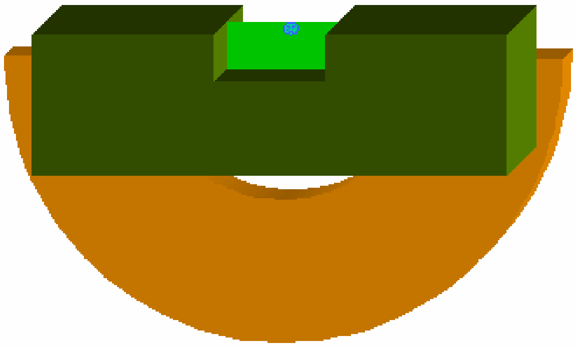
Small sample cut out from bulk using a diamond saw



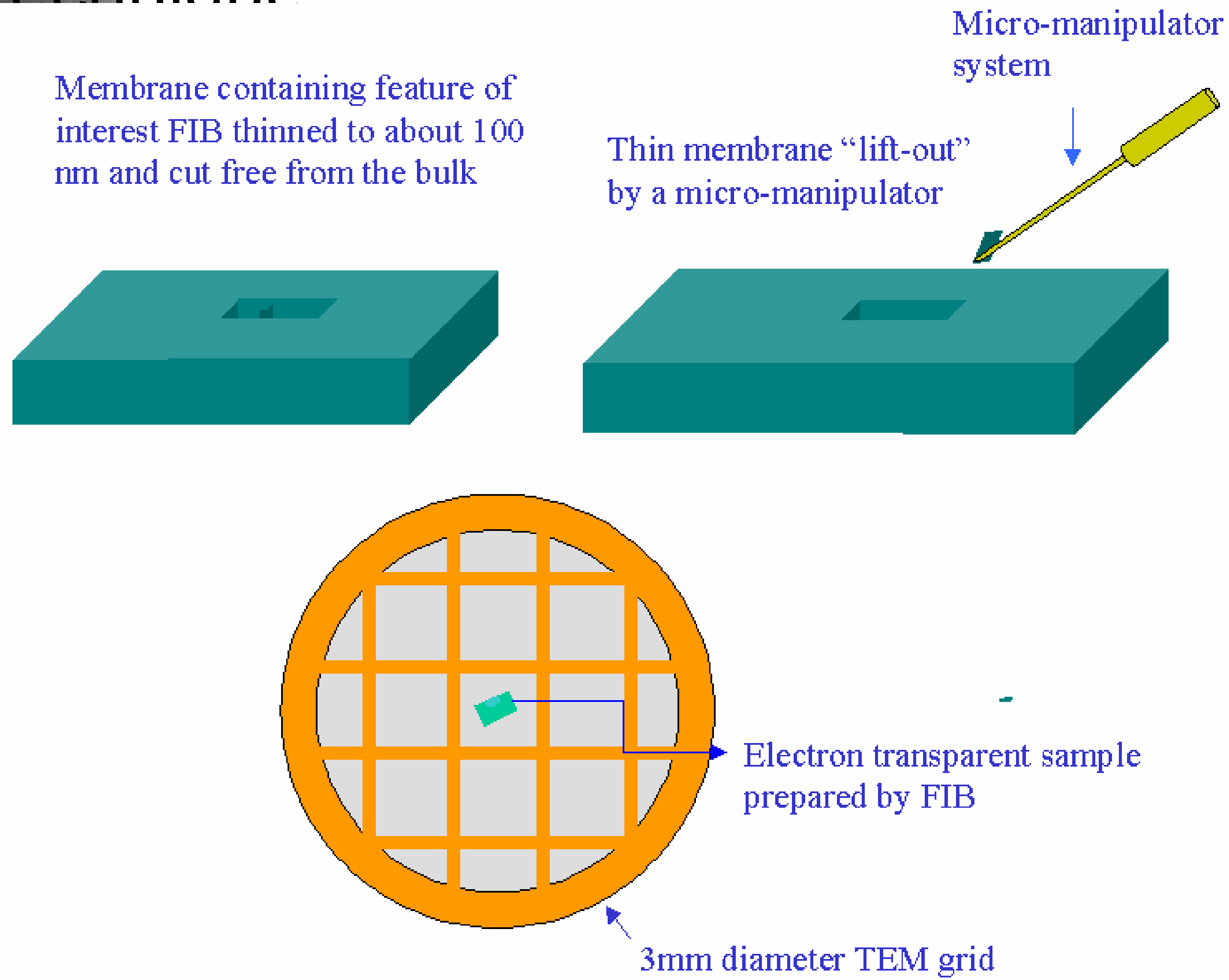
Sample mounted on a TEM grid
After carefully polished by a tripot polisher



