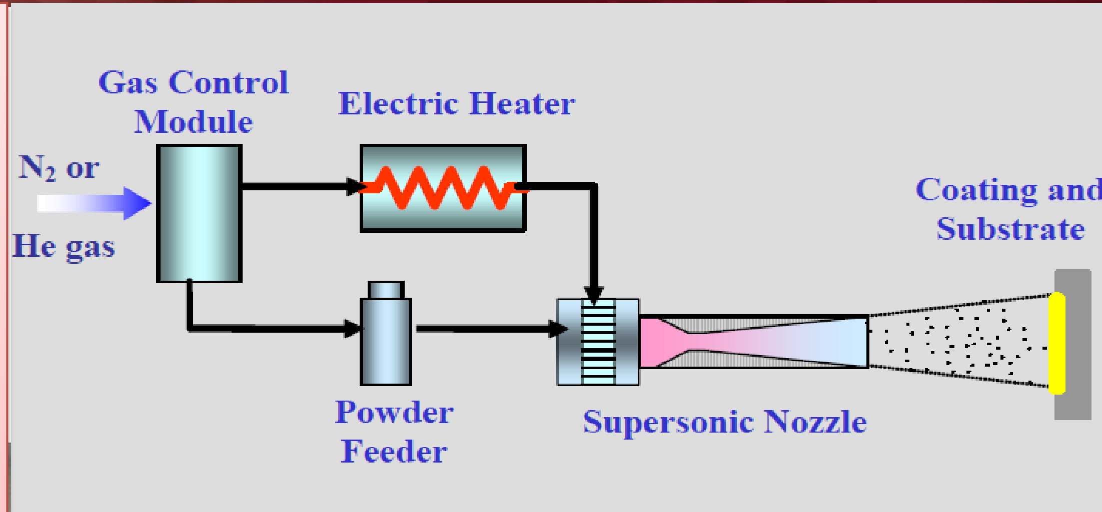
# Cold Spray Action Team

# Materials Characterization of Pure Copper Consolidated by Liquid Particle Acceleration and the Cold Gas-Dynamic Spray Process




Victor Champagne

# Objective

** Compare materials characterization data obtained from bulk samples of pure copper consolidated by Liquid Particle Acceleration (LPA) and the Cold Spray (CS) Process.*

- Description of how LPA and CS bulk samples were produced
- Powder Feedstock (powder size, shape and distribution)
- Surface Finish
- Microstructural Analysis (porosity content and grain refinement)
- Conductivity
- Hardness Testing
- Inert Gas Fusion (determination of oxygen content)
- Discussion of Results
- Conclusions

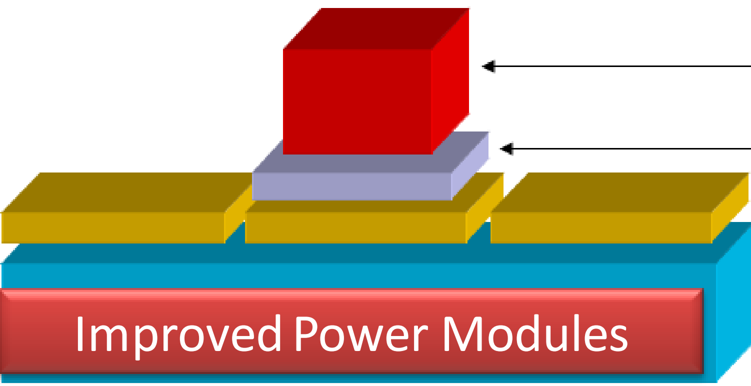
# Uses of Cold Spray Copper

## Antimicrobial Coatings

**Cold Spray Copper Coating has demonstrated UP TO >99.999% (log $_{10}$ >5.8), of Staphylococcus aureus-Methicillin resisant (MRSA) (ATCC 33592) following 2 hour exposure period at room temperature (23.0˚ C**

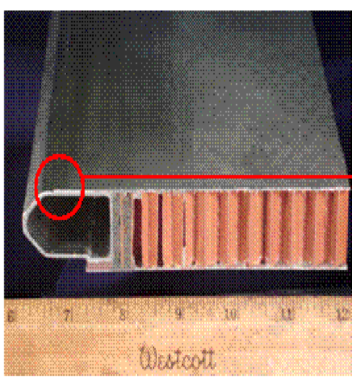
Navy Helicopter Gear

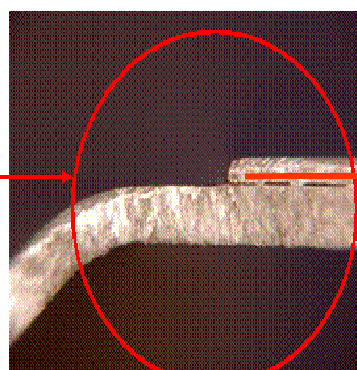
Thermally conductive copper coatings on steel.

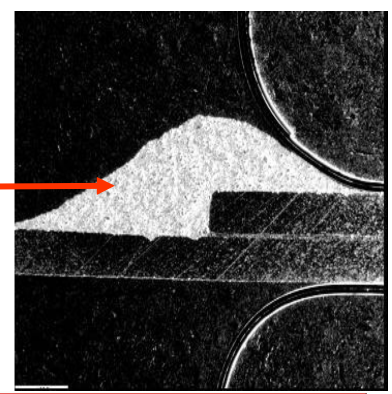


| Material | CTEx106 1 / K | Thermal Conductivity W / mK |
|---|---|---|
| Silicon | 3.6 | 150 |
| Solder | 25 | 50 |
| Copper | 17 | 400 |
| Aluminum Nitride | 4.4 | 180 |

Improved Power Modules







Provide adequate EMI shielding for HMMWV Shelters

# Specimen Fabrication and Determination of Process Parameters

**Phase II SBIR Topic:** A09-050
**Title:** Consolidation of Materials by Liquid Particle Acceleration
**Proposal:** A2-4284
**Title:** "Liquid Accelerated Cold Spray Using Ultra-High Pressure Jets"
**Awarded to:** Ormond LLC, Dr. Tom Butler

**Conventional Cold Spray:** MidAmerica, Webster, MA., Mike Parzych

- Ormond measured the velocity and temperature of the large and the small particles 750 m/s and 343 °C.

- ARL modeled the process parameters using nitrogen, yielding ~700 m/s and 344 °C at the nozzle exit
  - starting with gas temp. of 550 °C and 580 psi.

# Sample Identification

**CS = Cold Spray**

**LPA = Liquid Particle Acceleration**

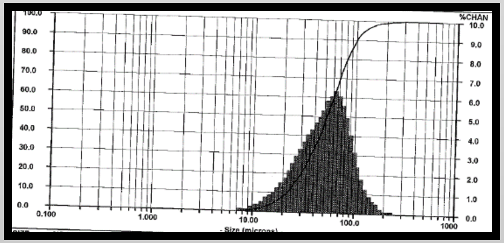
**Cu Powder – 500A (%Cu 99.73)**

- **D90 29.0um**
- **D50 18.0um**
- **D10 10.0um**

**Cu Powder– 151 (%Cu 99.81)**

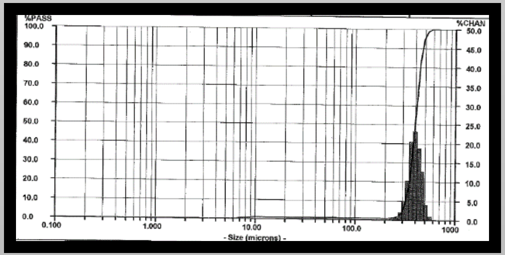
- **D90 101.3um**
- **D50 53.90um**
- **D10 21.90um**

Wider Particle Distribution

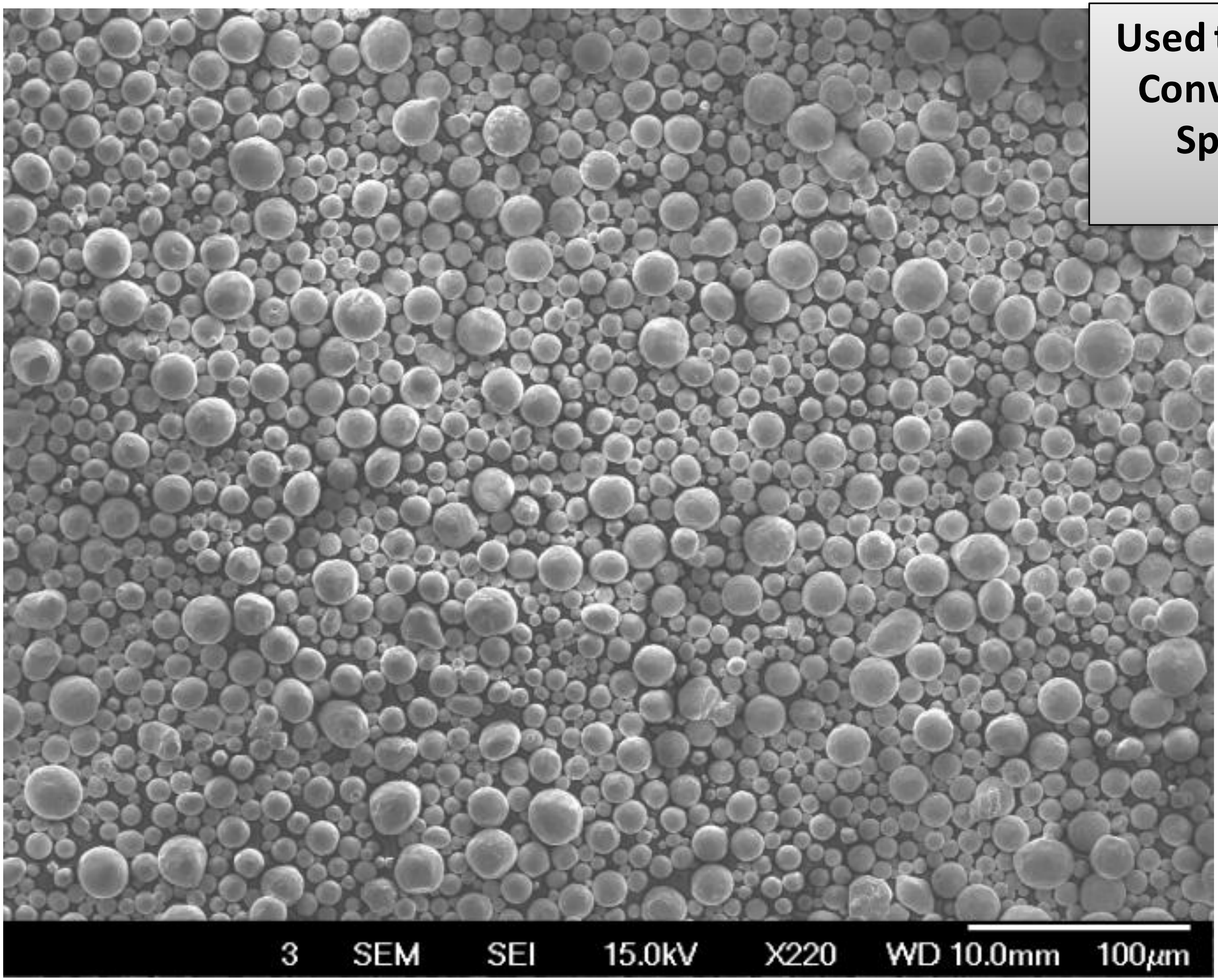


- **Cu Powder – 46HP (%Cu 99.83)**
  - **D90 478.9um**
  - **D50 398.3um**
  - **D10 326.2um**

