



Nanoparticles generated by Friction Stir Welding: First EM/ EDS results

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Reason for the Study

- FSW is being used in a lab at UW
 - Any exposure risks to lab and students?
 - Little known about emissions from FSW and opinion was that there would be none or minimal.
- The objective of this study was to characterize exposures to airborne particles during friction stir welding (FSW) of aluminum, with a special emphasis on nanoscale particles
- This is the first study¹ to report on airborne exposures during FSW of aluminum alloys

¹Characterization of Exposures to Airborne Nanoscale Particles during Friction Stir Welding of Aluminum, submitted to *Aerosol Science and Technology*, February 2009.



Study Goals

- Test the hypothesis that fine and ultrafine aerosols are generated during FSW
- Measure physical & chemical properties of aerosols generated during FSW
- Conduct a comparative assessment of several research grade (very expensive and bulky) and practitioner grade (inexpensive and portable) aerosol instruments
 - Identify suites of essential instruments necessary for adequate characterization of fine and ultrafine aerosols
 - Standpoint of an occupational hygienist practitioner

The comparison assessment¹ will be published elsewhere and only briefly referred to in this talk.



Expected physical & chemical properties

Physical: Nothing expected based on Current literature

Chemistry		Al	Mg	Zn	Fe	Cr	Mn	Mo
Workpiece	AA 6061-T6	95.8-98.6%	0.8-1.2%	≤0.25%	≤0.7%	0.04-0.35%	≤0.15%	-
Workpiece	AA 5083-H	92.5-95.6%	4.-4.9%	≤0.25	≤0.4	0.05-0.25	0.4-1.0	-
Tool	H13 steel	-	-	-	89.4-91.6	5.0-5.5	0.2-0.5	1.2-1.75%

¹ Note that the workpiece thicknesses for the 6061-T6 and the 5083-H111 samples were 3.175 mm and 5.08 mm, respectively, and that workpiece thickness was not considered a variable of influence for the study.



Instrumentation used in this study

Name (Model)	Measures	Size range (μm)
REAL-TIME SAMPLERS		
EEPS (TSI 3090)	Size distribution and total number concentration	0.0056-0.56
APS (TSI 3321)	Size distribution and total number concentration	<0.5-20
NSAM (TSI 3550)	Total lung deposited surface area (single number)	0.01-1
DustTrak, PM2.5 inlet (TSI 8520)	Mass concentration (particle diameter <2.5 (μm))	≤ 2.5
DustTrak, PM1.0 inlet (TSI 8520)	Mass concentration (particle diameter <1.0 (μm))	
CPC (TSI 3007)	Total number concentration	0.010->1
P-Trak (TSI 8525)	Total number concentration	0.020->1
INTEGRATED SAMPLERS		
TP (Fraunhofer Institute of Toxicology, Germany)	Collects particles on a TEM grid over a predefined time period using a thermal gradient.	Broad: 0.001->100
ESP (courtesy of Dr. A. Miller, NIOSH)	Collects particles on a TEM grid over a predefined time period using a point-to-plane electrostatic corona discharge.	Broad: 0.001->100
WRASS (Naneum Ltd., UK)	Collects and sizes the aerosol over a wide size range (0.001-35 (μm)) in 12 stages, five of which are in the 0.001-250 nm range.	0.001-35
Personal breathing zone respirable dust (GK 2.69 cyclone, BGI Inc., Waltham, MA)	Collects respirable dust on a filter when operated at 4.2 L min ⁻¹ .	1-10(μm)

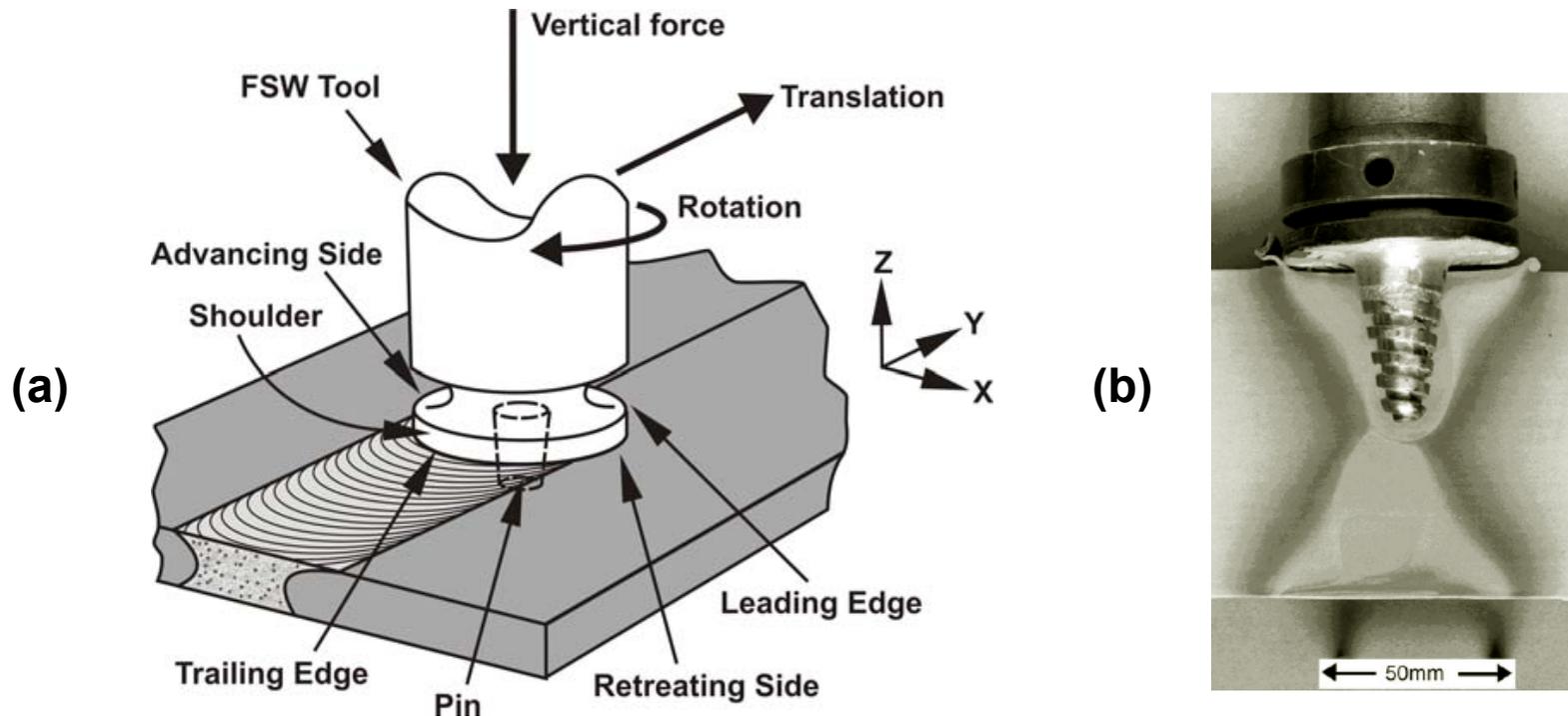


Outline

- Friction Stir Welding Experimental Overview
- EM Sample Collection and Analysis
- Results and Comparison to Other Instrument Data
- Next Steps