FIB thinning to create an electron transparent area



Lift-out FIB TEM Sample Preparation Technique



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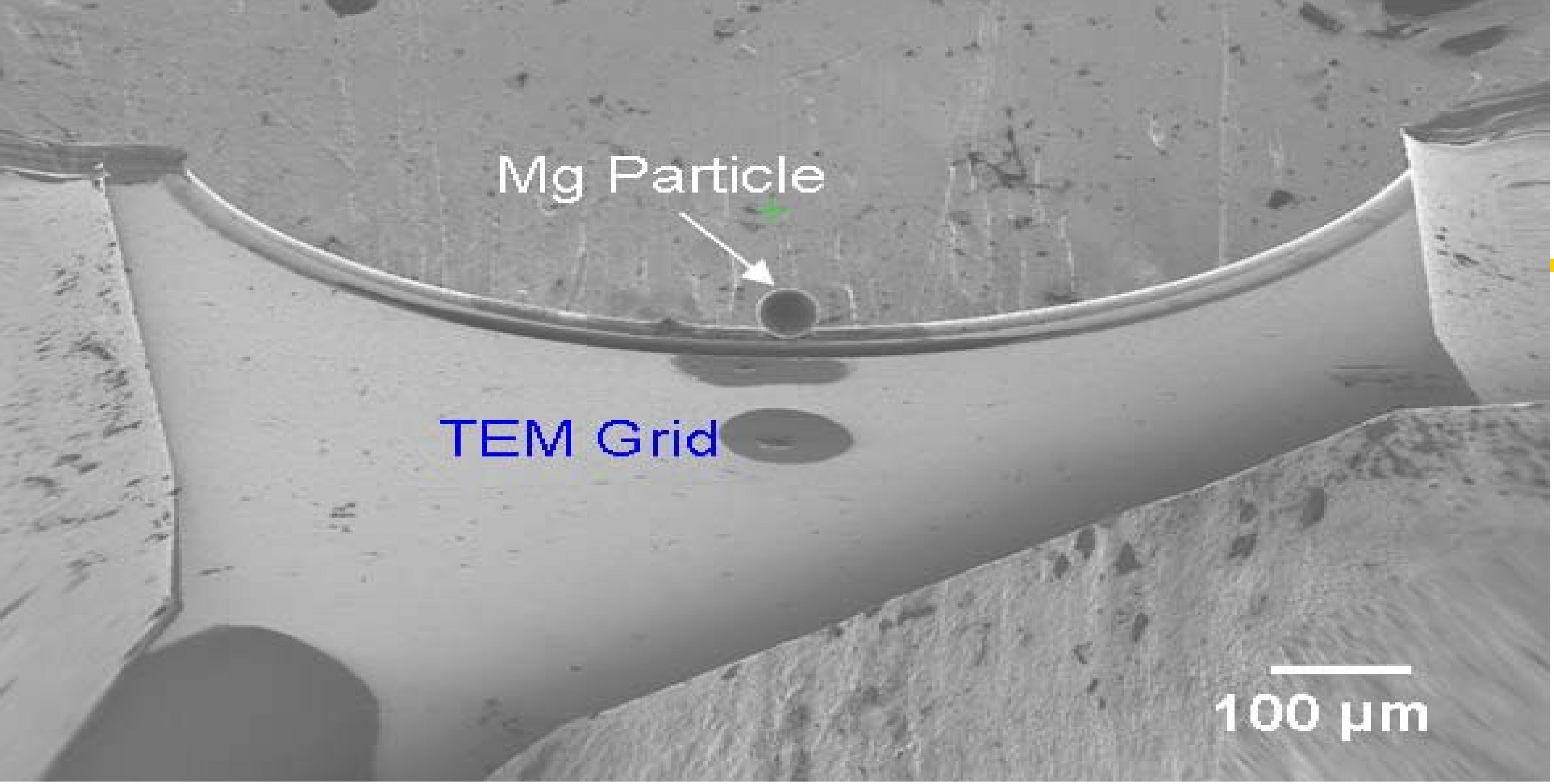