Narrow Particle Distribution



# Cu Powder – CS 500A

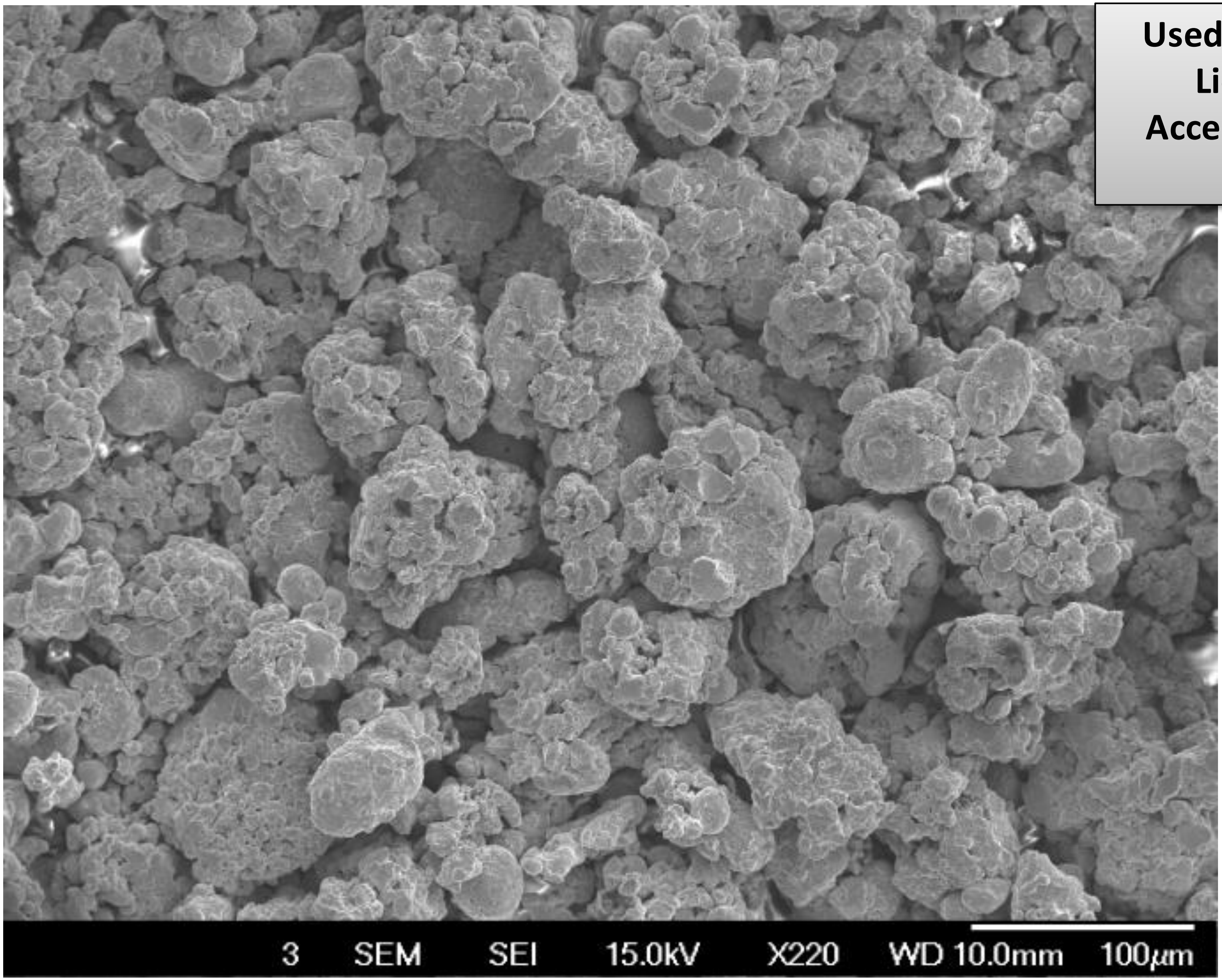



**Used to fabricate the Conventional Cold Spray Sample CS-500A**

- **%Cu 99.73**
- **D90 29.0um**
- **D50 18.0um**
- **D10 10.0um**

- Gas Atomized
- Spherical

# Cu Powder– LPA 151

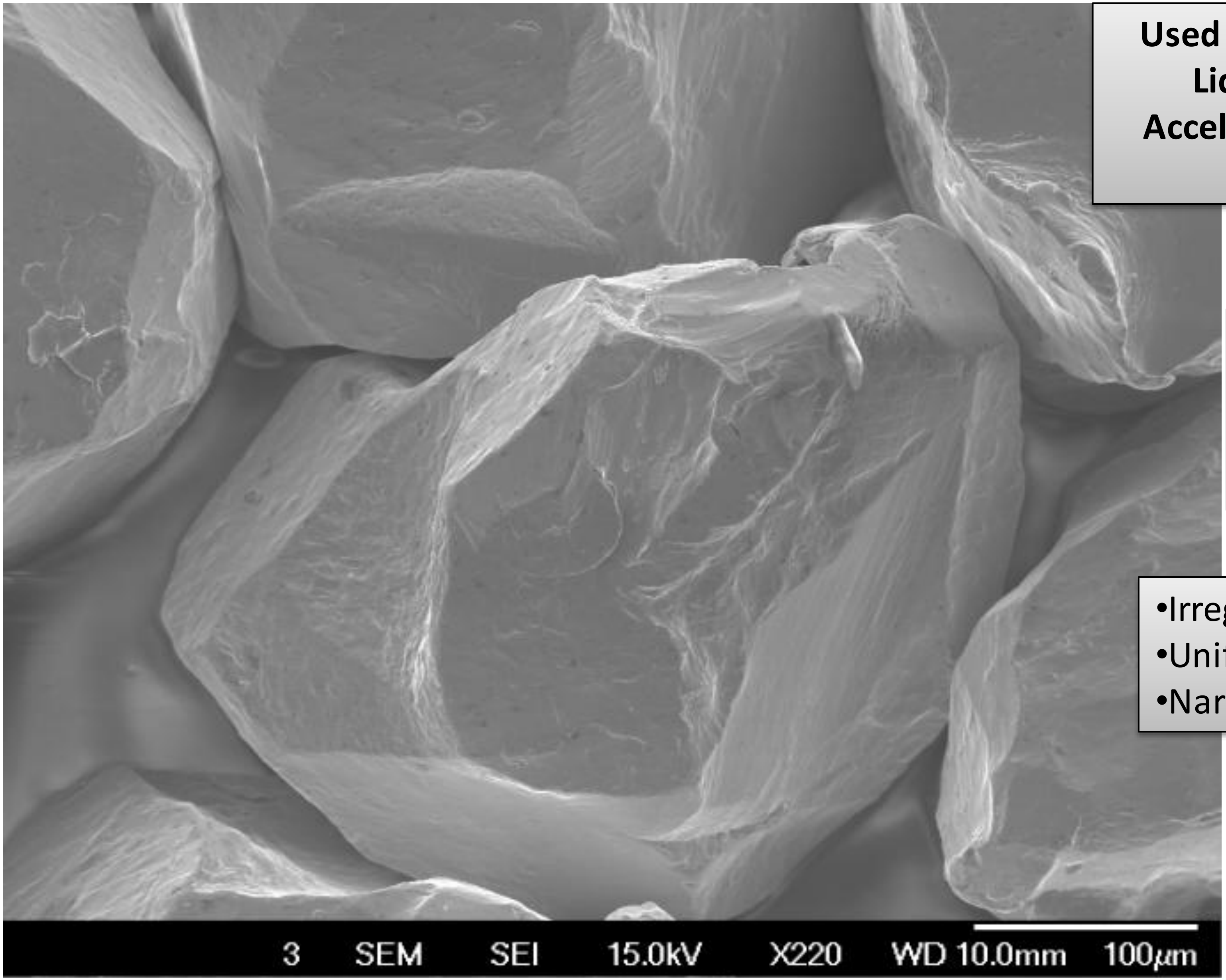



**Used to fabricate the Liquid Particle Acceleration Sample LPA-151**

- **%Cu 99.81**
- **D90 101.3um**
- **D50 53.90um**
- **D10 21.90um**

- Blocky
- Agglomerated
- Break up upon impact
- Better packing capacity

# Cu Powder – LPA 46HP

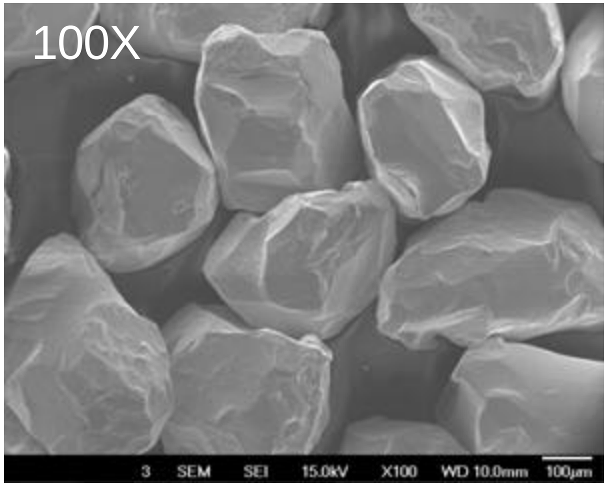


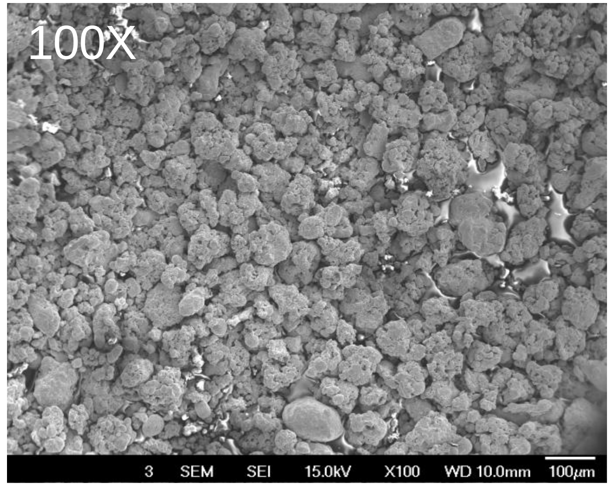

Used to fabricate the Liquid Particle Acceleration Sample LPA-46HP

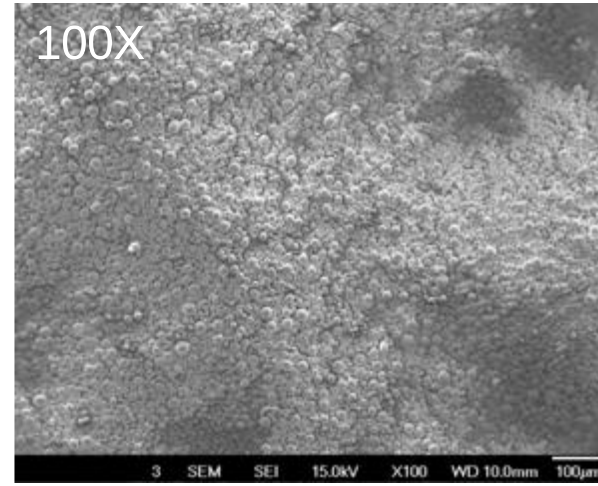
- %Cu 99.83
- D90 478.9um
- D50 398.3um
- D10 326.2um

