SOFC Tolerance Limits for Phosphorus and Arsenic

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INTRODUCTION

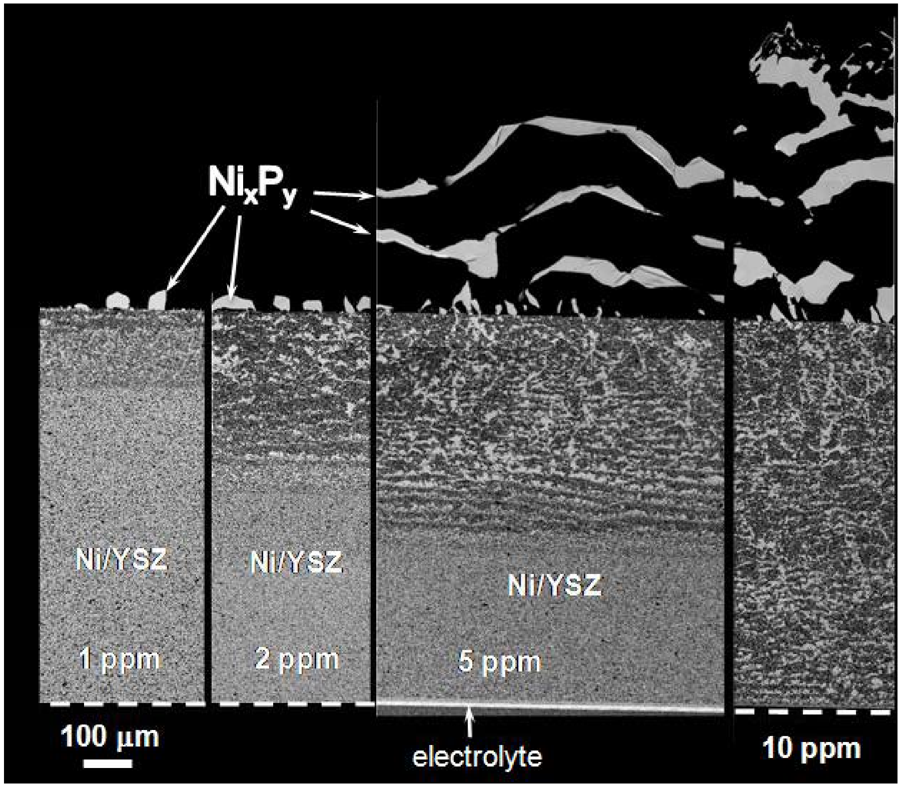
- Different coals, gasification processes, and cleanup processes result in different levels of impurities.
- Different contaminants lead to different types of interactions with SOFC anode.
- Performance degradation due to trace impurities is affected by various factors such as concentration of contaminants, temperature, operation time, cell voltage, and fuel utilization.
- Previous studies at PNNL focused on P, As, Sb, S, Se, Cl at ppm levels
- Current studies are focused on:
  - Effect of sub-ppm levels of P and As on anode chemistry/microstructure
  - Effect (if any) of electrical potential on reactions between contaminant and anode

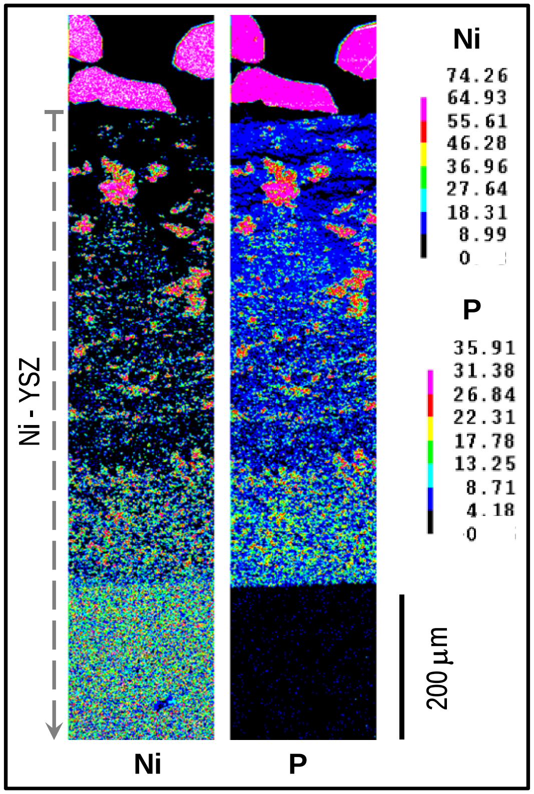
ANODE–PHOSPHORUS INTERACTIONS: CONCLUSIONS FROM PREVIOUS WORK

- Strong interaction between Ni and P-containing contaminants in coal gas (PH_3, PO_2, etc.)
  - Nickel phosphide solid phases: Ni_3P, Ni_5P_2, $Ni_{12}P_5$, Ni_2P, etc.
  - Phosphide formation predicted even at low P concentrations (< 0.01 ppb at 800ºC)
  - Sharp boundary observed between reacted and un-reacted parts of the anode
- Degradation Mechanisms
  - Increased Ohmic resistance due to
    - Loss of electrical connectivity in the anode support due to phosphide formation (Ni depletion)
    - Micro-crack formation due to particle coalescence

ANODE–PHOSPHOROUS Interaction

- **SEM Analysis of anode-supported button cells after exposure**





- ❑ Sharp Boundary Between Ni and Ni-P
- ❑ Considerable Coalescence of Ni-P
- ❑ WDS → P is associated only with nickel, not zirconia.
- ❑ Micro-cracks in Reacted Area

ANODE–PHOSPHORUS INTERACTIONS: CONCLUSIONS FROM PREVIOUS WORK

- Degradation Mechanisms (continued)
  - Poisoning due to slow migration of phosphorus to the active interface (increased electrodic polarization)
  - P adsorbs on surface of Ni grains in unreacted anode (observed by XPS, ToF-SIMS)