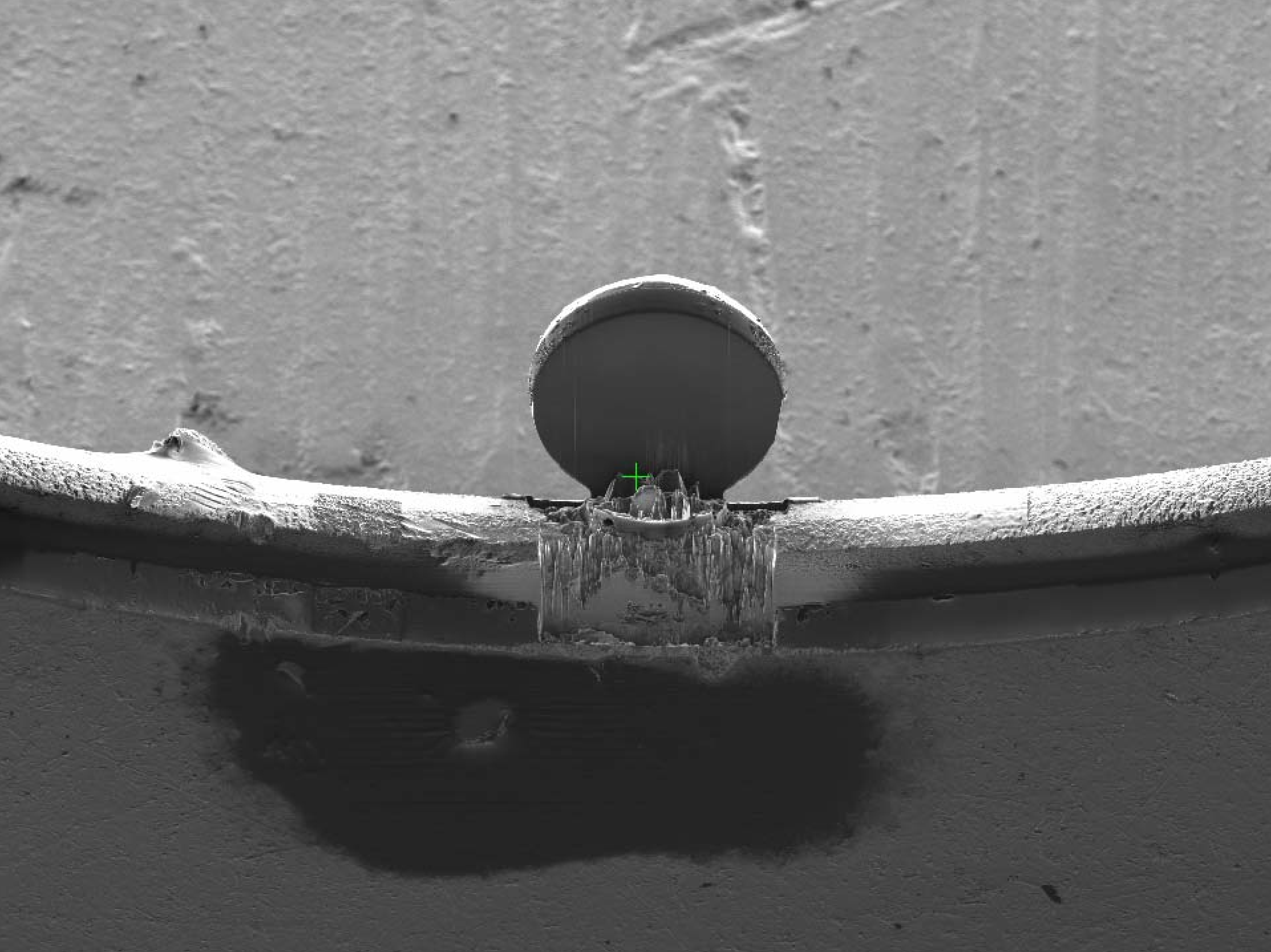
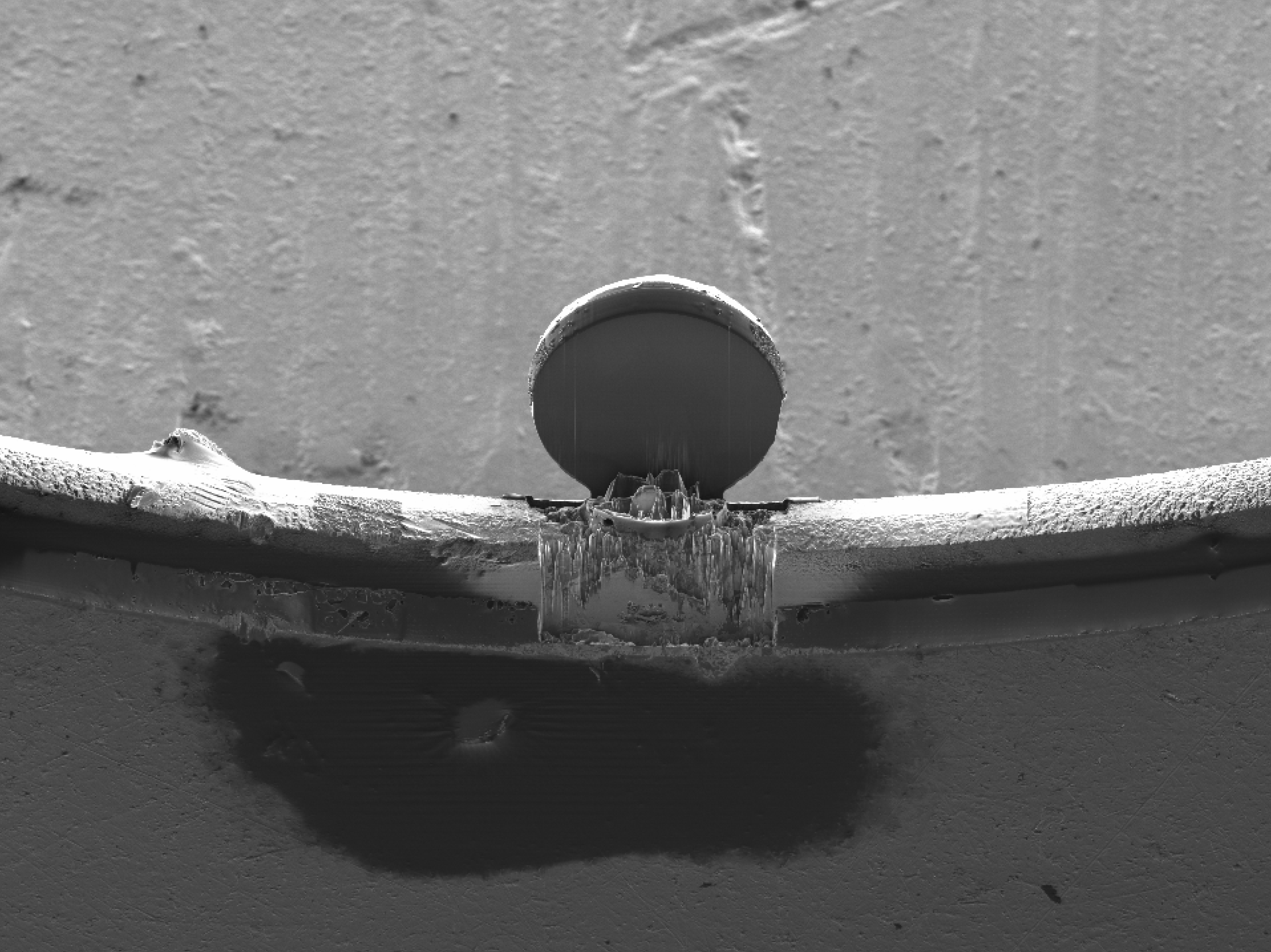