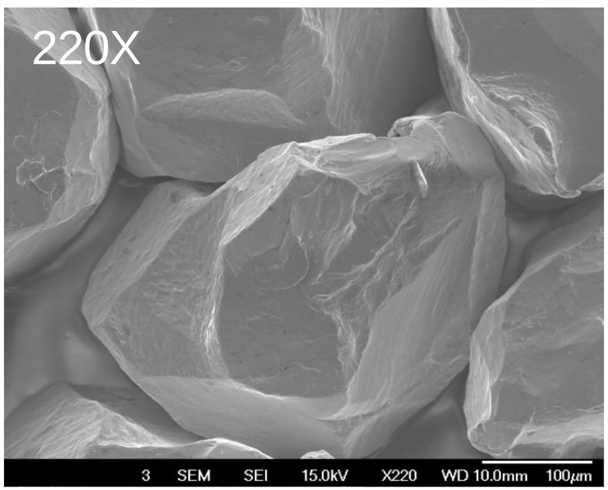
- Irregular
- Uniform
- Narrow Distribution

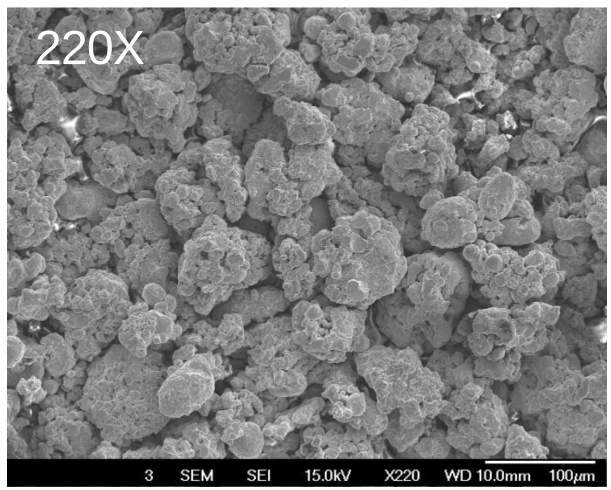
# SEM Summary 220X

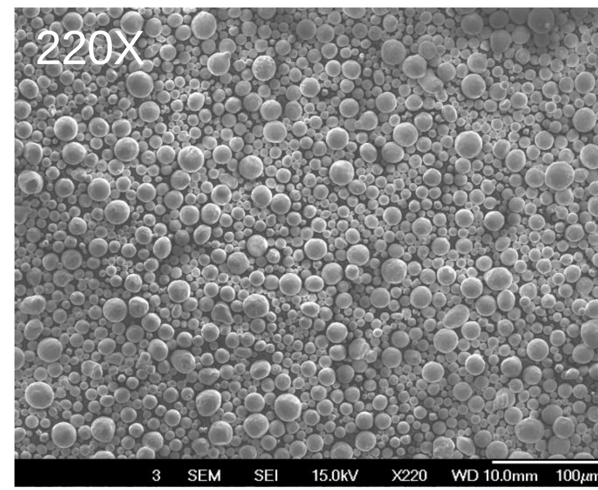



**Cu Powder – 46HP**

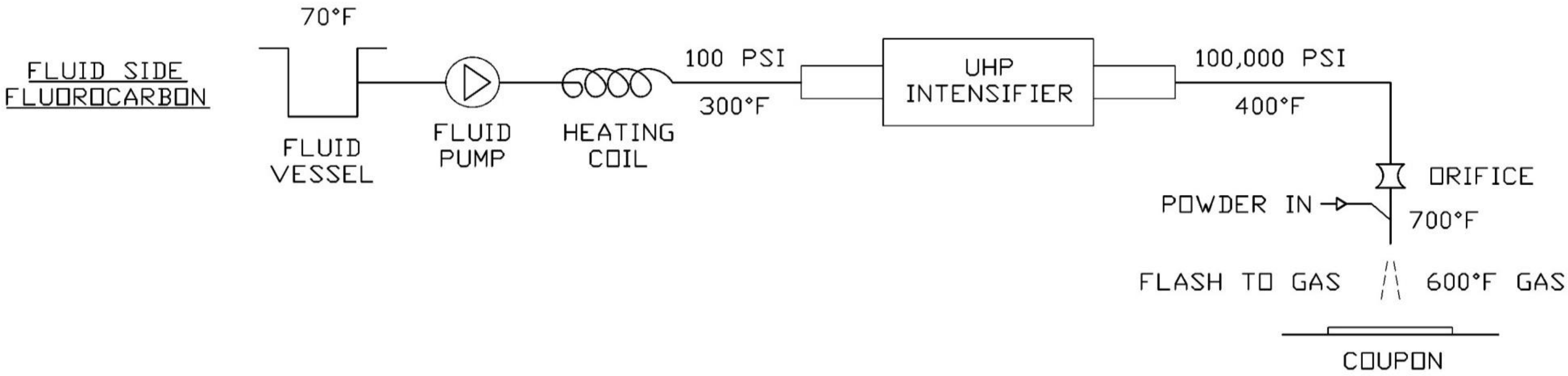
**Cu Powder – 151**

**Cu Powder – 500A**

* Acknowledgement: Baillie McNally from WPI for powder SEM photos

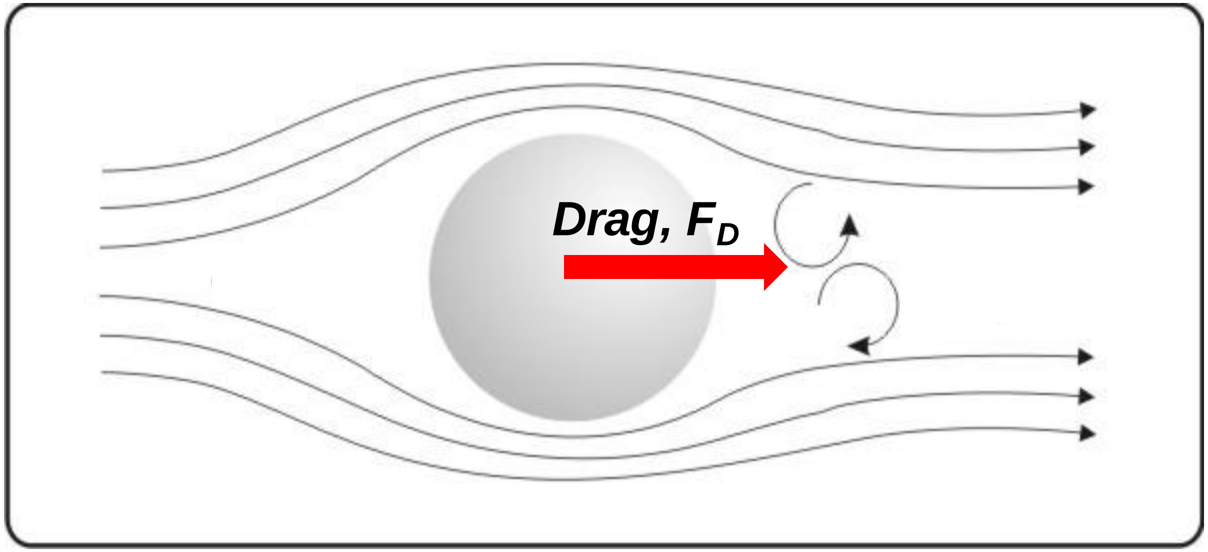
# LPA Process Parameters

- the velocity of the larger particles is the same as those for smaller because the velocity of the particles will reach about 70% of the fluid velocity for the mass loading used
- the temp was similar for both size particles, at least before they hit the fluid but the small particles would be cooled more by the fluid.
- the solvent used was a hydrofluorocarbon which has a low latent heat of vaporization
- shearing of fluid as it passes through the nozzle increases the temperature to cause vaporization




- Temperature was measured right at the nozzle before the powder hits the fluid.
- Fluid cools the powder slightly & the temp. as it hits the target is not known.