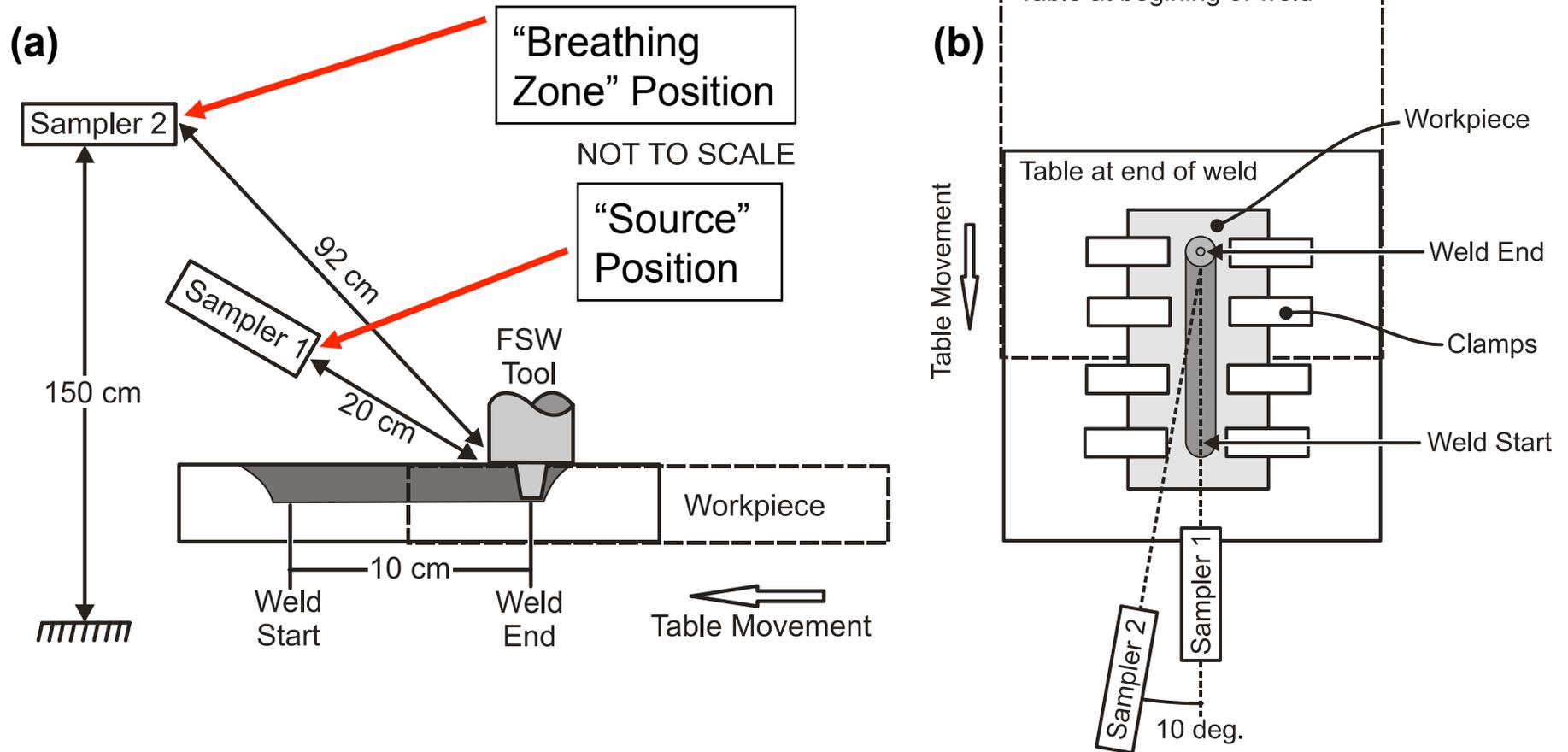
Friction stir welding (FSW) falls into the category of solid-state welding because it creates a joint without melting the workpiece.



(a) Schematic of FSW process and (b) FSW tool superimposed on a traverse section of a weld



Sampler Positions



Sampling locations: (a) side view, and (b) top view



Microscopes

LEO 1530 FESEM at UW



- Digital Controlled
- 1 nm resolution at 20 kV and 3 nm at 1 kV
- 200 V – 30 kV
- Large specimen chamber
- Motorized eucentric stage
- Thermo Scientific System 6 with 10mm² SDD at 35° TOA (not Shown)



Hitachi S-5500 FESEM/STEM at RJLG



- 0.4 nm at 30 kV and 1.6 nm at 1kV
- Magnifications up to 2,000,000x
- SE and BSE imaging
- BF-STEM and DF-STEM imaging
- Bruker Quantax EDS with 10mm² SDD at 35° TOA

VERY USEFUL for this study is the ability to simultaneously collect SE, BF-STEM or DF-STEM images, and EDS spectra without having to change the specimen position!



EM Sampling and Analysis Conditions

Sample Collection:

- Particles collected on Cu grids with SiO films
- Grids placed in a storage box and labeled by precipitator, case, and replicate number
- Samples coated with a thin (< 10 nm) layer of carbon to prevent particles from popping off the grid as the beam built up charge on the particles
- EDS peak artifacts from grids, film and coating include C, O, Si, and Cu spectrum peaks and should be disregarded

Acquisition conditions:

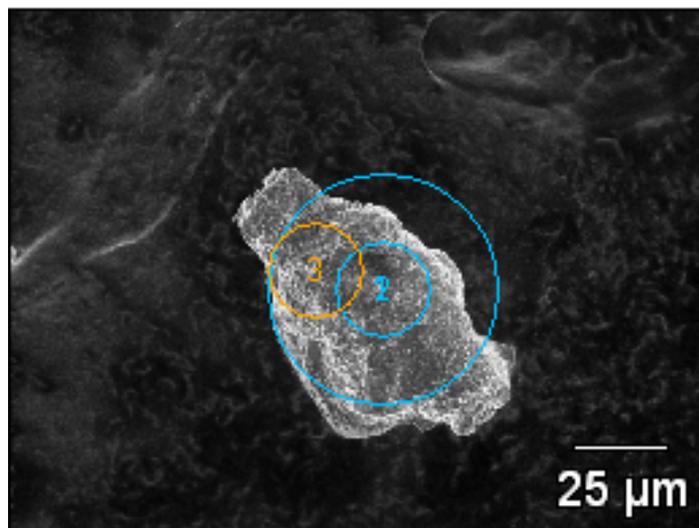
- Initial Data acquired on LEO 1530 FESEM at UW, but smaller (200nm) particles NG! No contrast. Look for a better machine!
- Data acquired on Hitachi S-5500 at RJ Lee Group, Inc. (RJLG)
- Secondary electron (SE) images collected at 2 kV and dark field- (DF) and bright field- (BF) STEM images collected at 20kV
- EDS spectra collected for 100 or 300 seconds at 5kV or 20kV with a 10 mm² silicon drift detector (SDD) at 35° takeoff angle (TOA) on both microscopes