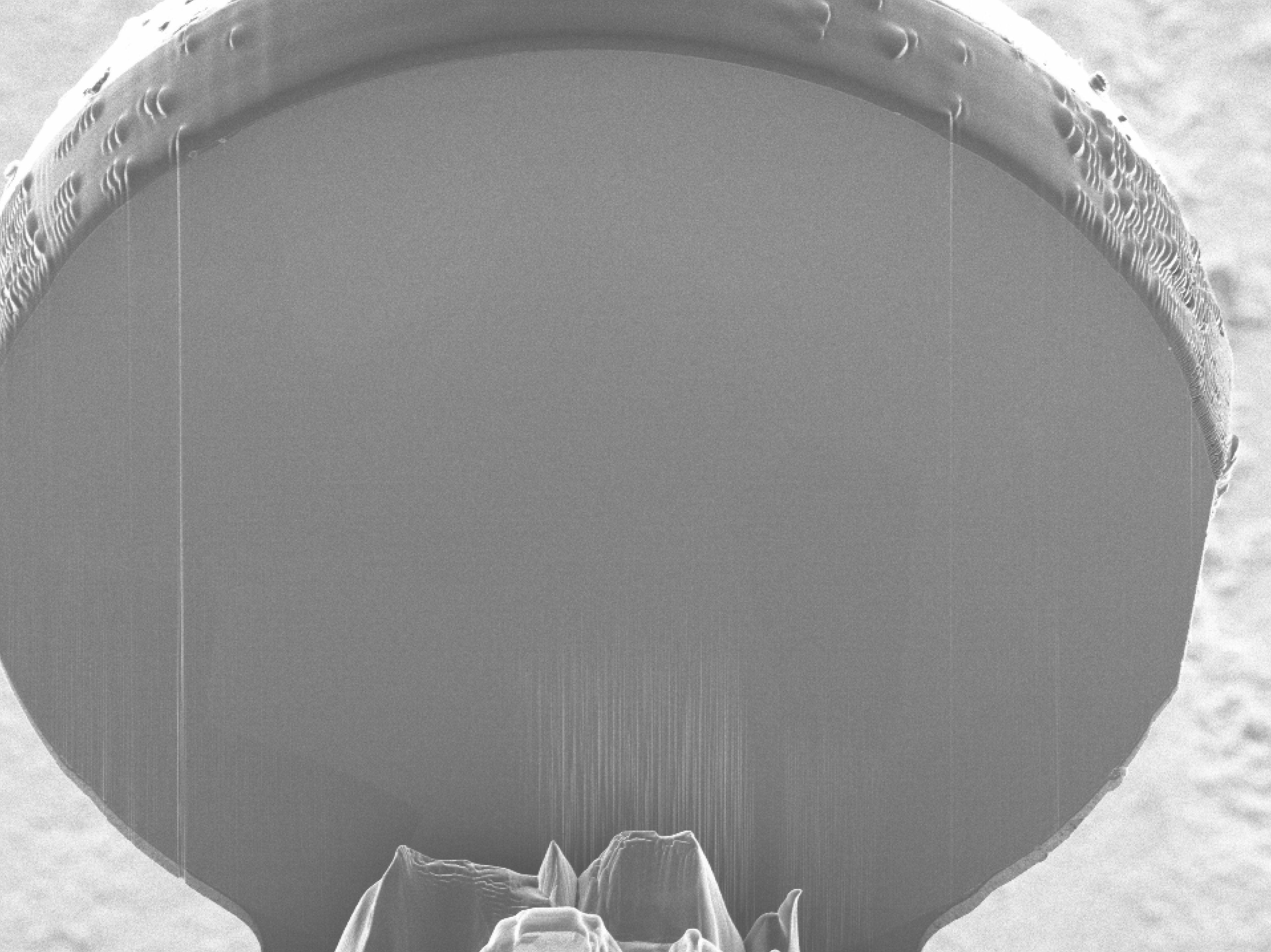
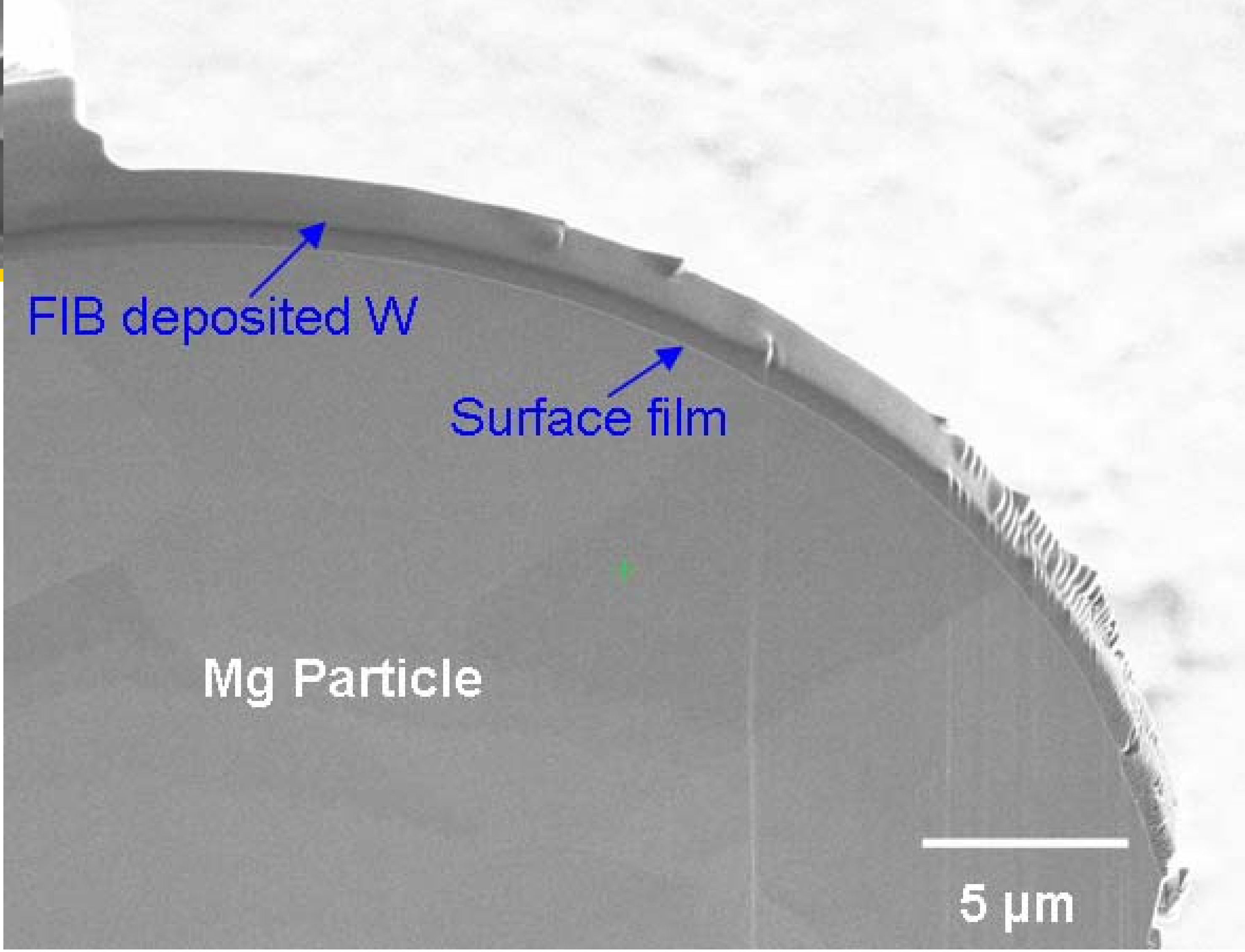


