# Effects of Phosphorus and Arsenic on SOFC Anodes

**J.W. Stevenson, O.A. Marina, C.A. Coyle, and D.J. Edwards**

Pacific Northwest National Laboratory
Richland, WA

July 26-28, 2011

12th Annual SECA Workshop

Pittsburgh, PA

Pacific Northwest NATIONAL LABORATORY

*Proudly Operated by* Battelle *Since 1965*

# Outline

- Introduction / Summary of Previous Work
- Objectives / Experimental Approach
- Experimental Results
- Summary
- Future Work
- Acknowledgements

# Introduction

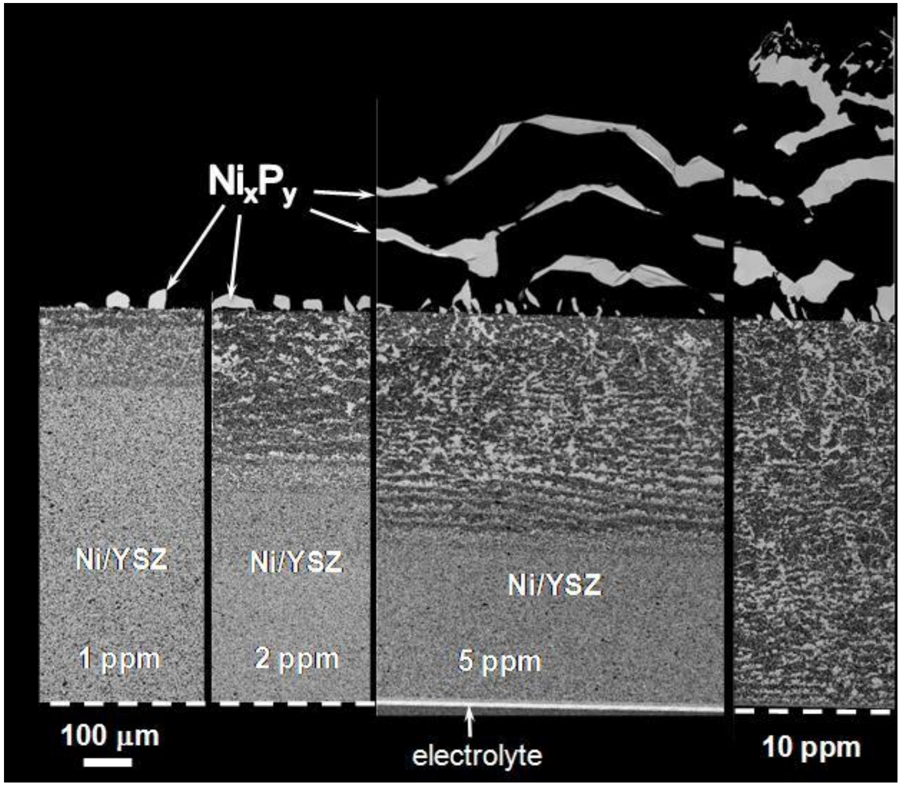
- Coals contain a wide variety of impurities.
- Different impurities lead to different types of interactions with SOFC anode.
- Anode performance degradation due to coal gas impurities is affected by various factors, such as concentration of contaminants, temperature, operation time, cell voltage, and fuel utilization.
- Previous studies at PNNL focused on effects of P, As, Sb, S, Se, Cl at ppm levels
- Current studies are focused effects of sub-ppm levels of P and/or As on anode chemistry/microstructure

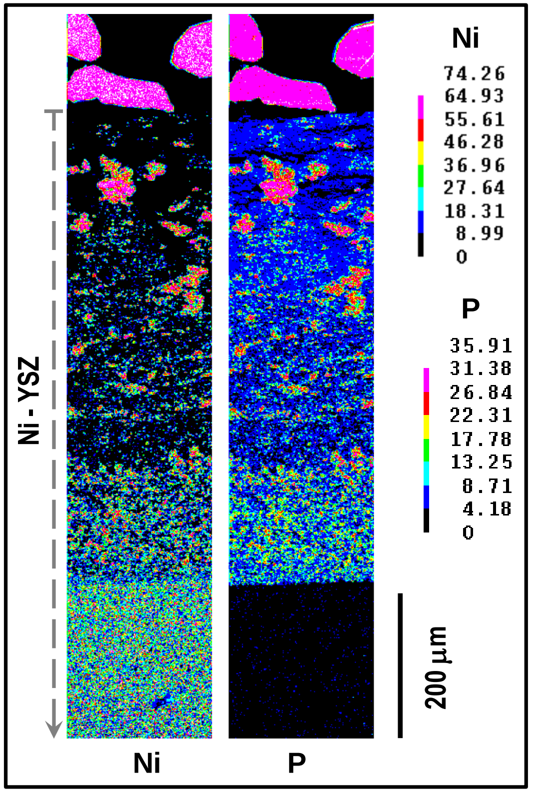
# Anode–Phosphorus Interactions: Conclusions from Previous Work