# Drag Force Comparison




$$F_D = \frac{1}{2}\rho A C_D v^2$$

**= *27 dynes (nitrogen)***

**= *22500 dynes (water)***

drag force — $F_D$

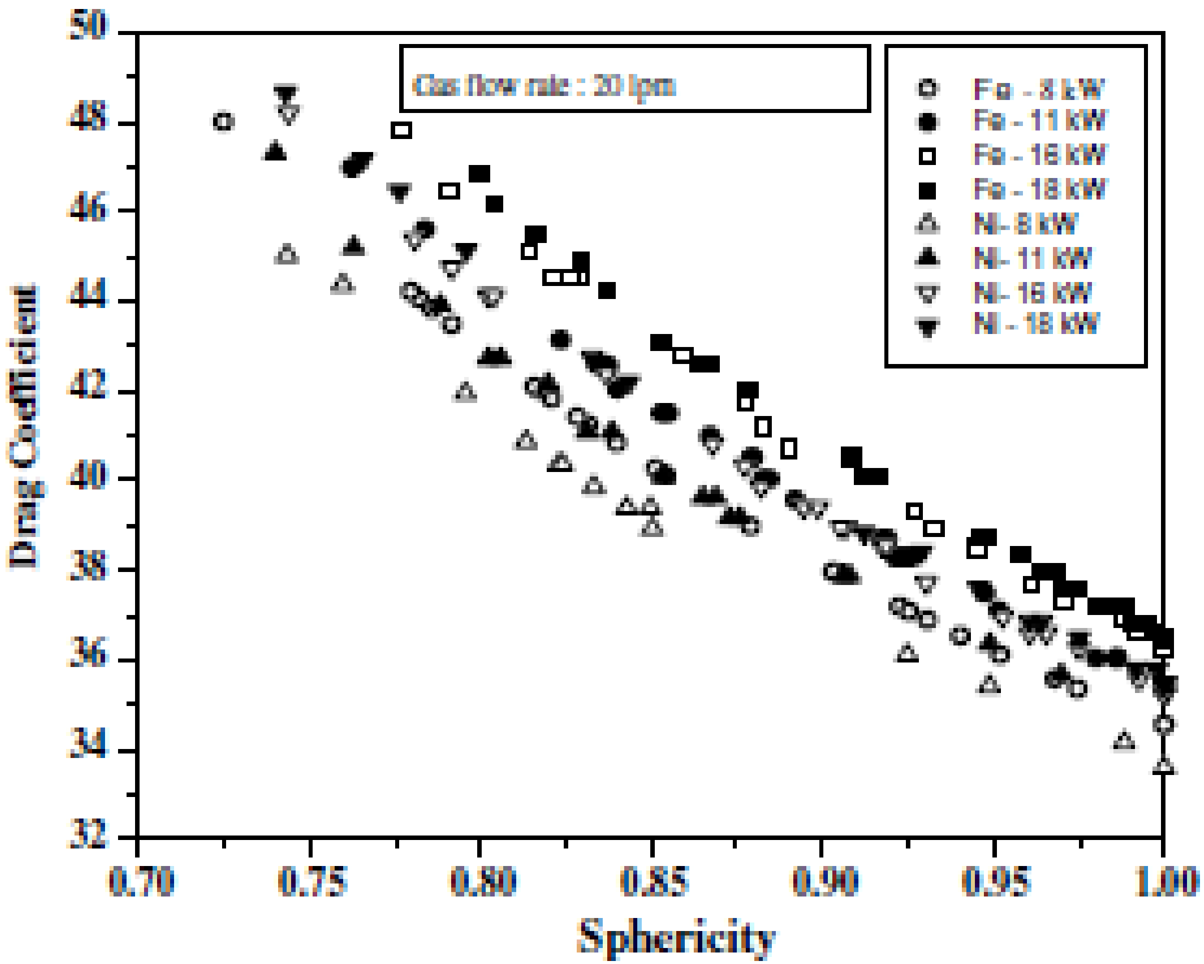
density — $\rho$

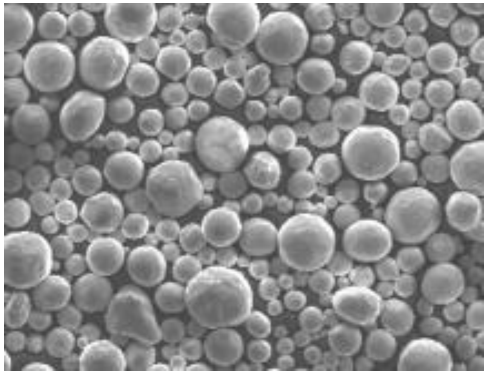
acceleration — $A$

drag coefficient — $C_D$

velocity — $v$

# Shape Affect on Drag (acceleration force, $F_D$)



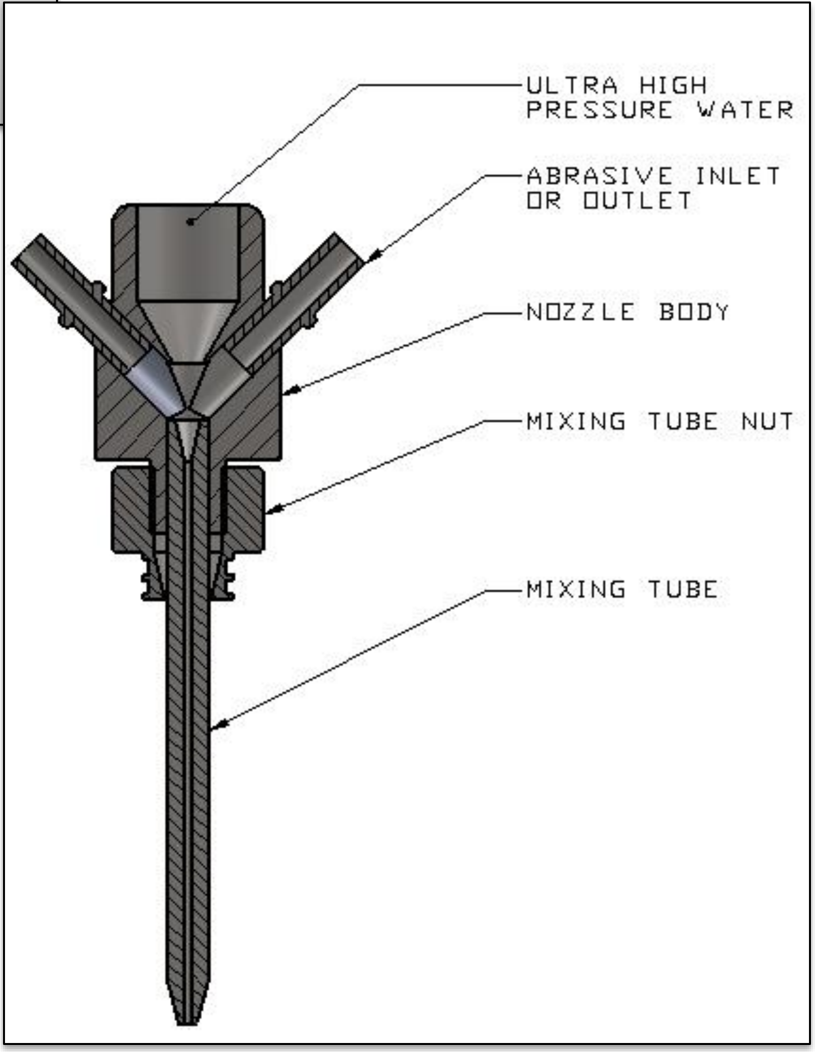



**Reference:** Kumar, et al, Influence of metal powder shape on drag coefficient in a spray jet, Current Applied Physics 9 (2009) 678–682

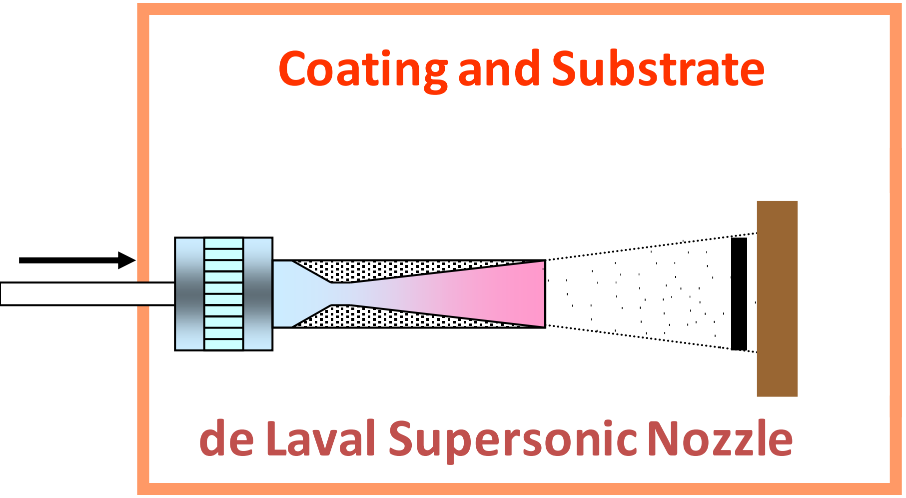
# Liquid Particle Acceleration Compared to Cold Spray

- •Uses 60-90,000 psi pumps and multi-axis robots
- •Entrain abrasives into fluid jet
- •Particle velocities of around 850 m/s
- •Particle size typically 180 microns
- •Particle flow rate up to 1,000 g/min.

## Liquid Particle Acceleration (LPA)



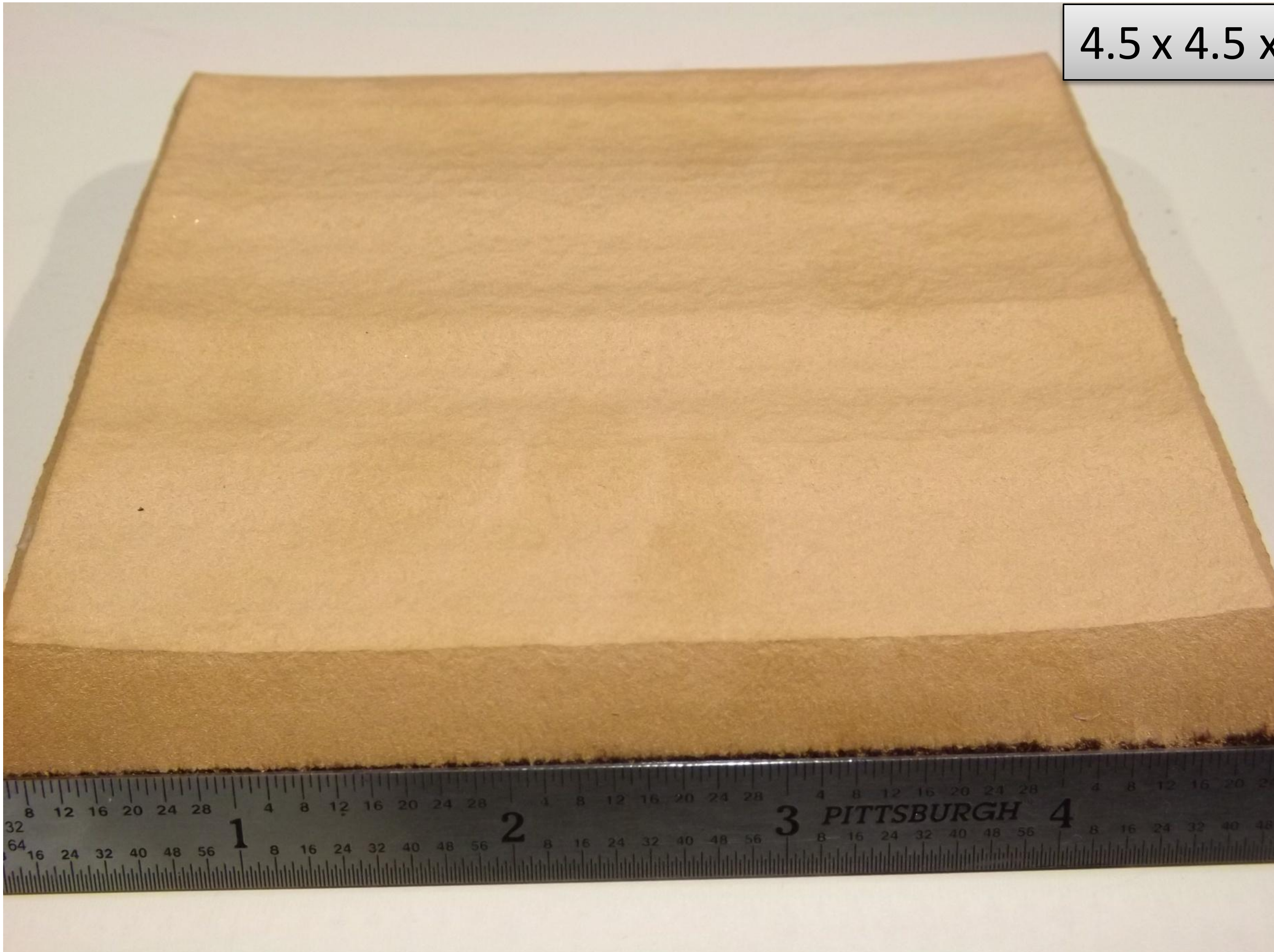

## Conventional Cold Gas-Dynamic Spray




- •Uses compressed gas (300-1,200psi)
- •Powder fed into gas up-stream of nozzle
- •Particle size typically ~20-44 microns
- •Particle flow rate up to 50-100g/min.