A Mg particle is mounted onto the edge of the TEM grid using an external lift-out tool

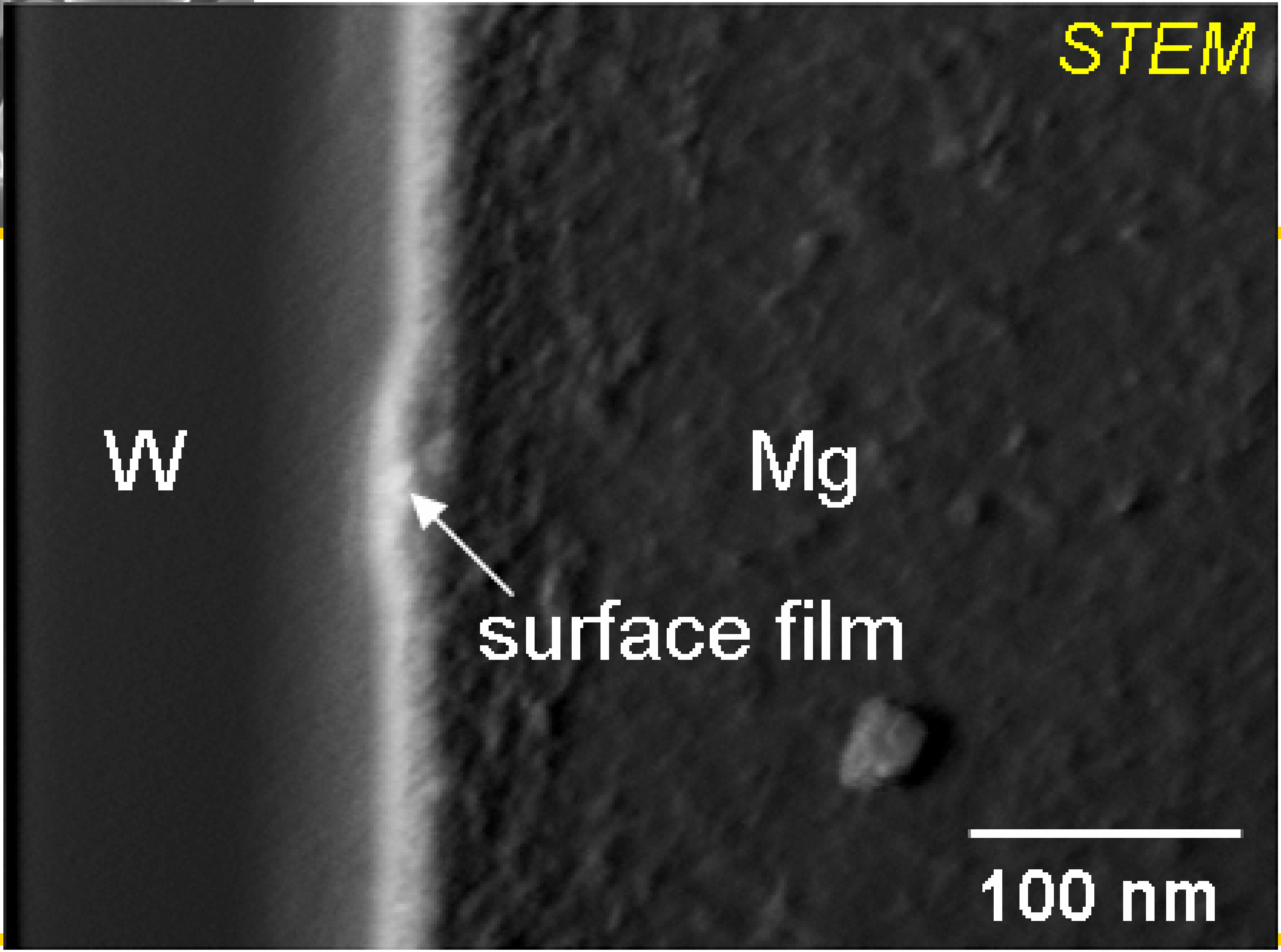








FIB secondary electron image showing the thin film formed on the Mg particle