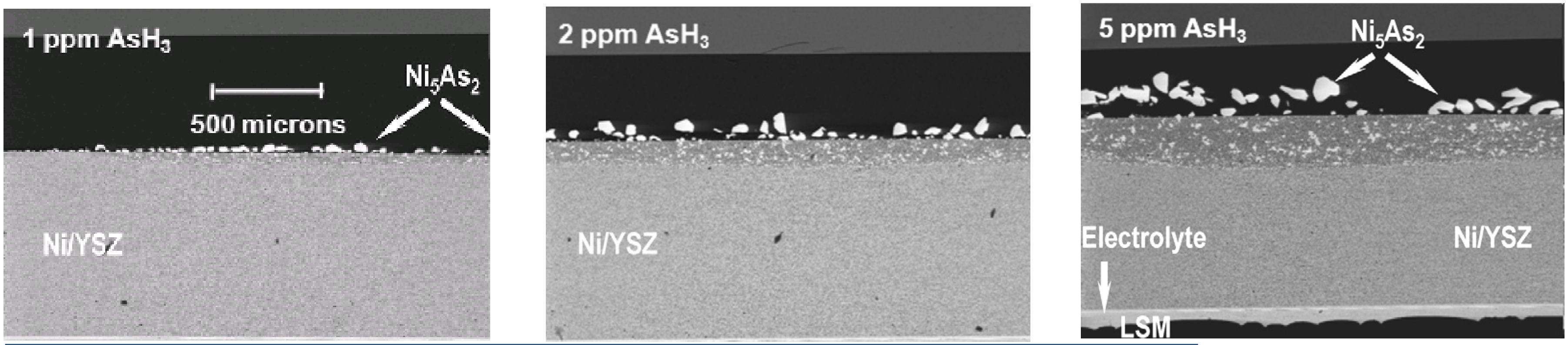
- Effect of Contaminant Level
  - For [PH_3] = 1-10 ppm, both ohmic and electrodic losses in tested cells increased substantially during 1000 hours of testing

Anode–Arsenic Interactions: Conclusions from Previous Work

- Strong interaction between Ni and As-containing contaminants in coal gas (AsH_3, As_2, etc.)
  - Nickel arsenide solid phases: Ni_5As_2, $Ni_{11}As_8$, etc.
  - Arsenide formation predicted even at low As concentrations (<0.1 ppb at 800ºC)
  - Sharp boundary observed between reacted and un-reacted parts of the anode
- Degradation Mechanisms
  - Loss of electrical connectivity in the anode support due to arsenide formation: Ni depletion (increased Ohmic resistance)
    - Abrupt failure after long-term operation upon loss of electrical percolation
  - Unlike case for P, poisoning effects due to adsorption of As at active anode interface were not observed
- For [AsH_3] = 0.5 – 10 ppm, substantial degradation of performance observed in 1000 hours or less

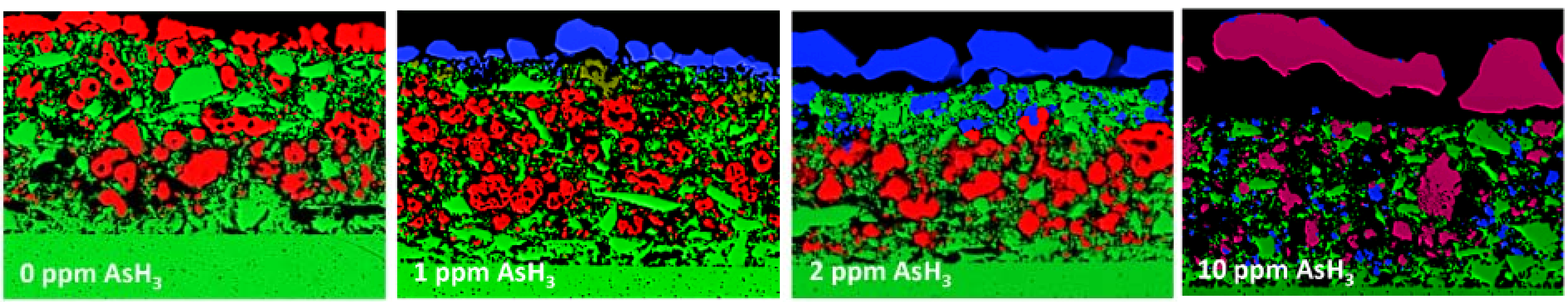
ANODE–ARSENIC INTERACTION

- **SEM Cross-Section Image (800ºC, 500 hours)**



❑ AsH_3 Concentration ↑ ~ Depth of Reaction ↑, Agglomeration↑

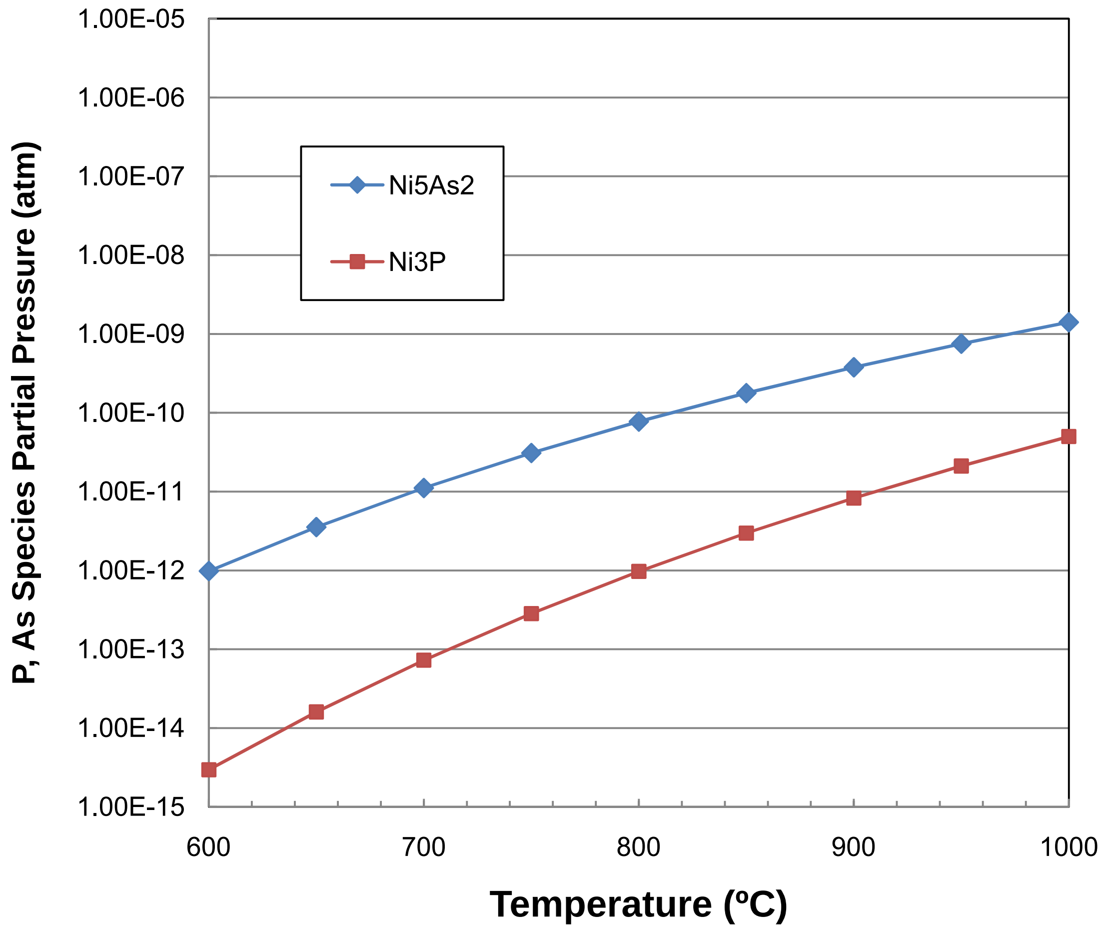
- **Conversion of Nickel to Nickel Arsenide (Ni_5As_2, $Ni_{11}As_8$)**