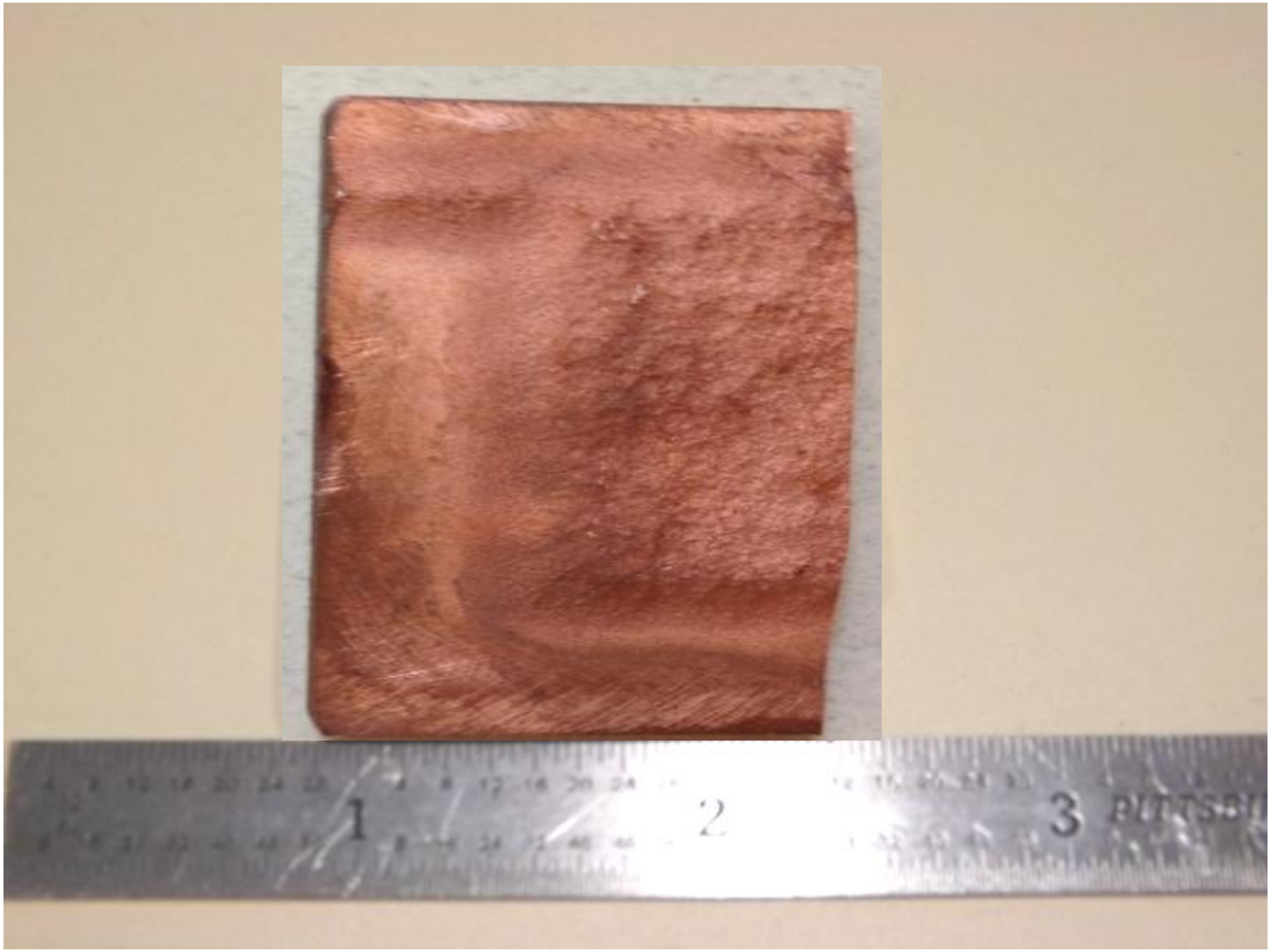
# Macro of CS 500A Block

4.5 x 4.5 x 3/8 inch



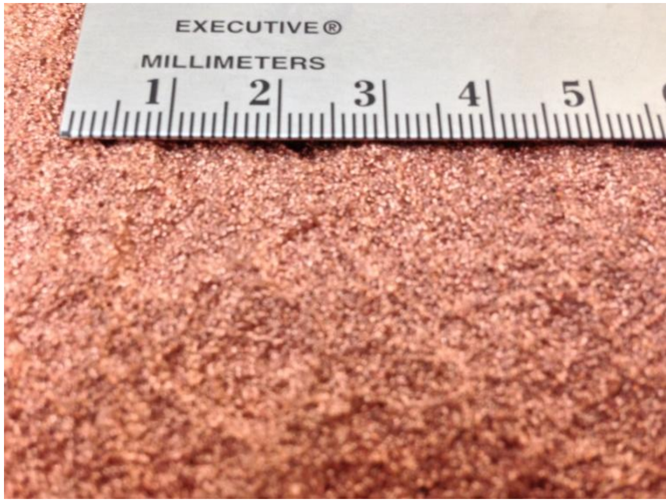
# Macro of LPA 151 Block

1.5 x 1.5 x 1/4 inch



# Macro of LPA HP46 Block


4.5 x 4.5 x 3/8 inch




Surface Finish was too rough to measure with a normal surface profilometer

# Surface Profile



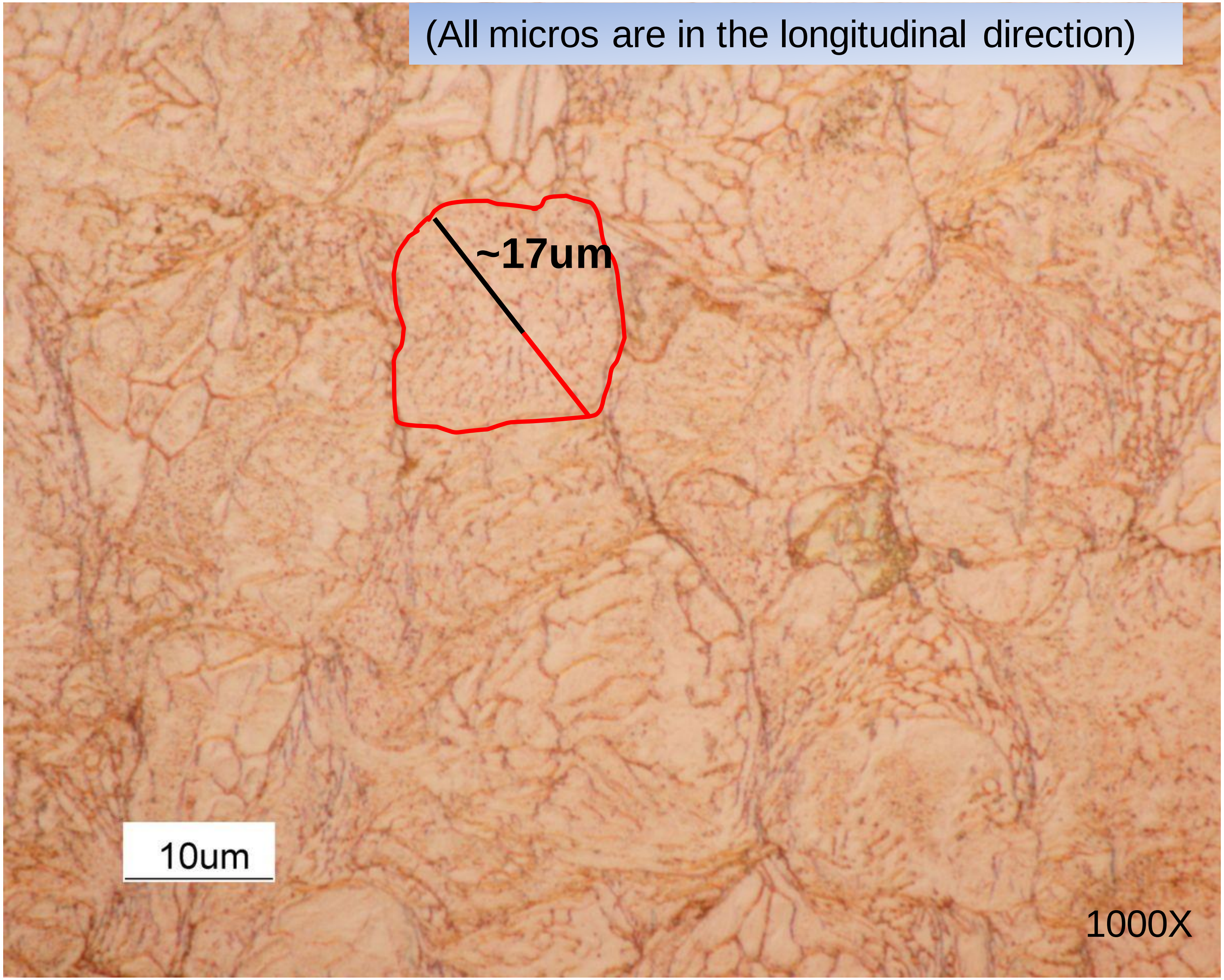
| CS 500A | LPA 151 | LPA 46HP |
|---|---|---|
| 247.21 Ra | 494.95 Ra | N/A |
| 222.95 Ra | 596.01 Ra | N/A |
| 233.77 Ra | 506.67 Ra | N/A |
| 243.08 Ra | 434.38 Ra | N/A |
| **AVG. 236.75 Ra** | **AVG. 508.00 Ra** | **N/A** |

**Mitutoyo Surface Roughness Tester (SJ-210)**

•diamond stylus profilometer runs perpendicular to the surface and traces along a straight line