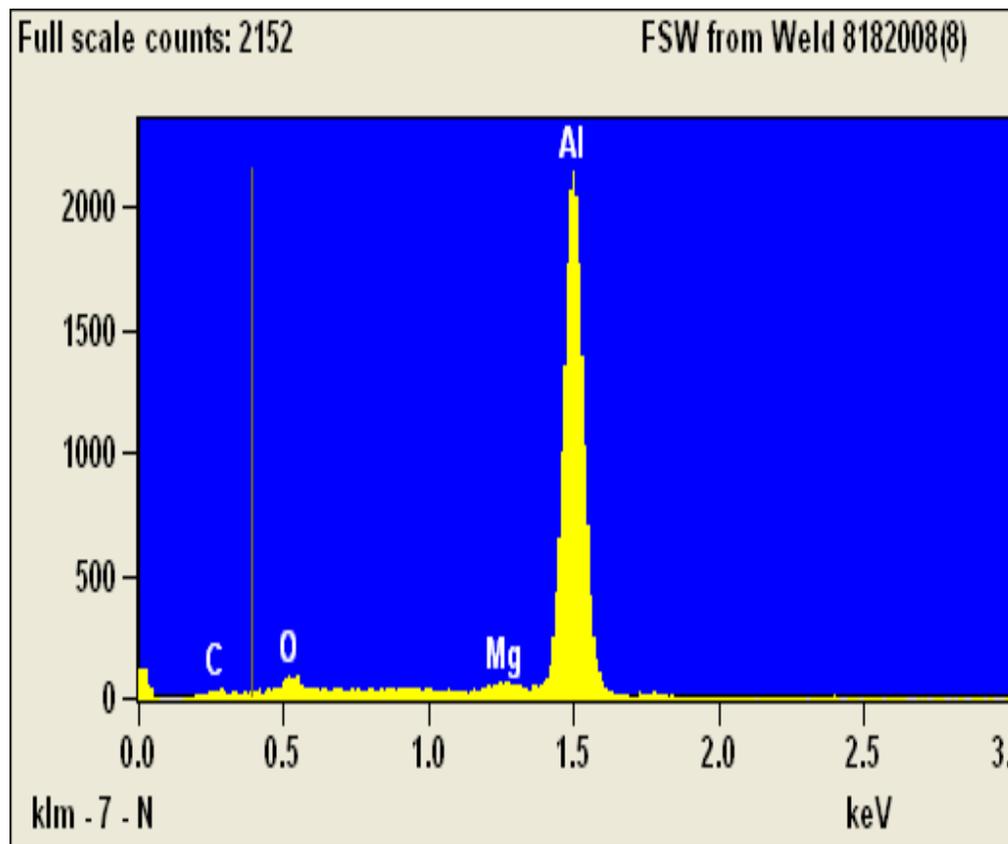
SEM Images and Particle Size Distribution



First “quick check”: Double sided carbon tape pressed into a weld



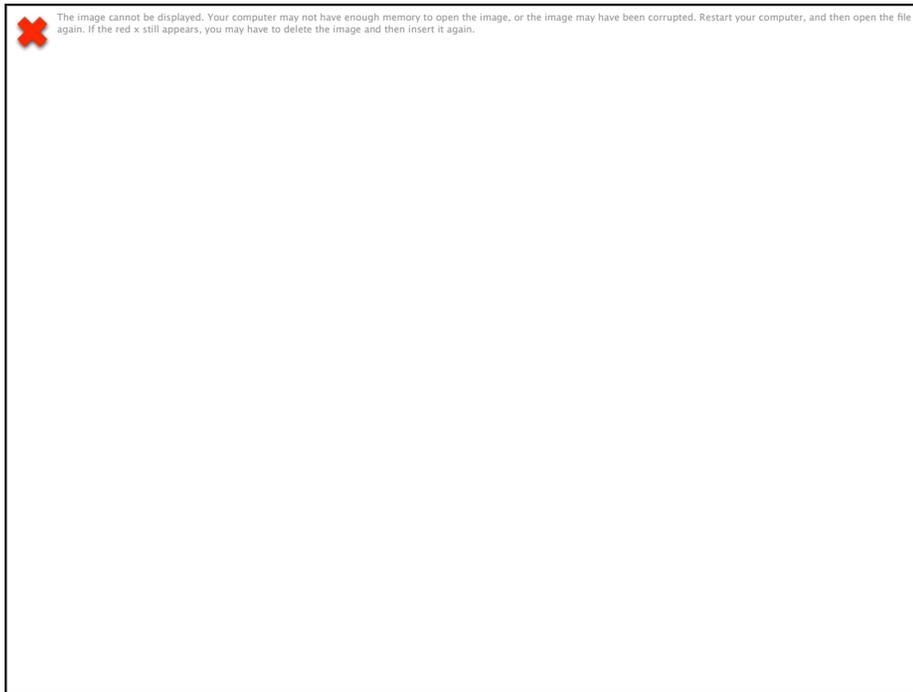
- Validated Particle Generation from 6061-T6 aluminum sample during FSW
- Particles this large were rarely collected on the samplers



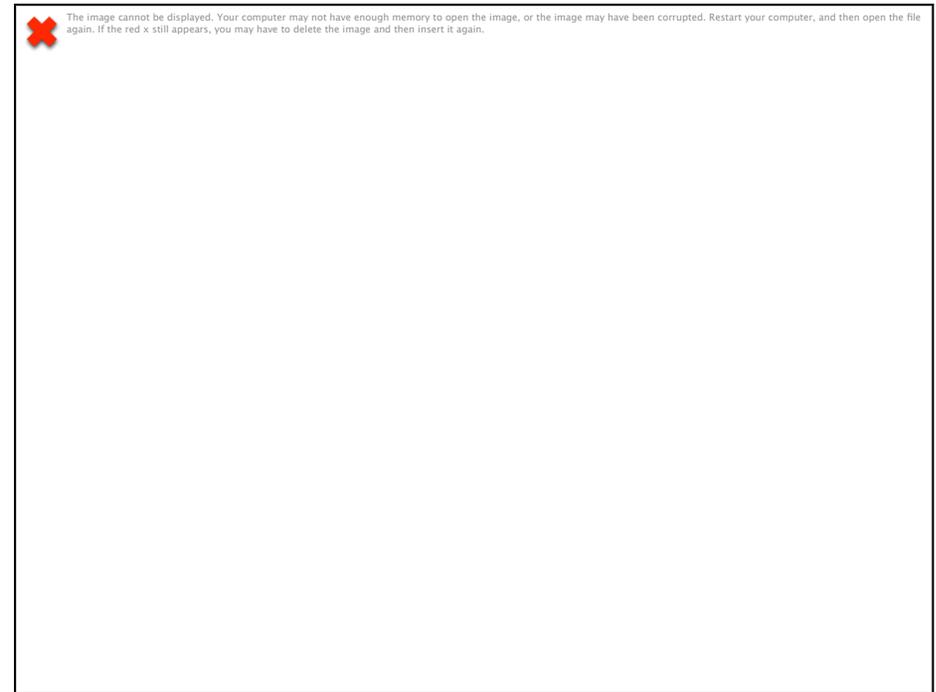
- LEO 1503: 5 KV, 30 second EDS acquisition