- 700ºC, 50 Hours
- Red: Ni, Dark Yellow: Ni-As Solid Solution, Green: YSZ, Blue: Ni_5As_2, Magenta: $Ni_{11}As_8$

Current Study: Effect of 10 ppb contaminant levels

- Ni Phosphide / Ni Arsenide formation expected to occur even at sub-ppb contaminant levels:



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Current Study: Effect of 10 ppb contaminant level

- Ni Phosphide / Ni Arsenide formation expected to occur even at sub-ppb contaminant levels
- However, also can expect low rate of reaction due to low contaminant delivery rate

- Calculated rates of Ni conversion
  - Assumptions:
    - 50/50 vol% Ni/YSZ anode w/ 40% porosity; 500 microns thick
    - 65% fuel utilization, 0.8 A/cm^2 current density
    - Complete capture of contaminant by anode (worst-case scenario)
    - Dominant phase formed:
      - P: Ni_3P
      - As: Ni_5As_2

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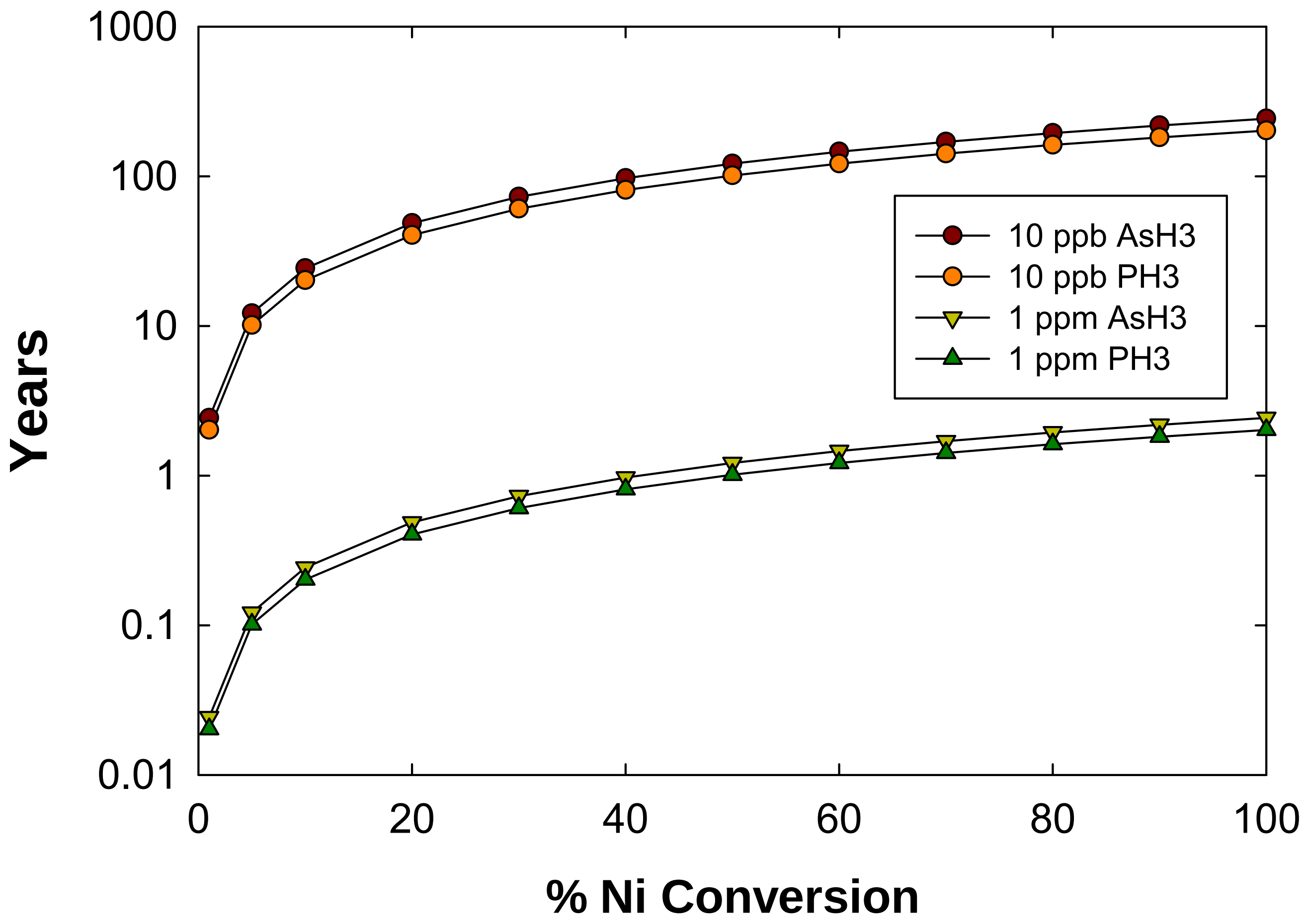
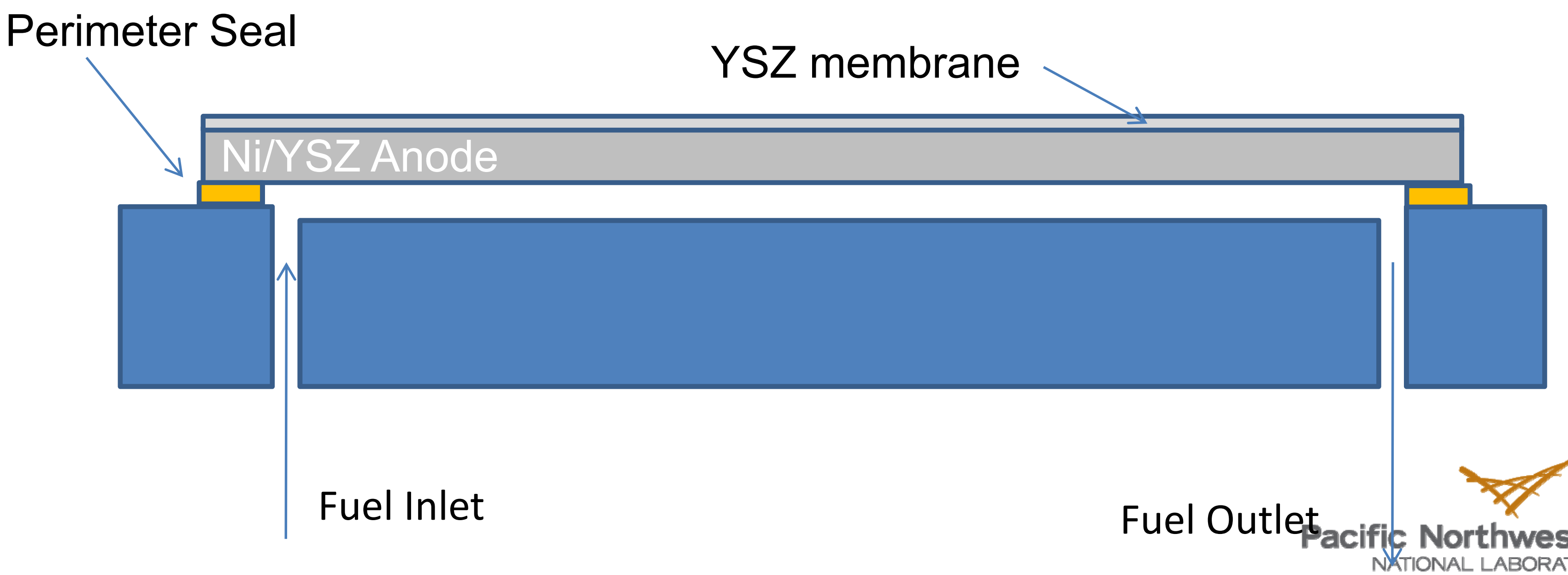
For 10 ppb contaminant level, expect low rate of Ni conversion