- 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.
  - 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
  - Poisoning due to transport 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–Phosphorus Interaction

- SEM Analysis of anode-supported button cells after exposure




- ❑ Sharp boundary between reacted and unreacted anode
- ❑ WDS confirmed P is associated only with nickel, not zirconia.
- ❑ Micro-crack formation in reacted area: W. Liu et al., "Effect of Nickel-Phosphorus Interactions on Structural Integrity of Anode-Supported SOFC," J. Power Sources, 195, 7140 (2010).

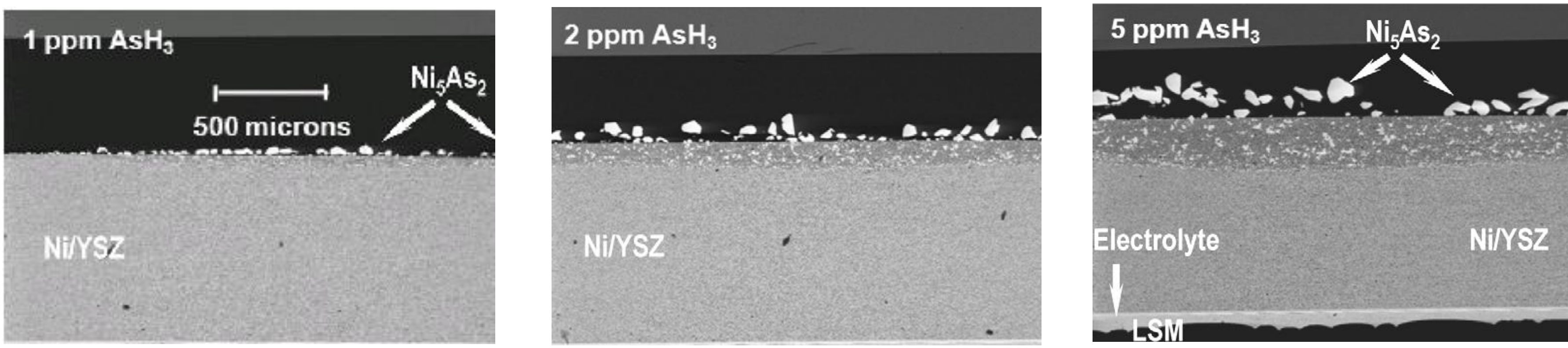
Pacific Northwest NATIONAL LABORATORY
Operated by Battelle Since 1965

# 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.
  - 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 [$AsH_3$] = 1 – 10 ppm, substantial degradation of performance observed in 1000 hours or less