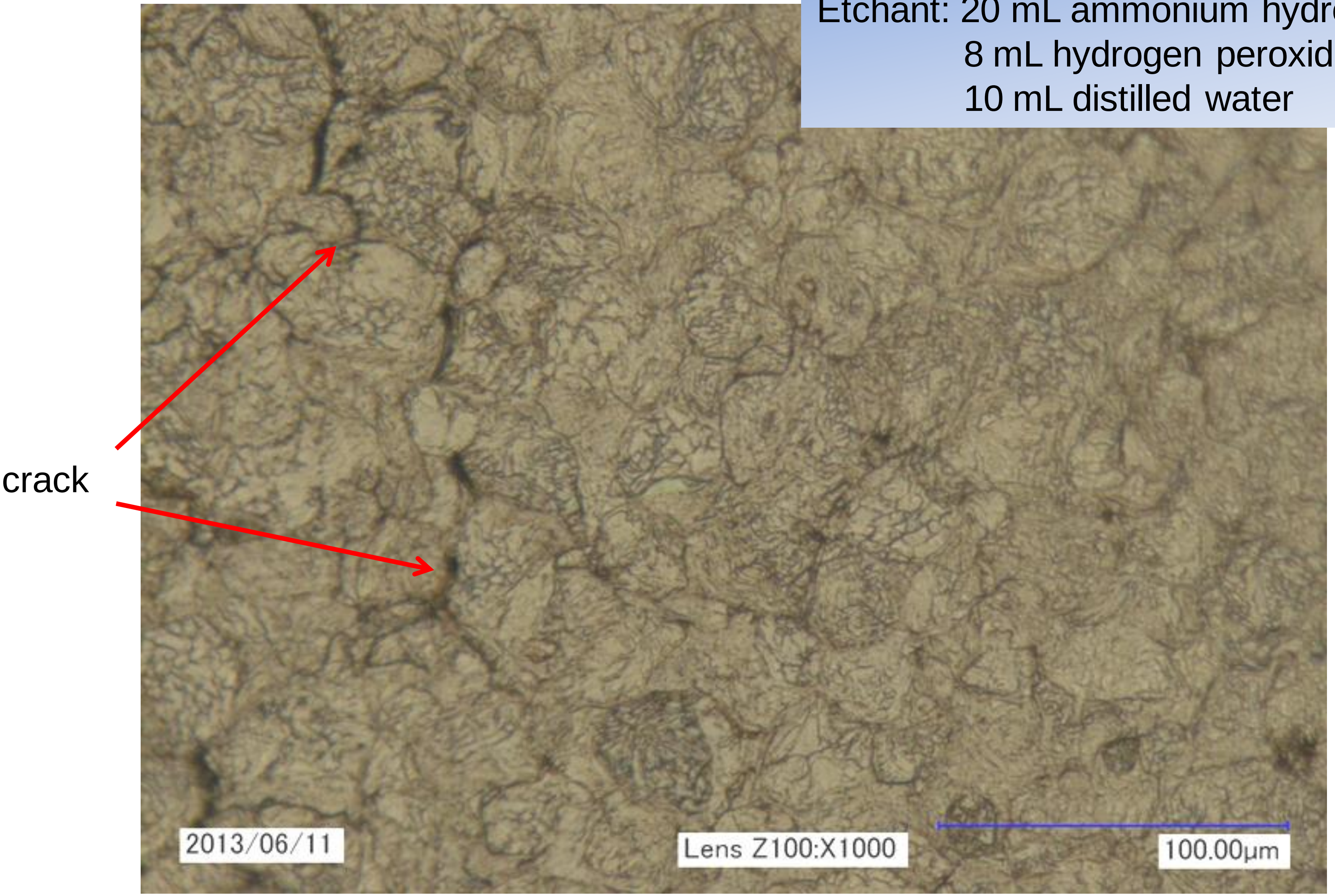
# CS 500A Microstructure

(All micros are in the longitudinal direction)

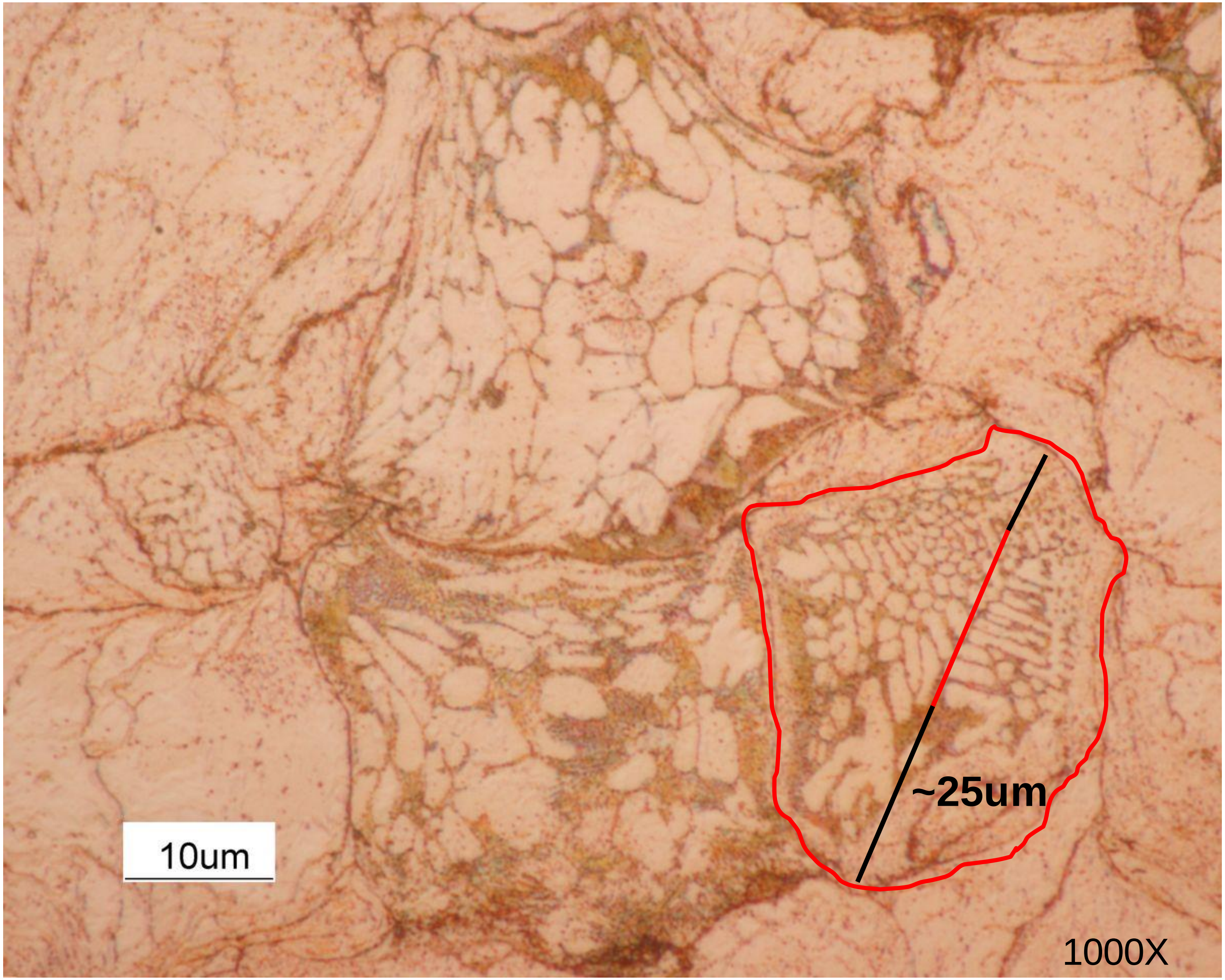


# CS 500A Microstructure

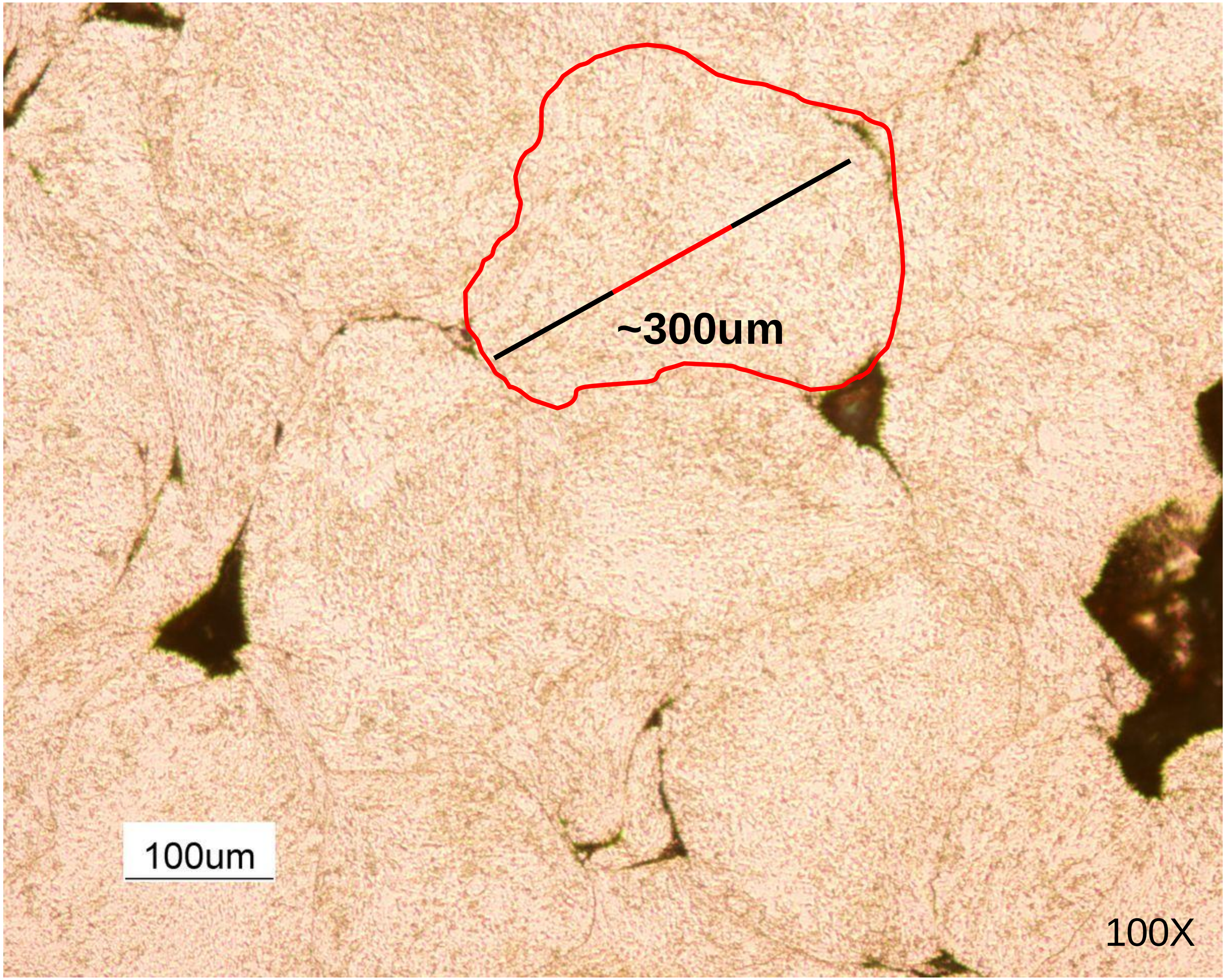
Etchant: 20 mL ammonium hydroxide
8 mL hydrogen peroxide
10 mL distilled water