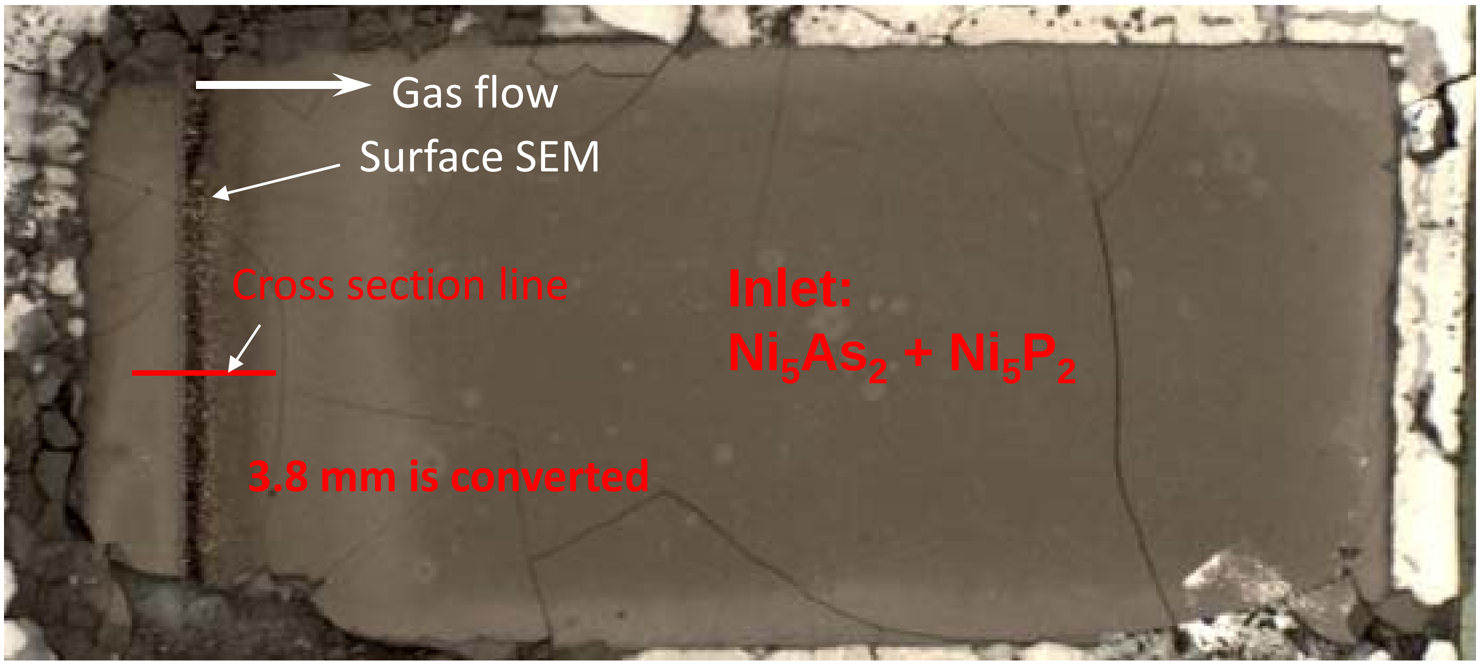


"Flow-by" anode contaminant tests

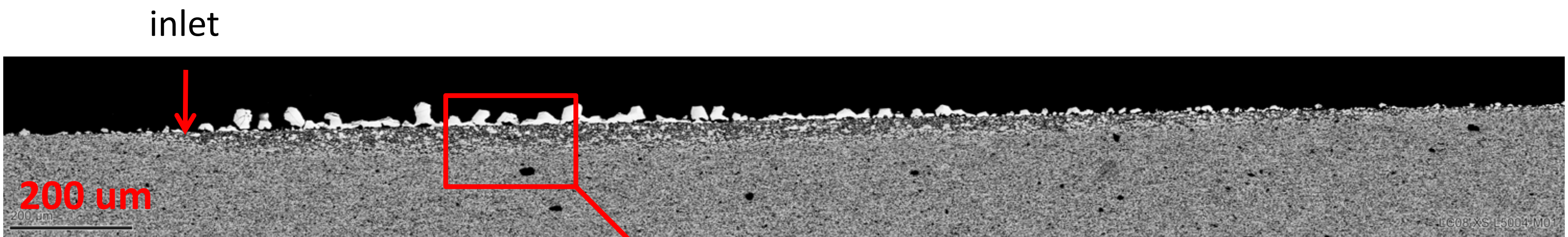
- Flow rate: 200 sccm, corresponding to ~65% fuel utilization at 0.8 A/cm^2
- Gas composition: Simulated coal gas (55% H_2; 45% CO_2)
- Contaminant type and level:
  - 10 ppb AsH_3
  - 10 ppb PH_3
  - 10 ppb AsH_3 + 10 ppb PH_3
- Temperature: 800ºC
- Exposure time: 2000 hours +