Typical SEI Images from the Source and Breathing Zone locations



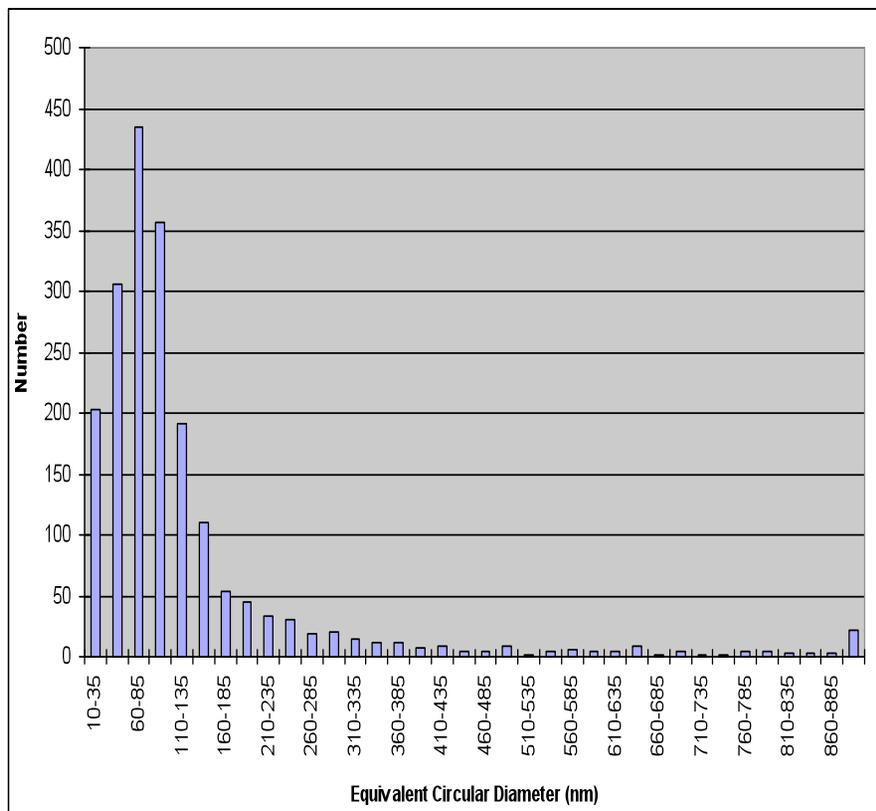
Secondary electron image at 2 kV and 4000X from a heavily loaded grid from ESP at the Source in Case 1



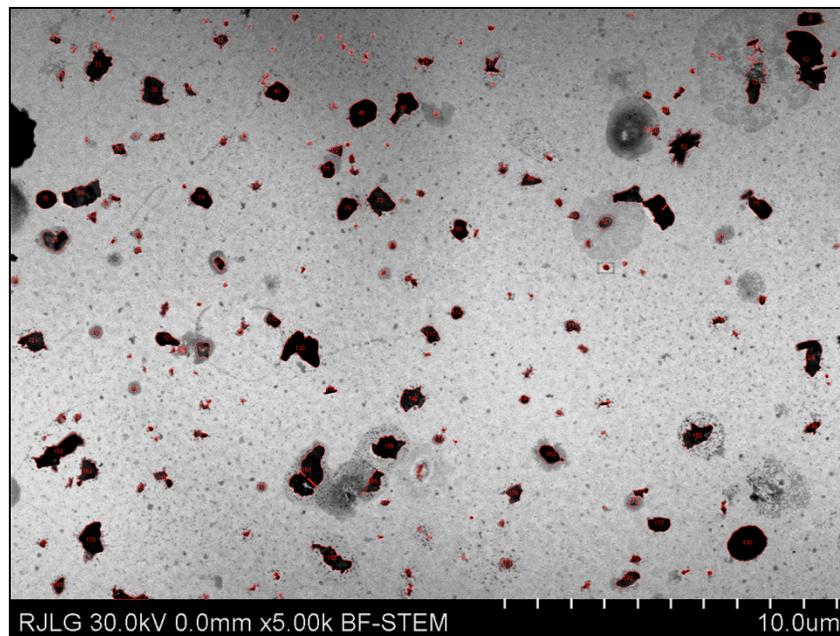
Secondary electron image at 2 kV and 4000X of a lightly loaded sample from TP at the Breathing Zone in Case 1



Particle Size distribution from 4 5000x BF-STEM Images (measured via IMAGEJ)



Particle size distribution obtained from the ESP source sample from a series of 4 images



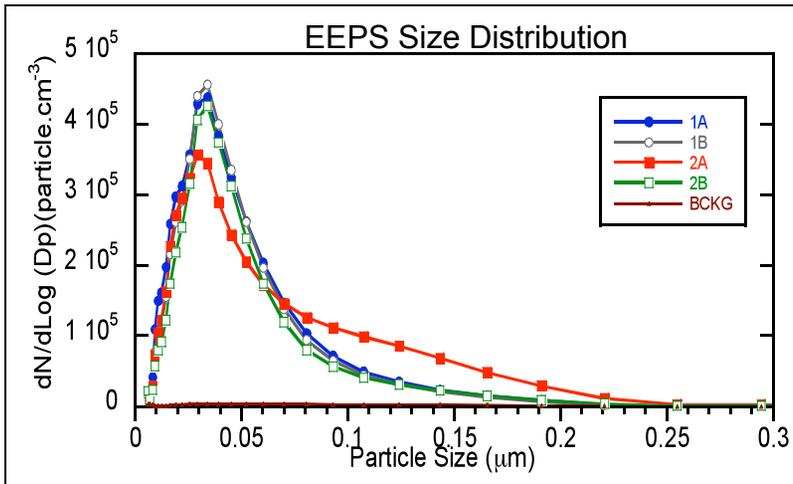
Sized Image: Most consistent using BF-STEM. Thresholding smaller particles is a difficult process.

Mystery! What are those big blotchy films(?) surrounding some Particles??





Size Distribution Comparison



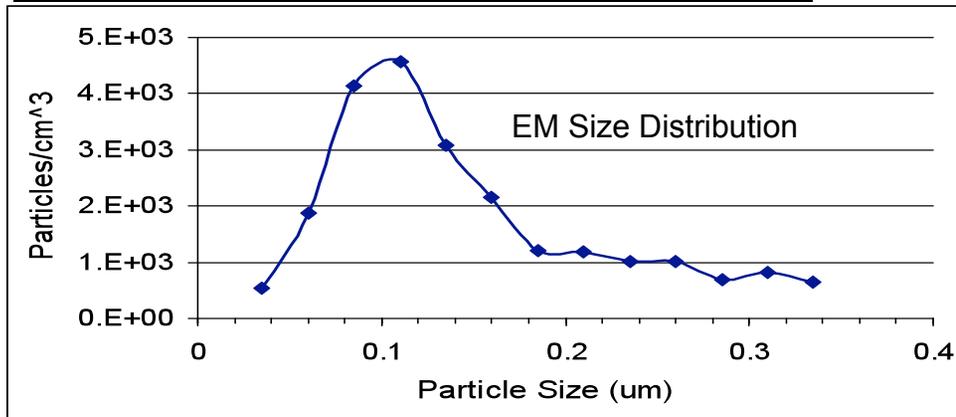
Basic results: Both EM and EEPS

- FSW generates significant amount of nanometer size particles at the Source AND BZ.
- Max at 30NM-40nm peak is 100X BKGND level
- A secondary peak at 550nm is 10X BKGND
- BZ maximum levels are 10X BKGND

NOTE: Levels at the BZ are reduced to background with the use of a local exhaust ventilator system near the workpiece

Differences: EM to EEPS

- Overall Qualitative agreement of methods is pretty good!
- EM Distribution cuts off at 20nm, minimum pixel size!
- EM Peaks at 100 nm and is broader
- Maximum shift and broadening may result from more agglomerated particles in EPS collection & longer sampling time versus EEPS



Note: Vertical scales are different! Calibration of EM data for sampled volume is a work in process. Also, EPS may not deposit sample uniformly on the grid-we are checking

Lesson Learned: Pick your pixel size intelligently based on an initial survey!