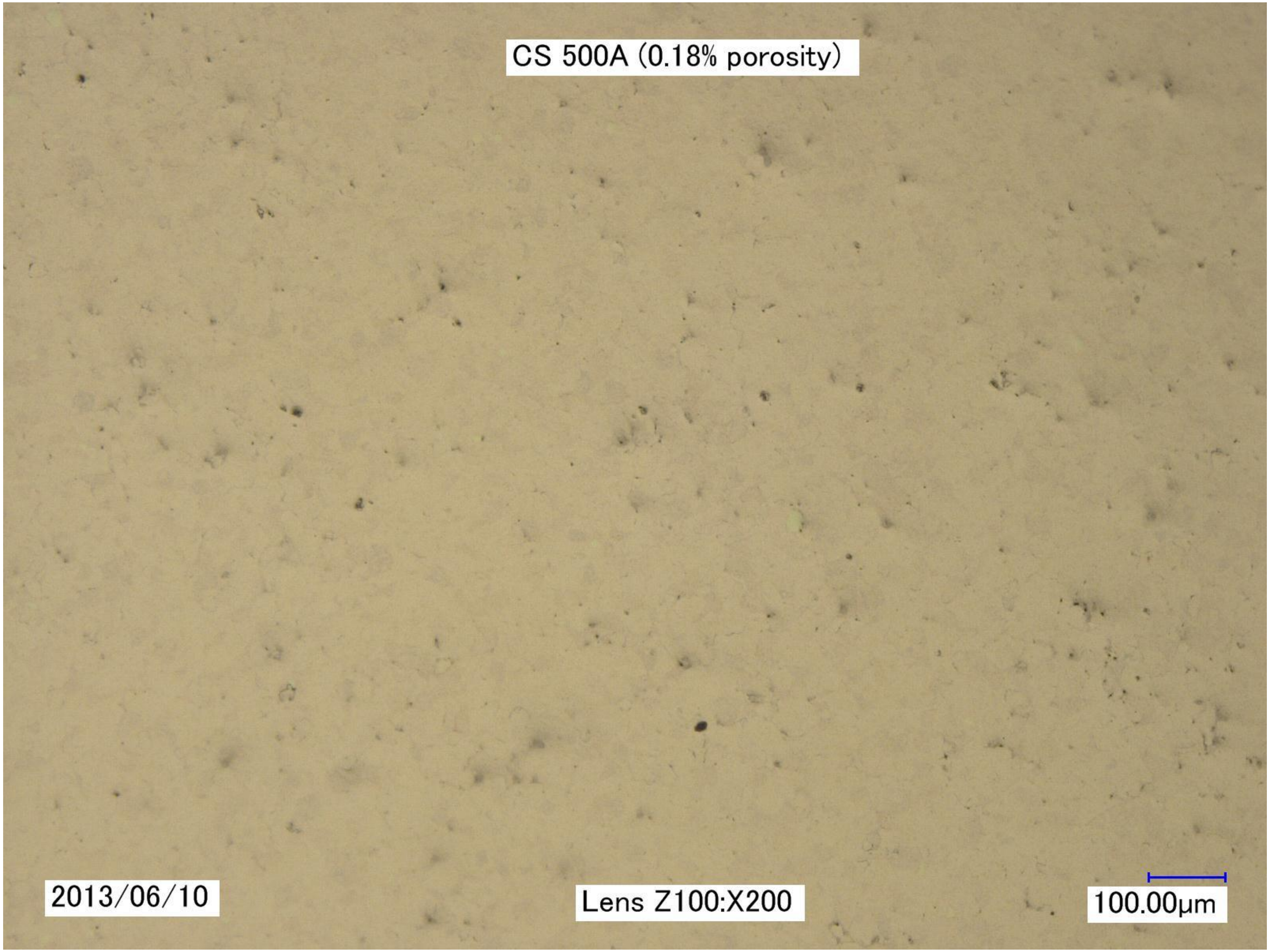
# LPA 151 Microstructure



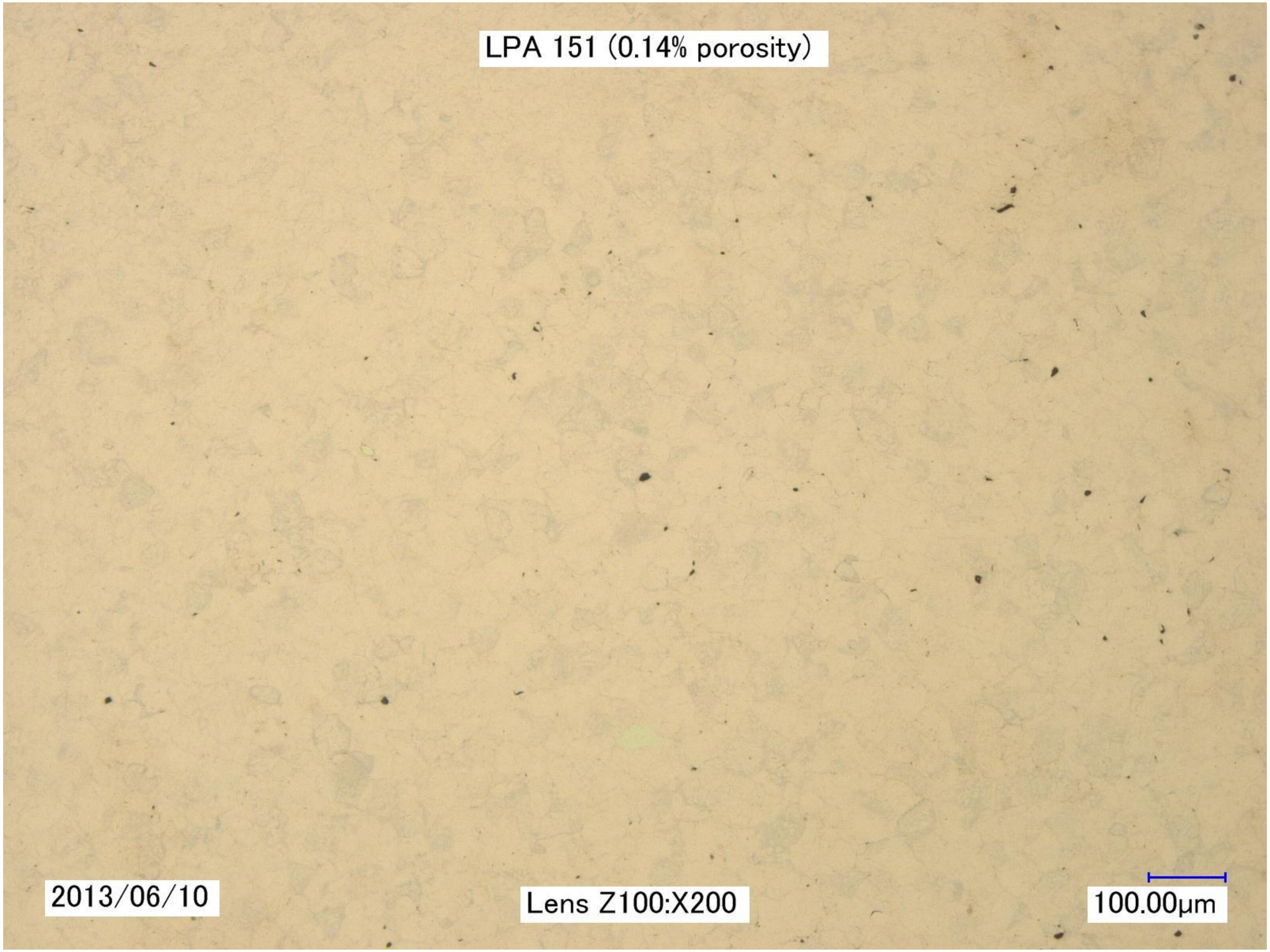
# LPA 46HP Microstructure



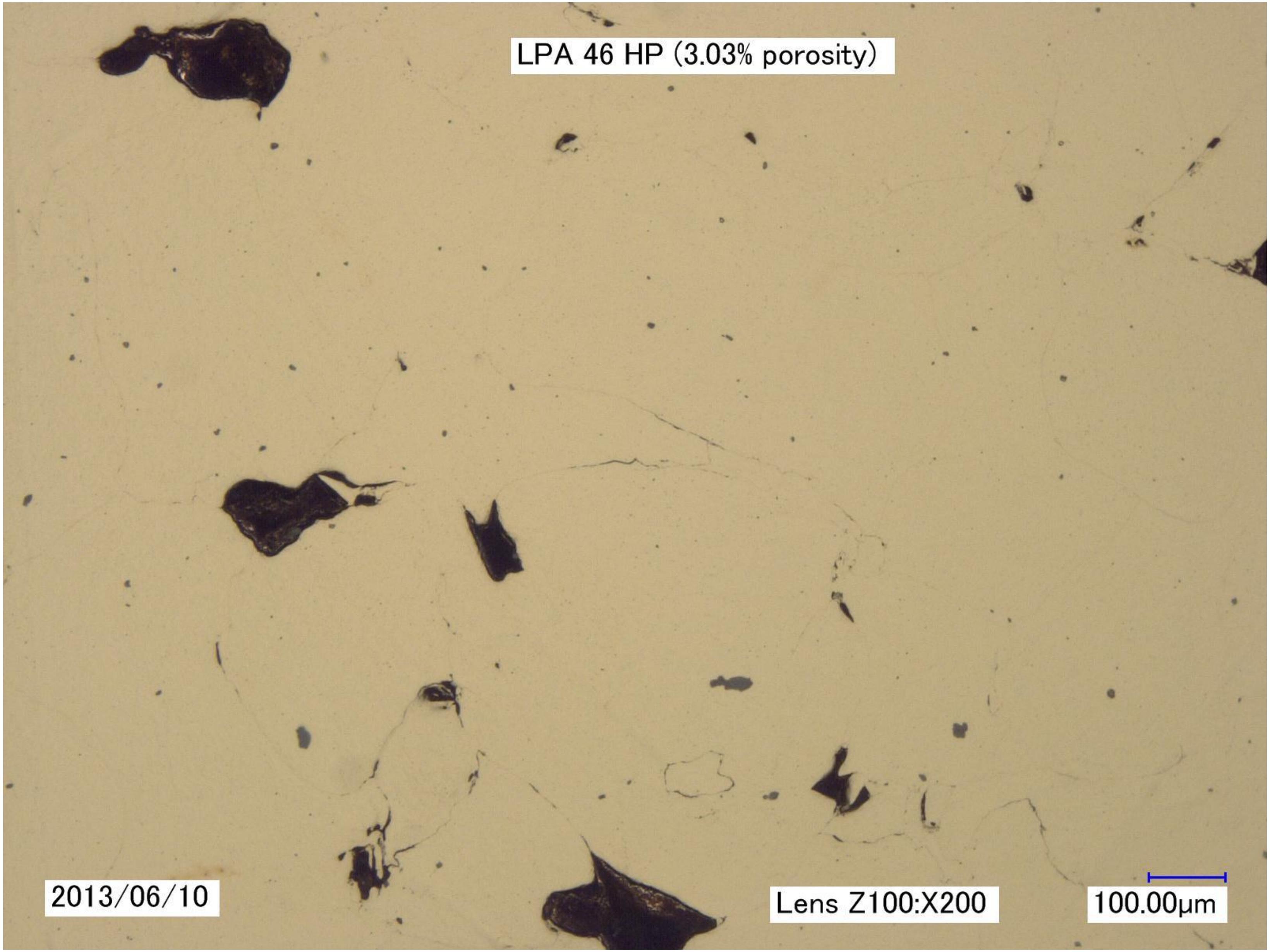
# Porosity of CS 500A



# Porosity of LPA 151



# Porosity of LPA 46HP



# Conductivity Measurements

| Sample | *Conductivity (%IACS) |
|---|---|
| CS 500A | AVG. 54.9 |
| LPA 151 | AVG. 73.8 |
| LPA 151 Cu Substrate | 102.5 |
| LPA 46HP | 10.7-34.4 |
| LPA 46HP Cu Substrate | 101.6 |

- **Olympus Nortec 500C Eddy Current System & Probe**
  - Used for LPA 46HP and CS 500A

- **Olympus 60kHz LEMO Eddy Current Probe**
  - 0.31” diameter pencil type
  - used for LPA 151
  - Calibrated with 29.75 & 59.56%IACS calibration standard
  - Provides conductivity in %IACS

*measurements taken by United Technologies Research Center

# Microhardness Testing (Vickers)

| Test # | CS 500A | LPA 151 | LPA 46 HP |
|---|---|---|---|
| 1 | 162.1 HV | 114.0 HV | 77.0 HV |
| 2 | 161.8 HV | 121.9 HV | 77.9 HV |
| 3 | 159.3 HV | 131.4 HV | 69.5 HV |
| 4 | 160.6 HV | 146.0 HV | 83.3 HV |
| 5 | 162.0 HV | 120.1 HV | 106.5 HV |
| 6 | 165.5 HV | 121.6 HV | 62.3 HV |
| 7 | 154.7 HV | 116.8 HV | 66.8 HV |
| 8 | 154.0 HV | 117.0 HV | 80.1 HV |
| 9 | 166.1 HV | 144.2 HV | 70.5 HV |
| 10 | 167.5 HV | 123.3 HV | 81.4 HV |
| **Average** | **161.4 HV** | **125.6 HV** | **77.5 HV** |

Wilson Hardness Vickers 402 MVD
Test Load: 300 gf
Test Duration (Dwell Time): 12 sec.

# Inert Gas Fusion Testing

**Definition:** Inert gas fusion is a quantitative analytical technique for determining the concentrations of nitrogen, oxygen, and hydrogen in ferrous and nonferrous materials.

**Objective:** *To compare the oxygen concentration of the feedstock powder to the consolidated material.*

**ASTM E 2575-08**: *Standard Test Method for Determination of Oxygen in Copper and Copper Alloys*

- The consolidated samples are etched with a solution of nitric acid ($HNO_3$) for a time sufficient to produce a visible reaction.
- ***ASTM B170-99(2004) Standard Specification for Oxygen-Free Electrolytic Copper***


**Leco TC-436 Oxygen-Nitrogen Analyzer**

- Analysis performed by Luvak, Boylston, MA 01505

# Inert Gas Fusion Testing ASTM E 2575-08

1. The sample is weighed and melted in a graphite crucible in a stream of helium.
2. The oxygen in the sample combines with carbon to form CO which is converted by a catalyst to $CO_2$.
3. An infrared cell determines the $CO_2$ content from which the weight % of oxygen in the sample is calculated.
4. Molecular nitrogen is released from the sample and is separated from any hydrogen and carbon monoxide liberated from the sample.
5. A thermal conductivity cell determines the nitrogen content from which the weight % of nitrogen in the sample is calculated.
6. A nickel flux is used for metals that melt at high temperatures.
7. Calibration is verified with NIST or NIST traceable standard reference materials of known oxygen and nitrogen content.