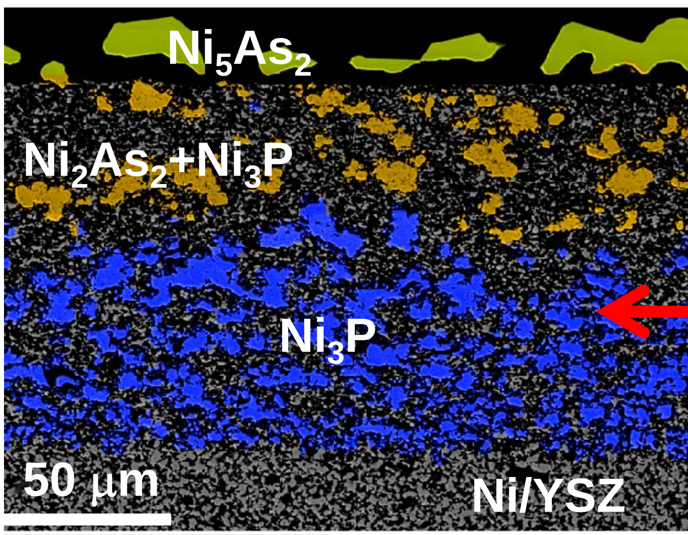


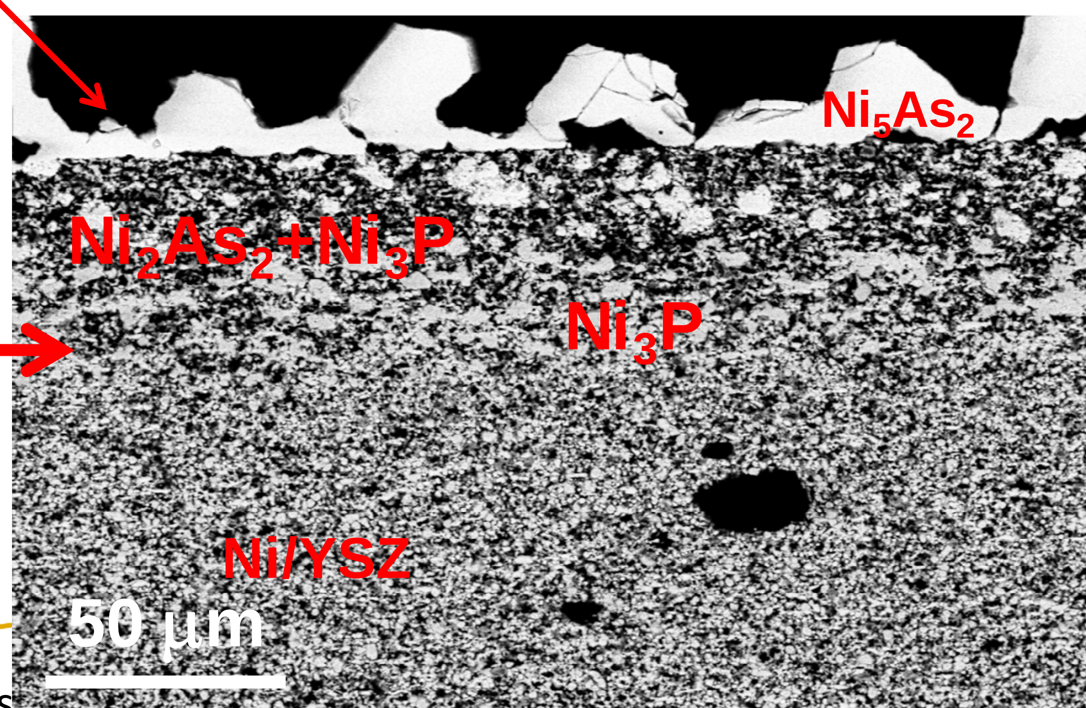
1 ppm PH_3 + 1 ppm AsH_3, 800^oC, 100h



Surface crystals are Ni-As; Ni-P is. The P penetration at the inlet was ~70.