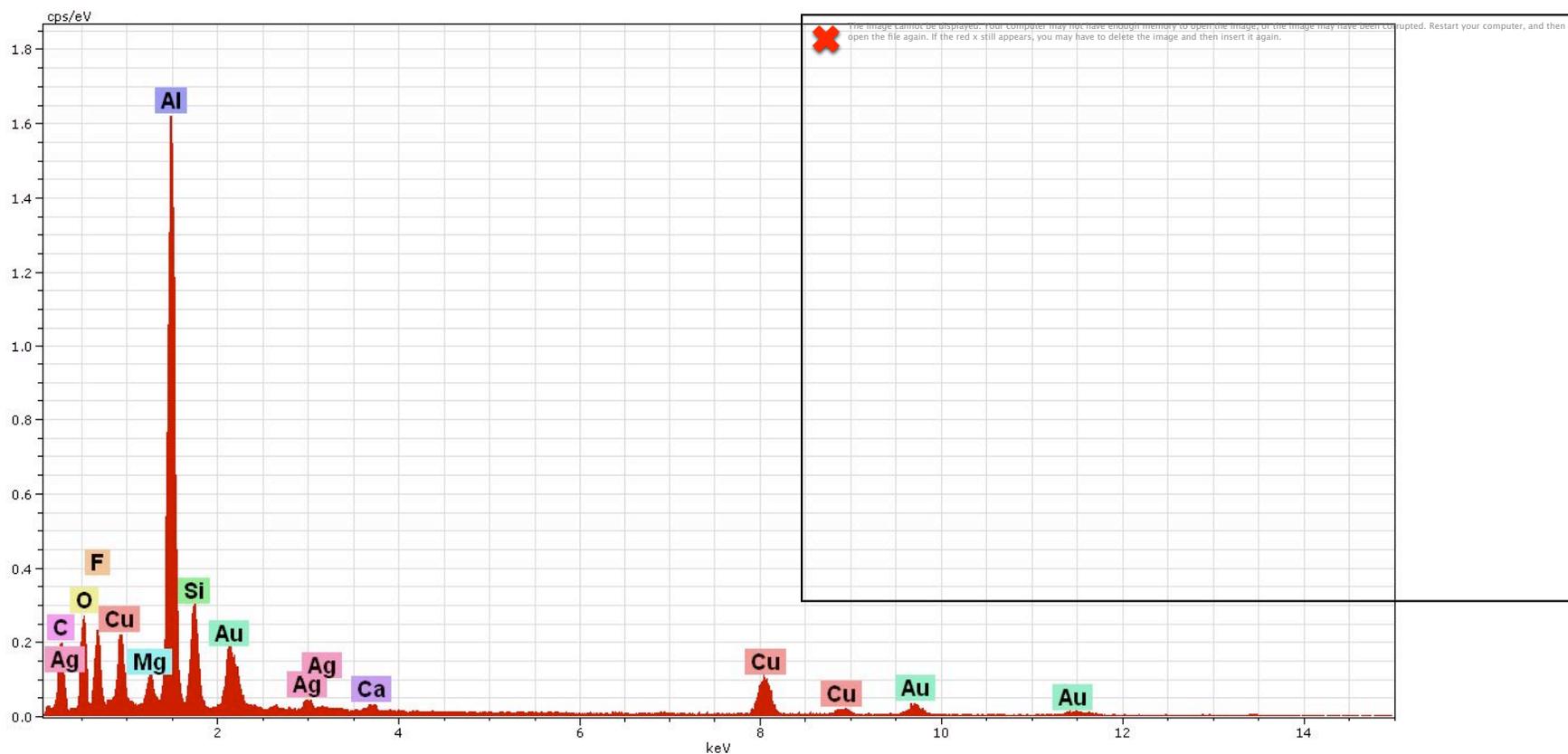


Morphology and Chemistry

Examples shown in the following slides cover the peaks in the extended size distribution and show distinct variation in morphology versus size



Large Particle Source Position

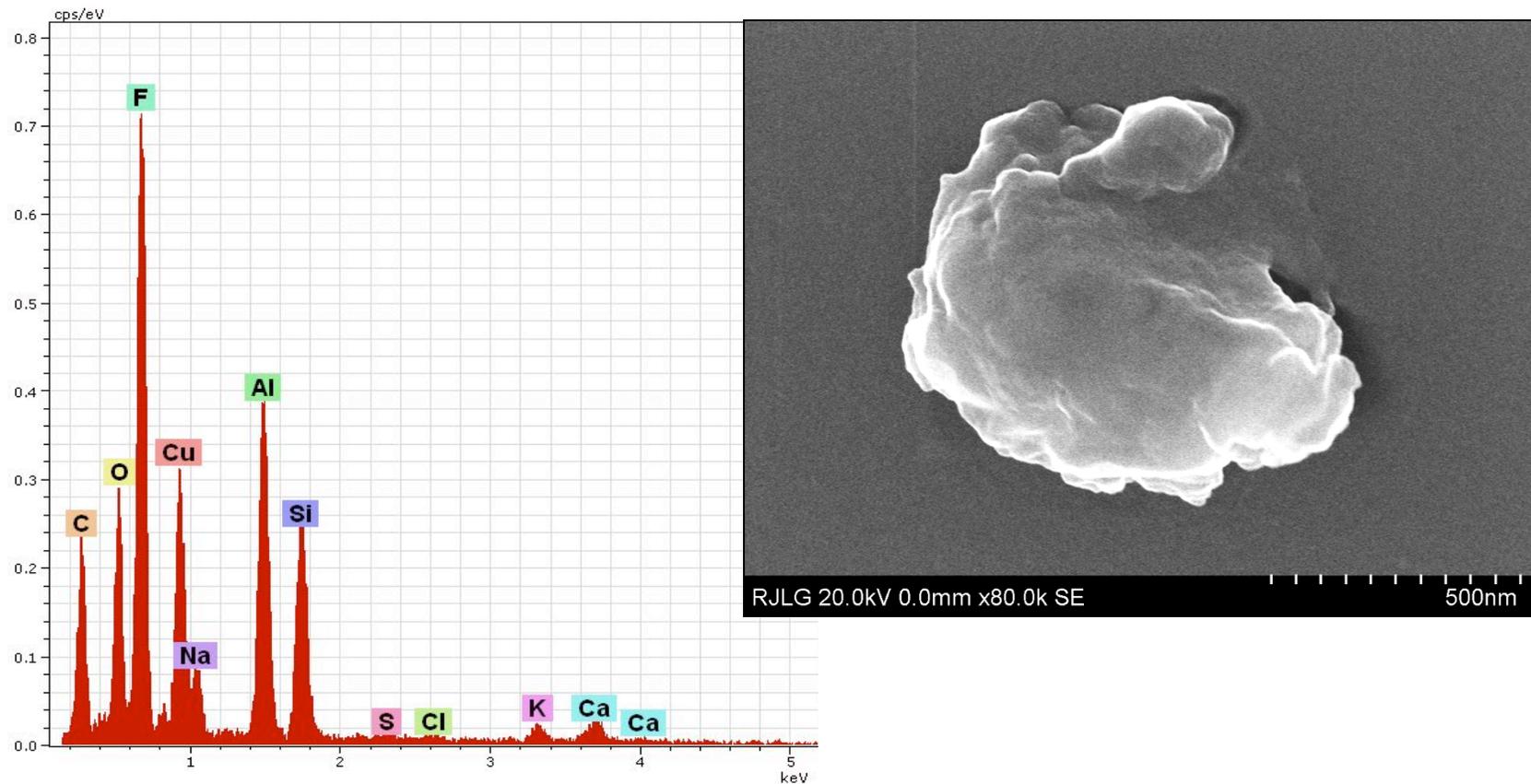


SE image of a flake-like larger particle with EDS showing high Mg, Al content, but also Ag, Ca and Au. This aluminum particle was collected with ESP (Source Position)