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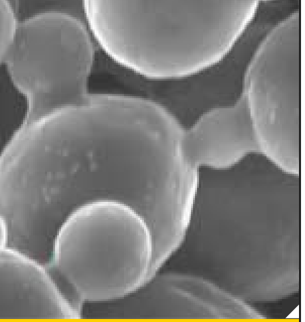
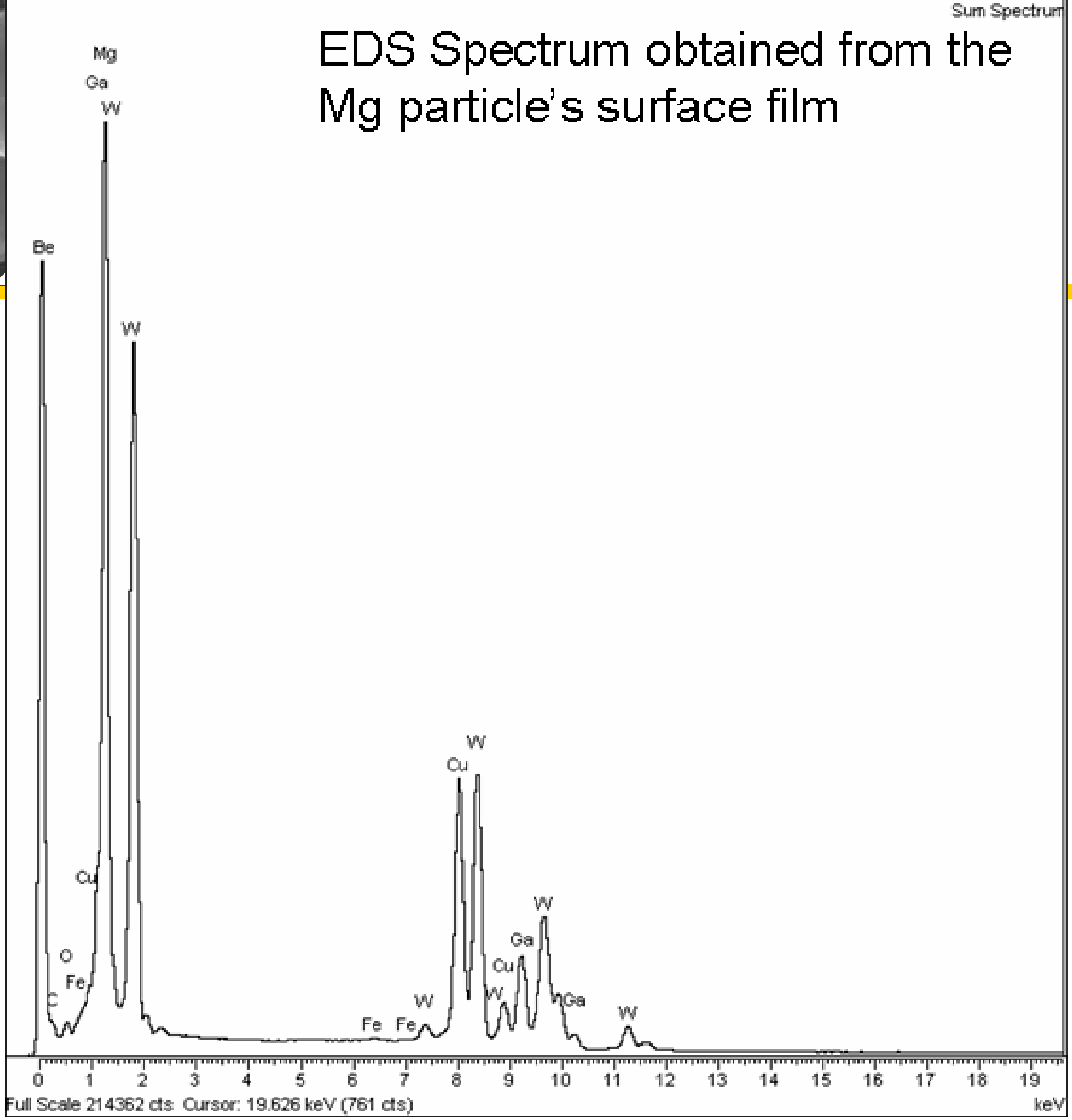
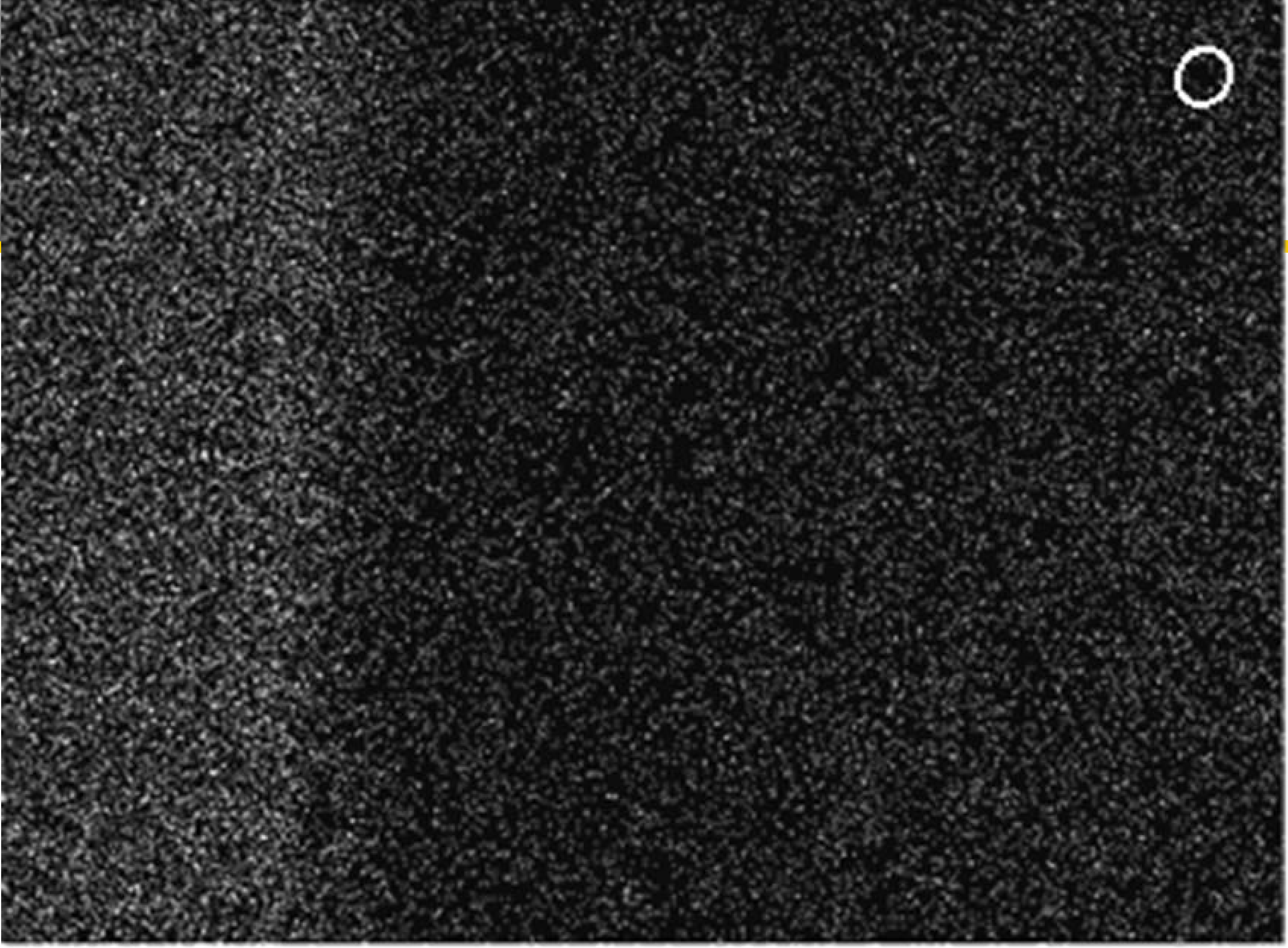