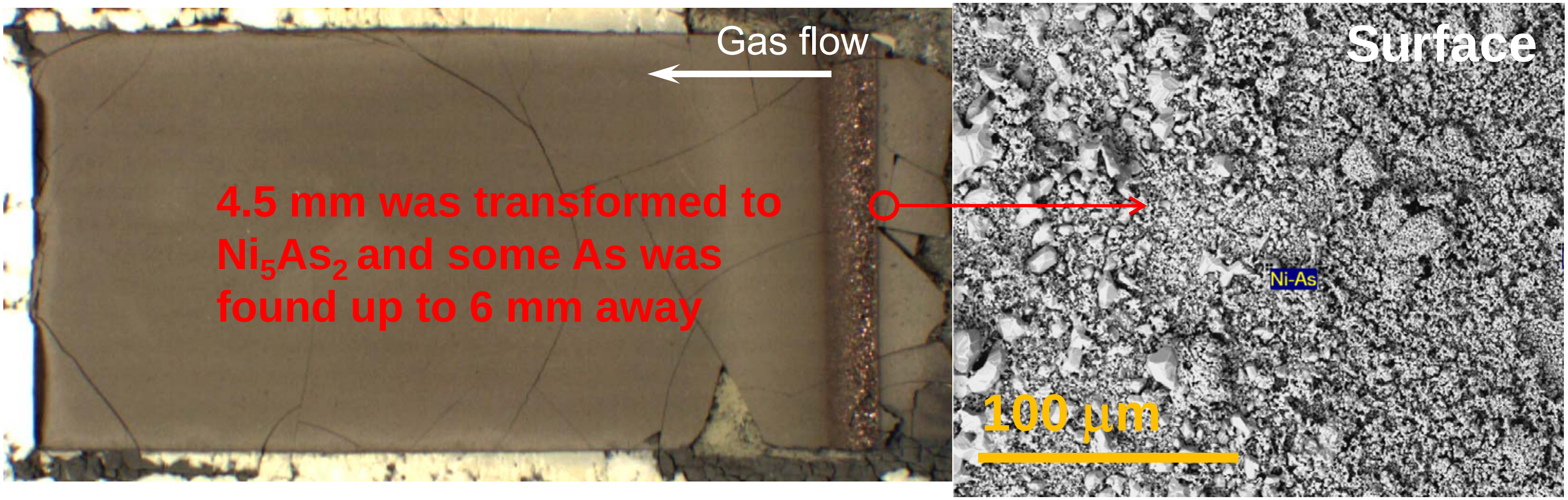


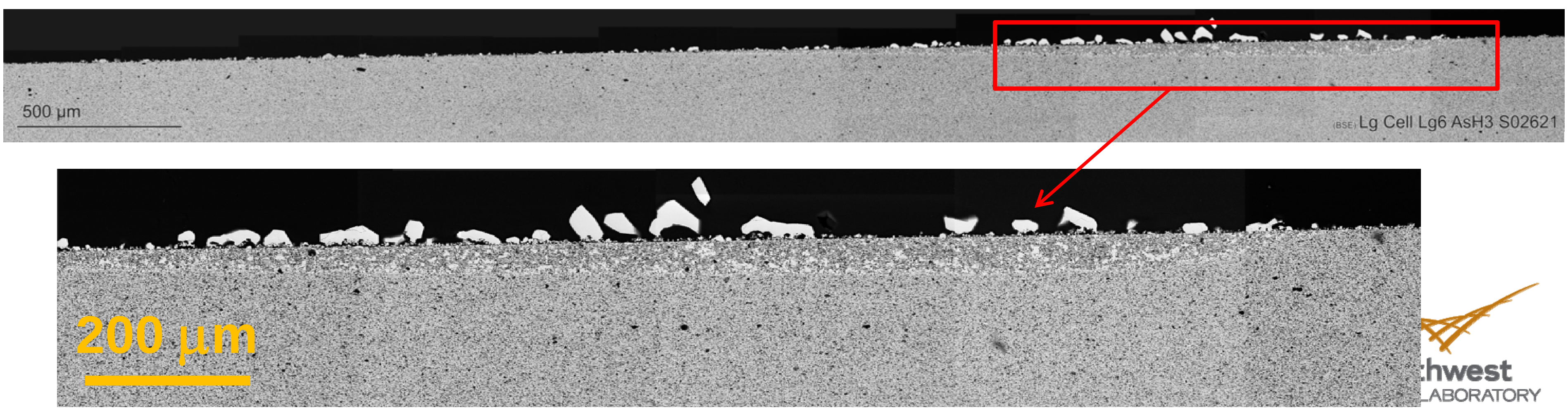




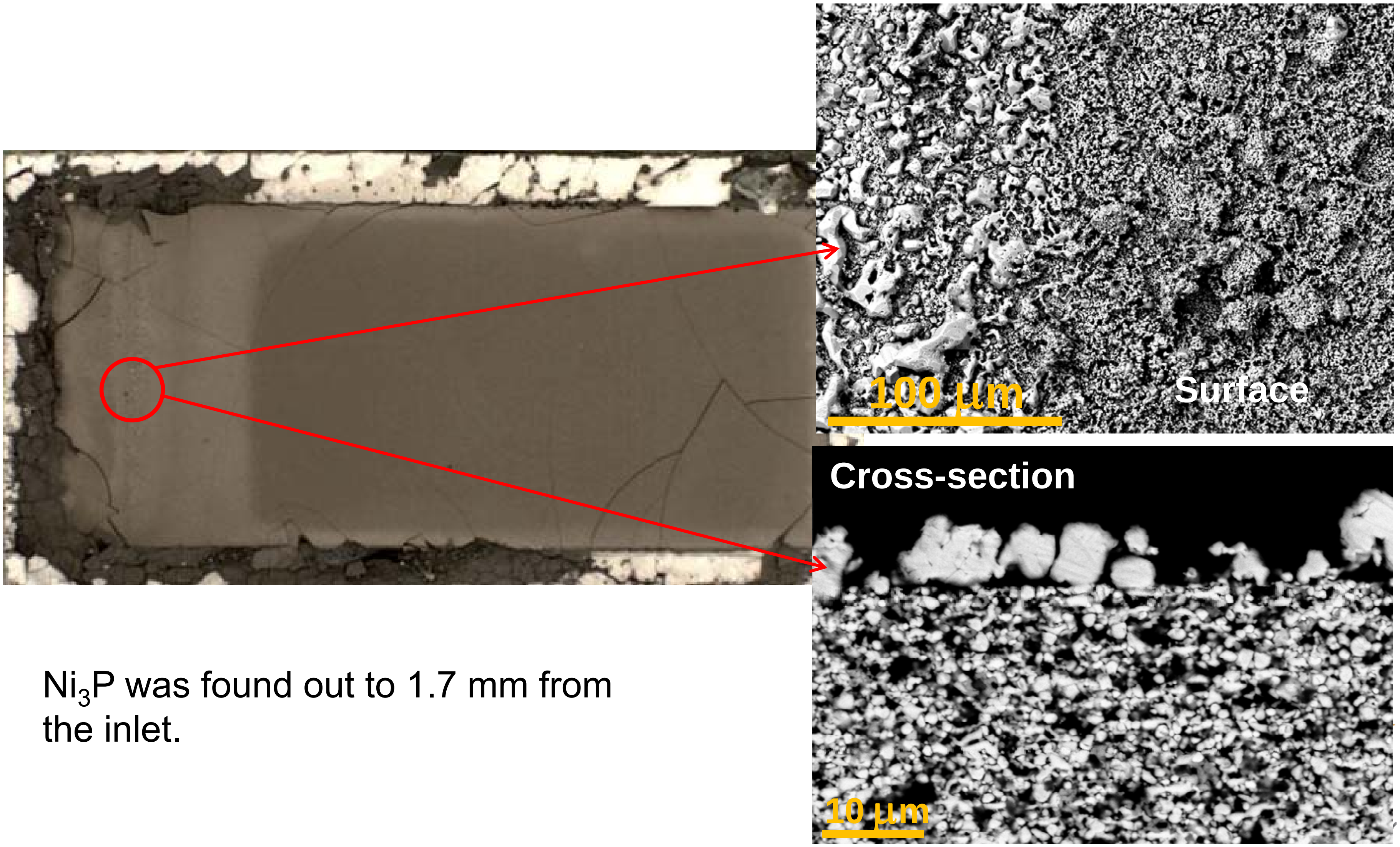
This map was obtained from a cell (A10-3) tested with 1 ppm P+1 ppm As at 800°C.