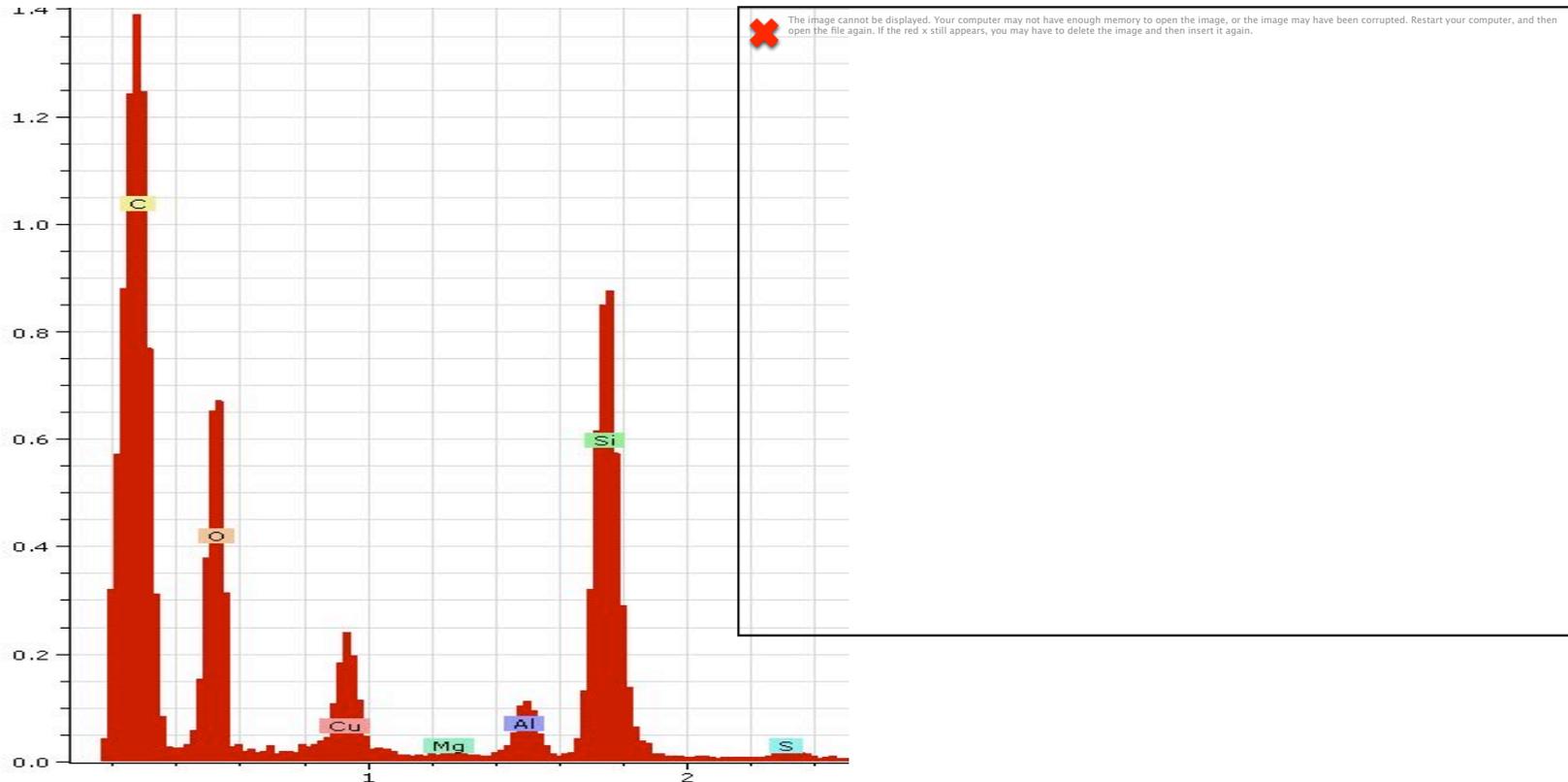
Large Particle BZ Position



Large Al particle collected with TP (Case 2 BZ sample position) The EDS spectra shows Al, F and small amounts of other elements. The fluorine is believed to come from overheating the tip of the TP