EDS Spectrum obtained from the Mg particle's surface film



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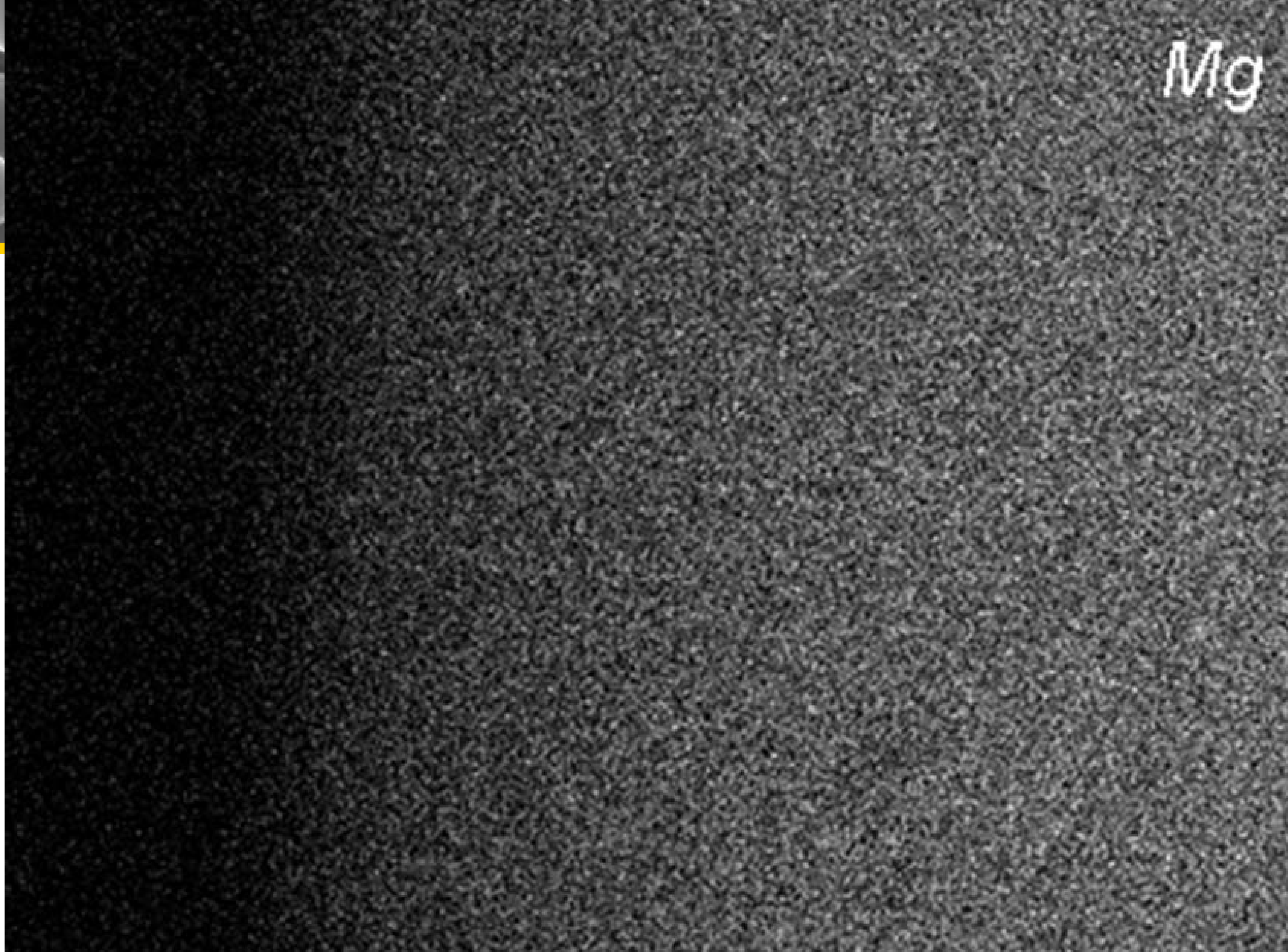
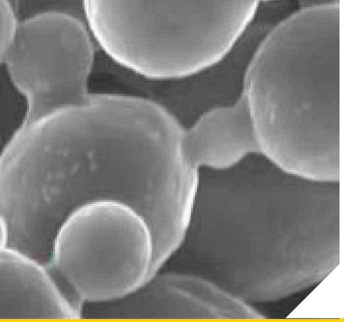
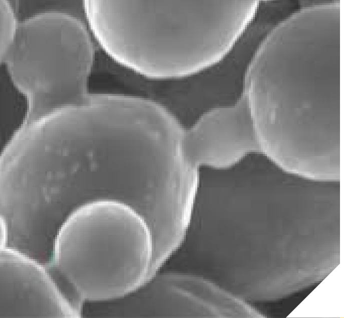

Mg



Future Work

- Continue FIB/TEM and XPS to identify layer constituents and thickness
- Confirm findings with AES, SIMS
- Determine decomposition reactions by thermal analysis (DSC, DTA, TGA)
- Identify reduction mechanisms of Ca and Y
- Add alloying additions for liquid formation, strengthening and corrosion resistance



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- Dr. Craig Bennett, Dr. Zeynel Bayindir

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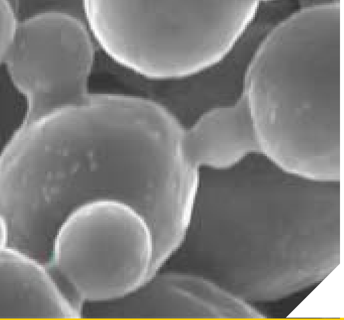

Thank you