1 ppm AsH_3 at 800^oC, 100h





0.5 ppm PH_3 at 800°C, 100h



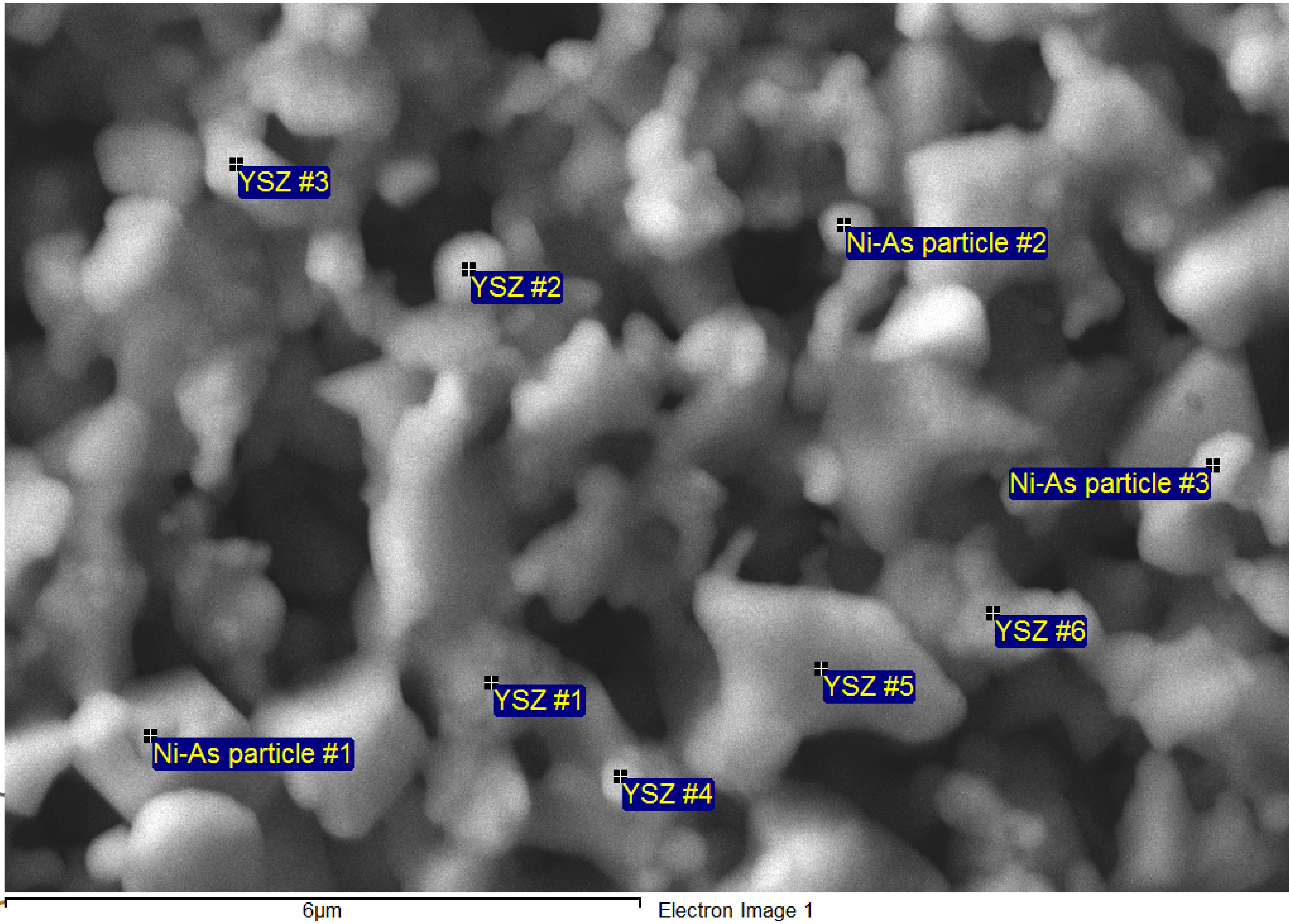
Ni_3P was found out to 1.7 mm from the inlet.

"Flow-by" anode contaminant tests at 10 ppb

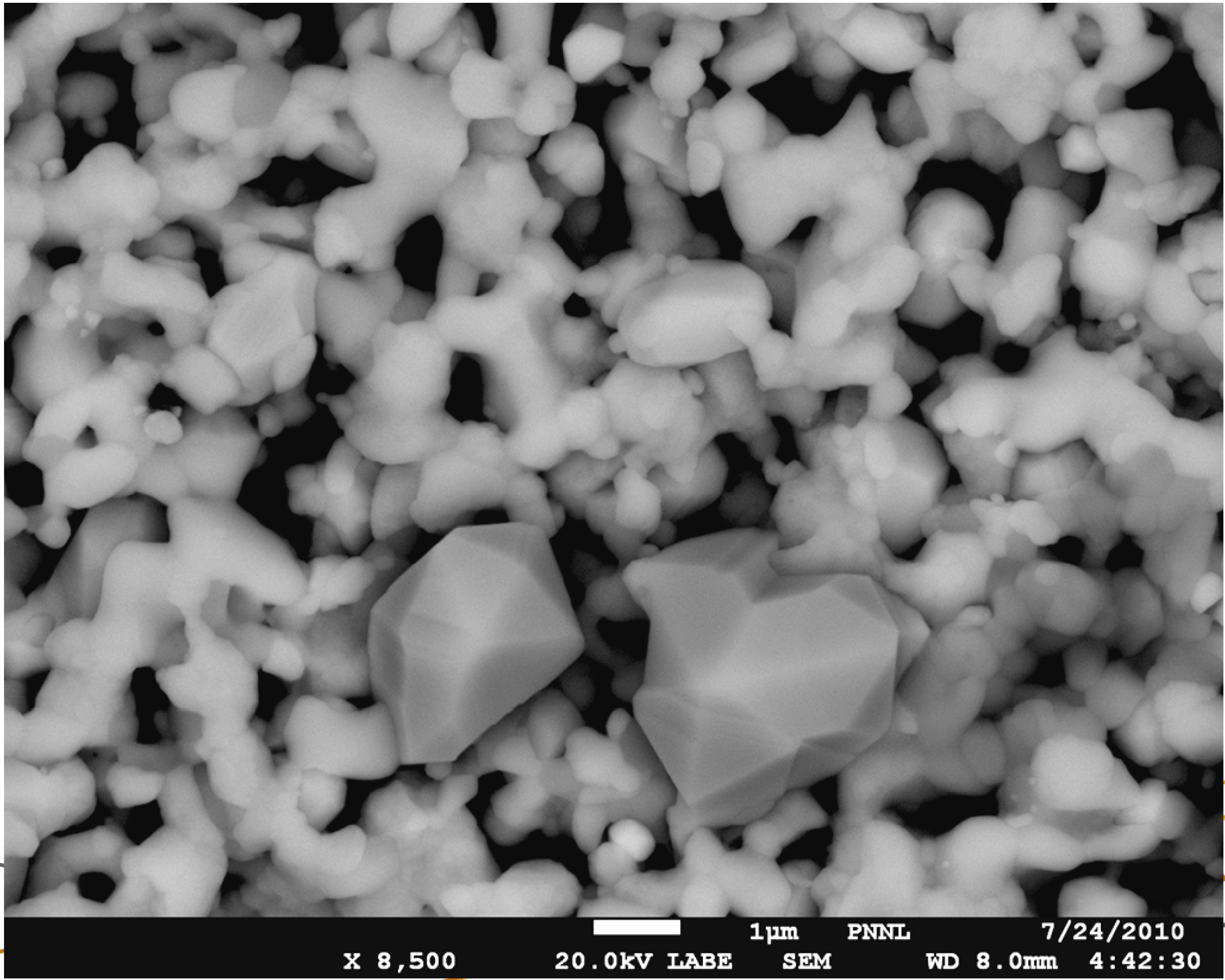
- 2000 hour tests completed
  - Total As supplied: 0.8 mg
  - Total P supplied: 0.3 mg
  - Total contaminant dosage was 40% of dosage in 0.5 ppm, 100 h tests
- Nickel arsenide detected by surface SEM/EDS
  - "Needle in a haystack"; unclear why secondary phase is so hard to find
  - Confirmed that 10 ppb is higher than minimum As concentration for secondary phase formation