Agglomerated Particle Source Position

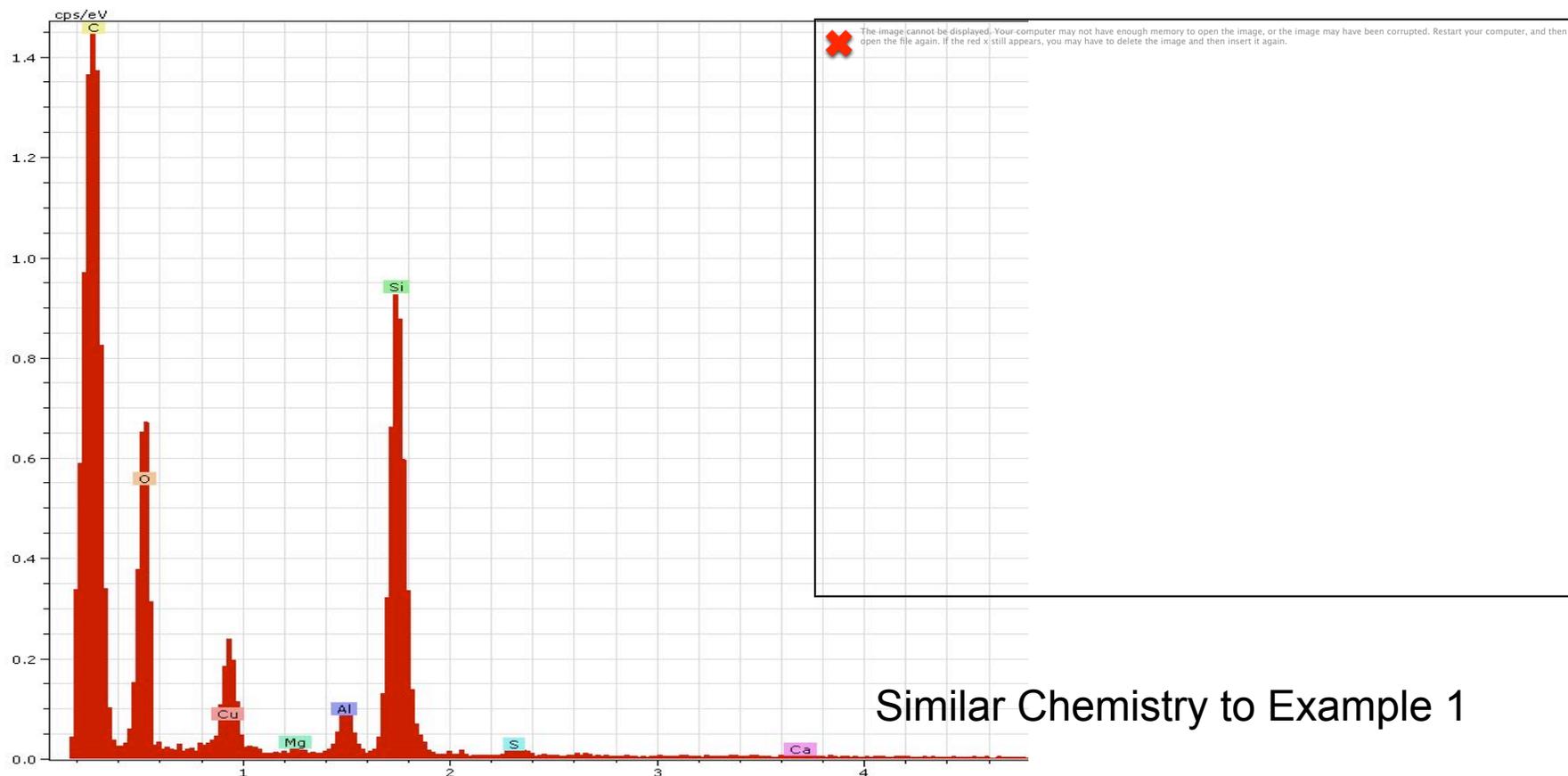


Agglomerated particle collected from ESP at source, and EDS from that particle showing presence of major elements (Mg, Al) present in 6061-T6 aluminum, as well as S, an artifact peaks



Agglomerated Particle Source Position

Example 2

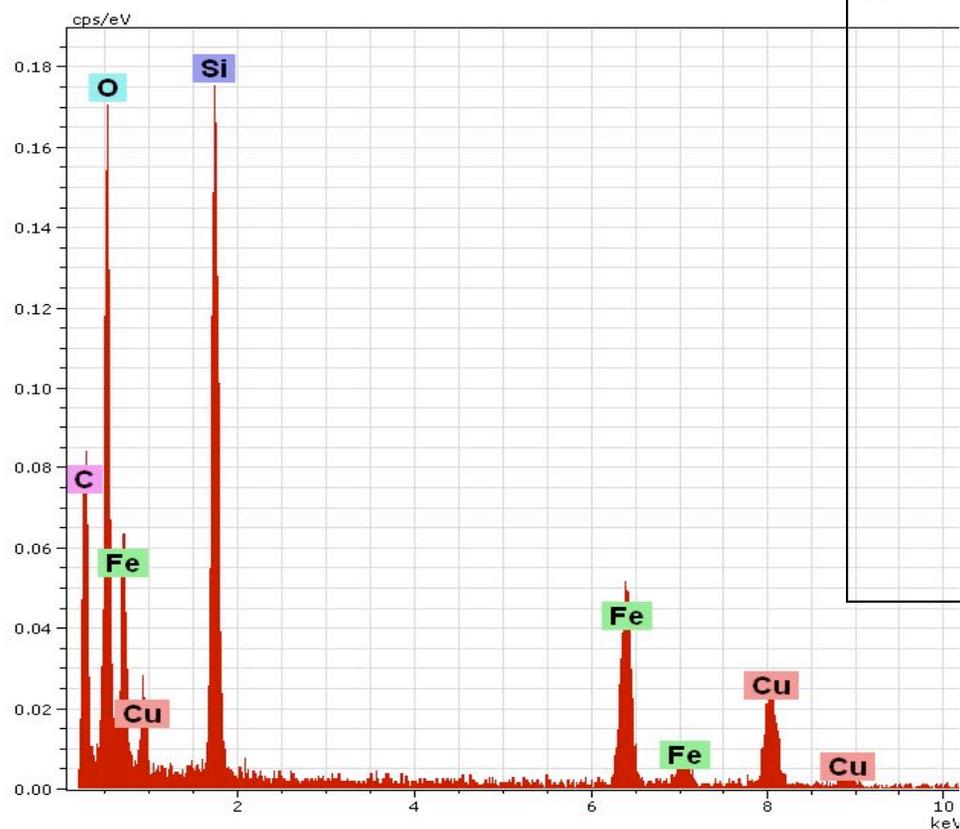


Similar Chemistry to Example 1





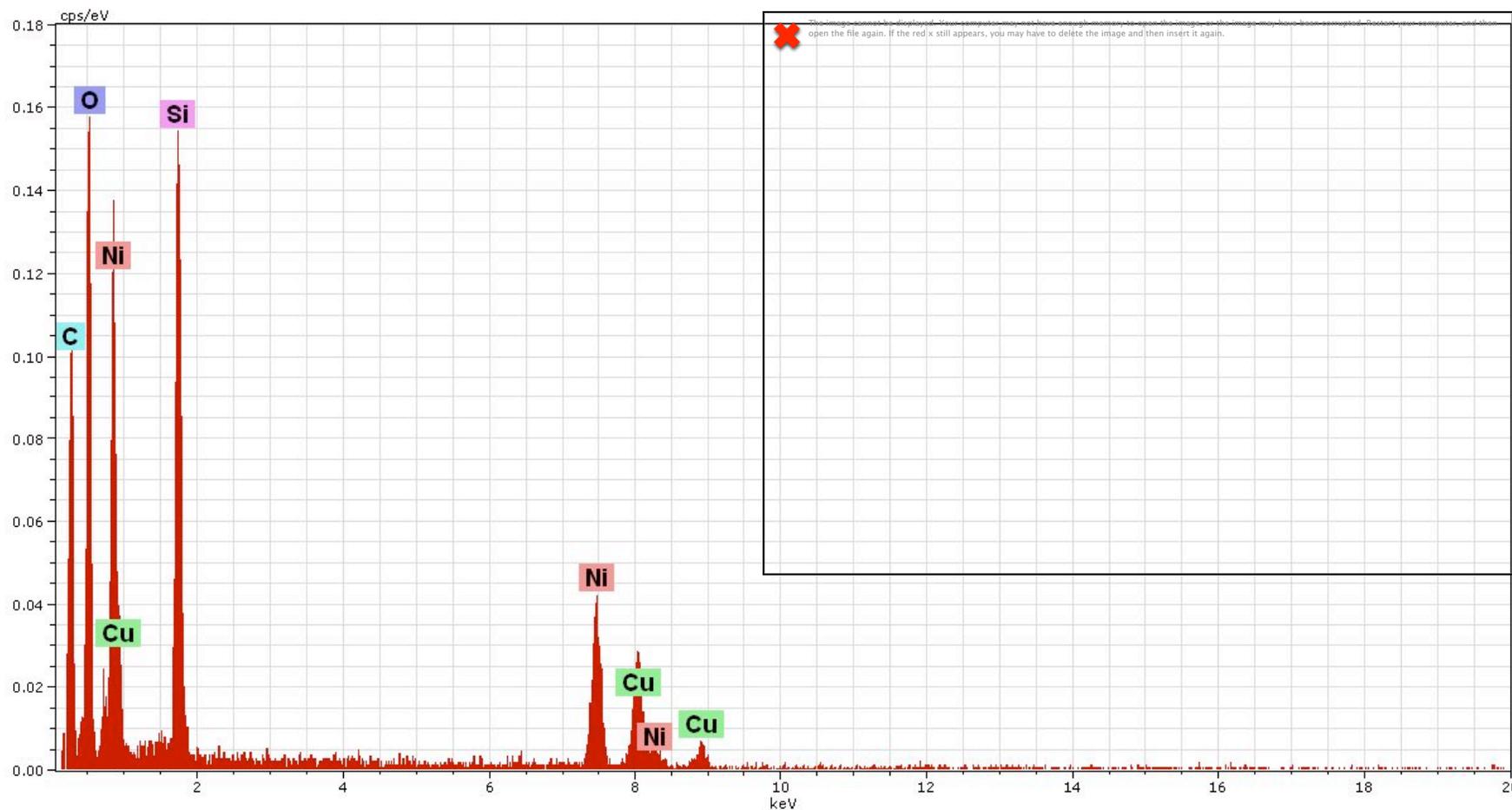
Spherical Particles: Seem to be smaller, and pure elements