8. Luvak Inc. has experience with determination of oxygen and nitrogen content ranging from trace amounts less than 5 ppm to the percentages present in metal oxides and nitrides.

**Reference:** http://www.luvak.com/index.html (Luvak Incorporated)

# Inert Gas Fusion Test Results

**Oxygen Analysis of Aluminum & Copper Powders and Cold Spray Deposits.**

| Powder Type | % Oxygen (Powder) | % Oxygen (Deposit) | % Change |
|---|---|---|---|
| *CP-Al (Brodmann) | 0.34 | 0.25 | -36% |
| *HP-Al (Valimet) | 0.88 | 0.58 | -51% |
| **Copper (Sandia Labs) | 0.34 | 0.28 | -21% |
| CS 500A -Copper | .162 | .141 | -15% |
| LPA 151-Copper | .182 | .240 | +32% |
| LPA 46HP-Copper | .027 | .056 | +107% |

**References:**

*Gabriel, Champagne ,et al. "Cold Spray for Repair of Magnesium Components", ESTCP Project WP-0620

**Smith" Cold Spray Direct Fabrication-High Rate, Solid State, Material Consolidation",

# Summary of Test Results

| TEST | CS 500A | LPA 151 | LPA 46HP |
|---|---|---|---|
| Powder Size | ~20um | ~55um | ~400um |
| Powder Geometry | Spherical | Agglomerated | Blocky and Uniform |
| Surface Finish | 237 Ra | 508 Ra | >508 Ra-Rough |
| Porosity | 0.18% | 0.14% | 3.03% |
| Microstructure | Highly Worked-Stress Cracks | Highly Worked-Recrystallization | Least Worked-No Recrystallization |
| Conductivity | 55%IACS | 74%IACS | 10-34%IACS |
| Micro-Hardness | 161 HV | 126 HV | 62-107 HV |
| Oxygen [ ] | -15% | +32 % | +107 % |

# Conclusions

➢**LPA 151 compared favorably with conventional cold spray**

***Why did the oxygen [ ] increase for the LPA samples but decreased for the conventional cold spray material?***

•Smith hypothesized that the slightly lower oxide content of the cold-sprayed material might result from a somewhat lower sticking probability for particles that have more surface oxide.

➢***Larger particles stick and the fines do not***

•ARL has shown the deposit efficiency of aluminum is ~100% so this explanation cannot be universally applied.

•The deposit efficiency of the all the copper sprayed was < 100%

- •LPA 46HP is about 75%
- •LPA 151 is about 25%
- •CS 500A is 80%

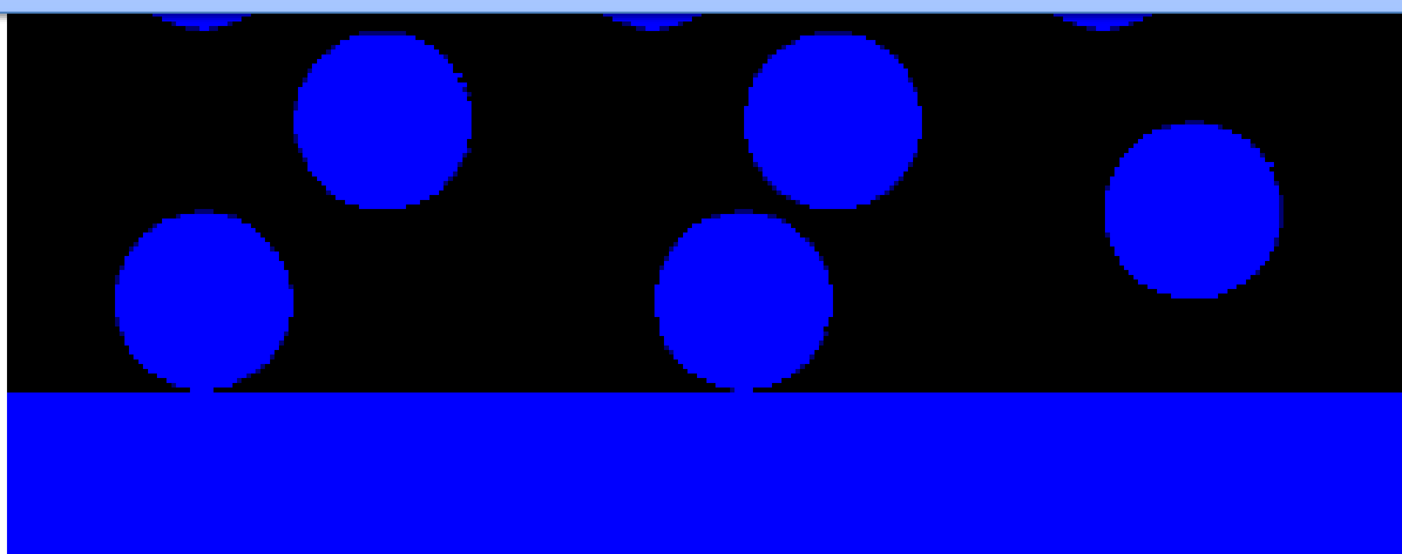
***The hydrofluorocarbon reacts with copper in the presence of water and most likely resulted in oxidation of the powder.***

# Conclusions

***Why did the LPA material produced using smaller particles (LPA151) have better properties than that of the larger particles (LPA 46HP)?***

- LPA 46HP contained greater porosity and voids and lower hardness
- LPA 151 had better consolidation & greater conductivity and deposit efficiency

➢**Adiabatic plastic deformation**: localized temperature increases and strain concentration play a major part in high speed deformation of metals and was recognized by Zener & Hollomon in 1944. Approximately 90% of the work of plastic deformation is converted to heat, and the flow stress of most metals is sensitive to temperature, decreasing as temperature increases. **Need to increase temp. of 46HP**



*from H. Assadi, www.modares.ac.ir/eng/ha10003/CGS.htm