- Will follow up with cross-section SEM/EDS
- Longer term are tests in progress

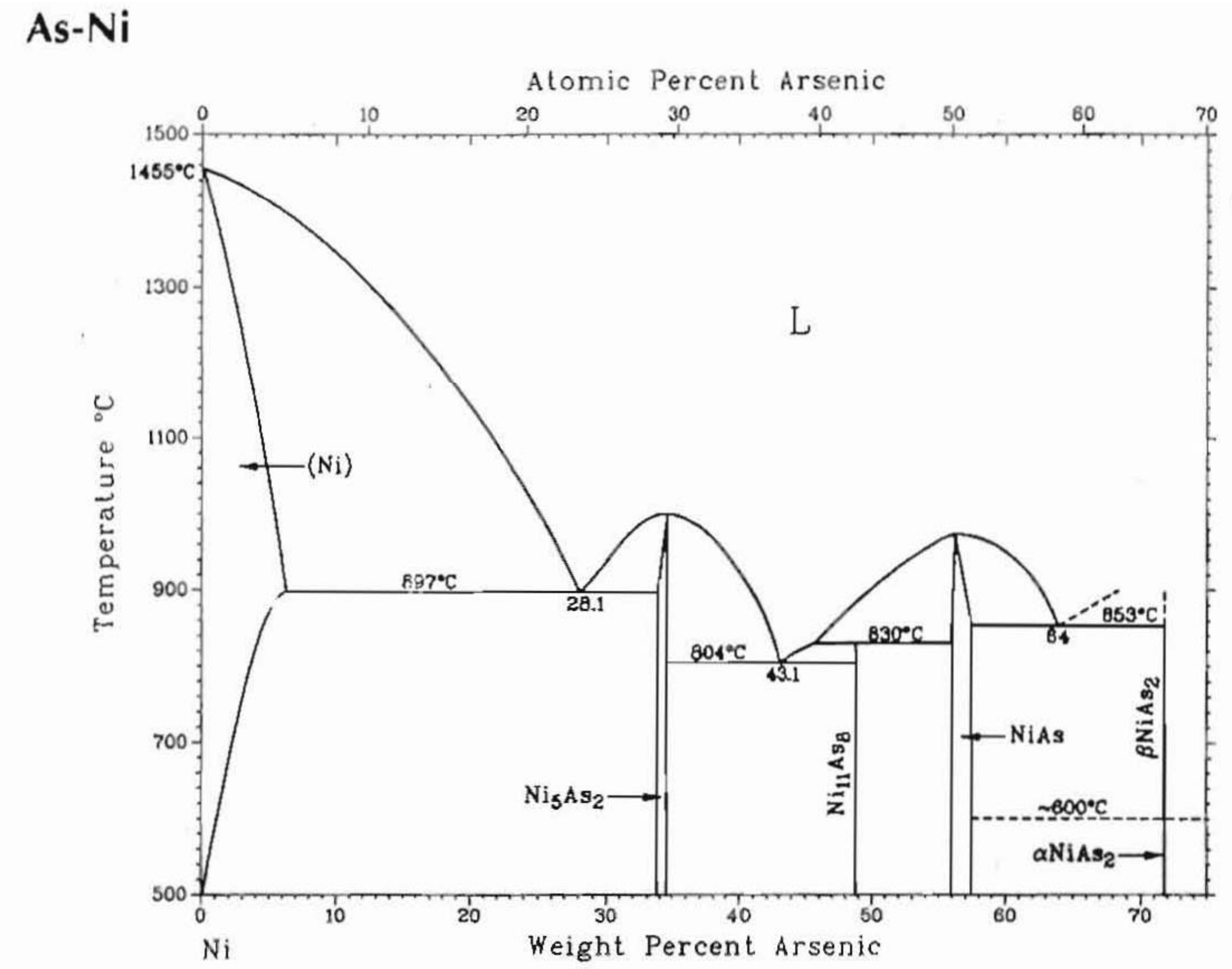
“Flow-by” anode contaminant tests at 10 ppb



"Flow-by" anode contaminant tests at 10 ppb



Arsenic – Nickel Phase Diagram



Note eutectics at 897 and 804ºC

ASM Handbook, Volume 3, “Alloy Phase Diagrams,” 1992

Effect of Electrical Potential on Ni Conversion

- Flow rate: 200 sccm, corresponding to ~65% fuel utilization at 0.8 A/cm^2
- Gas composition: Simulated coal gas (55% H_2; 45% CO_2)
- Contaminant type and level:
  - 1 ppm AsH_3
- Temperature: 800ºC
- Exposure time: 2000 hours (ending date: 7/29/10)

Case 1: No electric potential/current (baseline)
Case 2: Anode at 0V potential (connected to ground) /1.5 A/cm^2
Case 3: Anode at 40V potential / 1.5 A/cm^2

SUMMARY

- Strong interactions occur between Ni-based anodes and P and/or As contaminants in coal
- These interactions result in formation of secondary phases
  - Nickel phosphide solid phases: Ni_3P, Ni_5P_2, $Ni_{12}P_5$, Ni_2P, etc.
  - Nickel arsenide solid phases: Ni_5As_2, $Ni_{11}As_8$, etc.
  - Phosphide/arsenide formation were observed at ppm levels, and are predicted at much lower concentrations (< 1 ppb at 800ºC)
  - Sharp boundaries are observed between reacted and un-reacted parts of the anode
- At ppm levels, interactions result in ohmic (P, As) and non-ohmic degradation (P) of cell performance
- Tests with P and As at 10 ppb are in progress
  - For coal gas fuels cleaned to ppb levels, secondary phase formation is expected, but low rate of contaminant delivery may significantly reduce degradation rates, and also simplify upstream mitigation.

Future Work

- Complete longer term tests at 10 ppb level (P, As, P+As)
- Perform tests at intermediate contaminant levels (between 10 ppb and 0.5 ppm)
  - Equivalent total dosage (concentration x time)
- Correlate dosing level and time with extent of observed Ni conversion
- Complete electric potential tests

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