60 nm Fe sphere on irregular SiO₂ particle collected from the Source position, ESP



Spherical Particles: Seem to be smaller, and pure elements



50 nm Ni particle, Source Grid, ESP, Case 1



Morphology and Chemistry Results

- **Morphology results**

- Observed three morphologies and a “mystery” in both Source and Breathing Zone grid samples:

- Larger “Chip like” Particles, (500 nm to several microns)
- Agglomerations, (200 to 500 nm)
- Small spherical particles, (<100nm)
- Mystery splatter in BF-STEM images

- **Chemistry results:**

- All major elements (Al, Mg) and some minor ones (Fe, Zn, Cr) present in the 6061-T6 sample were qualitatively identified by EDS, suggesting that the FSW workpiece is the source of abundant nanoparticles!

- Larger particle and agglomerated particles (500 nm to 2 μ m) contained unexpected elements (S, Ca, Cl, Na, K, Ag) whose origin is unknown, but suspected to come from ambient background
- Smaller particles (<100nm) appear to be spherical and pure elements. Origin is unknown, but suggests local heating in FSW can exceed the melting point of materials which melt at higher temperature than the base alloy! This is unexpected!



Conclusions and Future Work

- FSW emits measurable concentrations of ultra-fine aerosols!
- The levels can be controlled effectively with local exhaust ventilation. If particulate emissions from FSW are properly controlled, the process appears to be safer than fusion welding
- EM/EDS is an effective tool for qualitative measurement of the size distributions and chemistry of ultra-fine aerosols
- Quantitative aerosol analysis requires EM/EDS to be correlated to other monitoring data
- Future work:
 - Refining the EM size distribution data and comparison to EEPS
 - Checking the uniformity of the EPS deposition on grids
 - Determining the origin of the “mystery” splatter blobs in the BF-STEM images



Acknowledgments

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Thank You!
Questions?



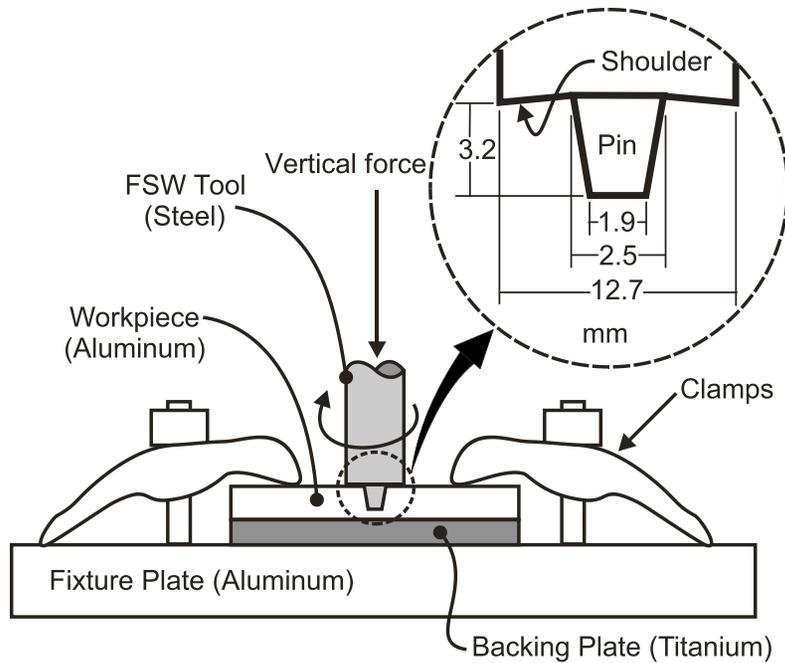


A Complex Study

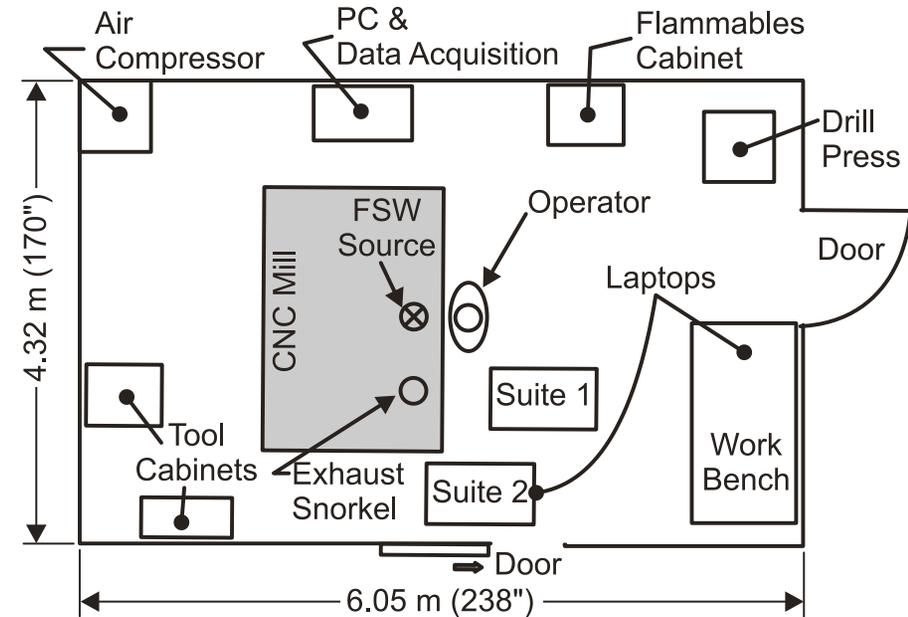
- Complex because:
 - Lack of prior exposure data on FSW process
 - What instruments should or can be used?
 - What protocols to adopt for sampling?
- Complexity required a collaboration
 - 11 researchers from 5 institutions
 - 12 different monitoring instruments
 - 2 instruments collected samples for EM analysis on 3 mm TEM grids
- This Paper focuses on EM/EDS analysis and results



Welding and Lab Layout



Schematic of friction stir welding apparatus



Friction stir weld laboratory layout



Spherical Particles: Seem to be smaller, and pure elements