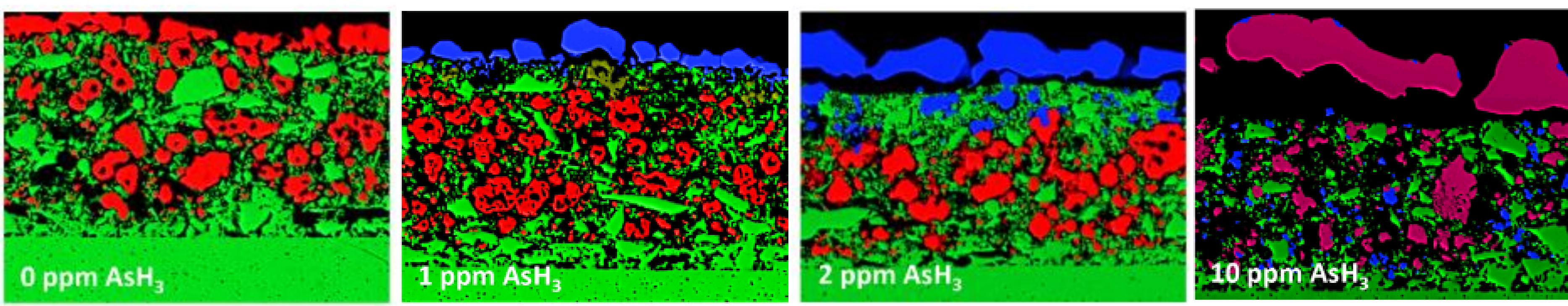
# Anode–Arsenic Interaction

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




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

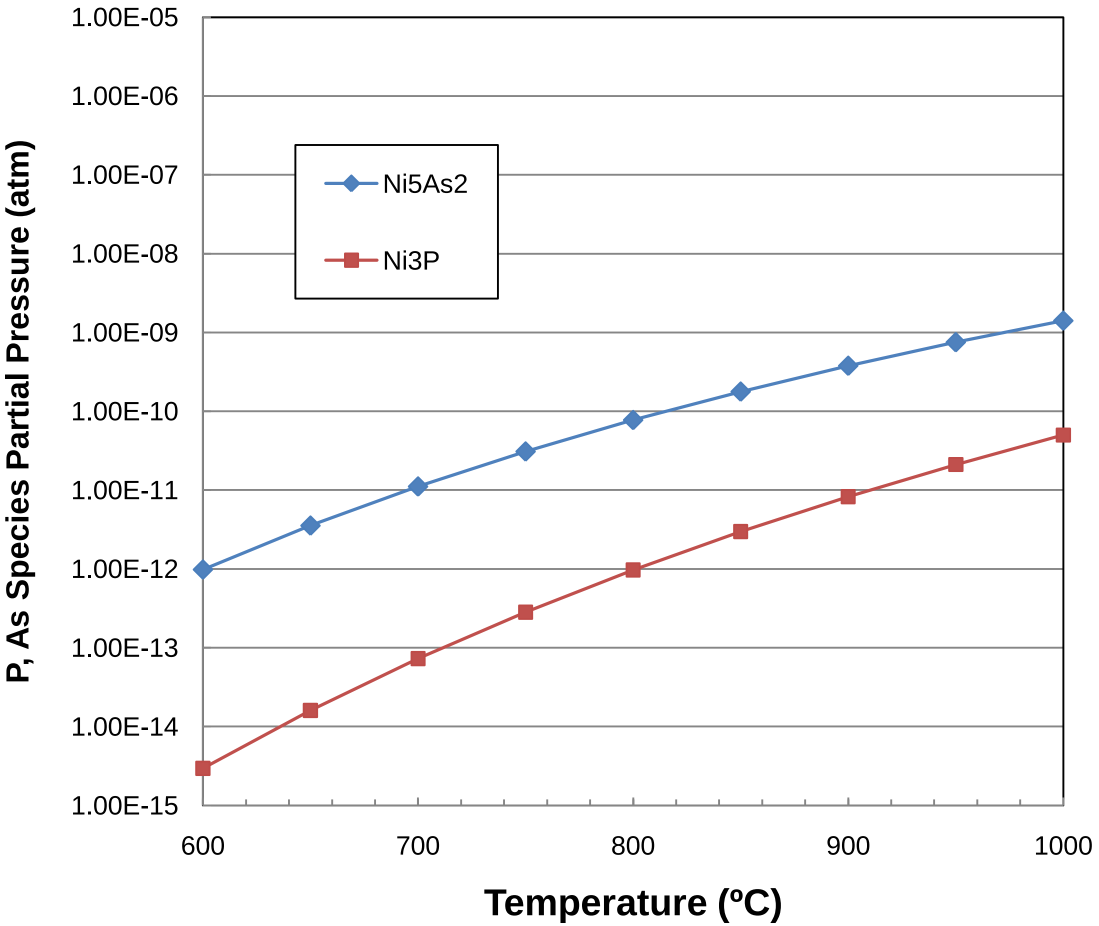
- **Conversion of Nickel to Nickel Arsenide ($Ni_5As_2$, $Ni_{11}As_8$)**




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

# Phosphide/Arsenide Formation

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

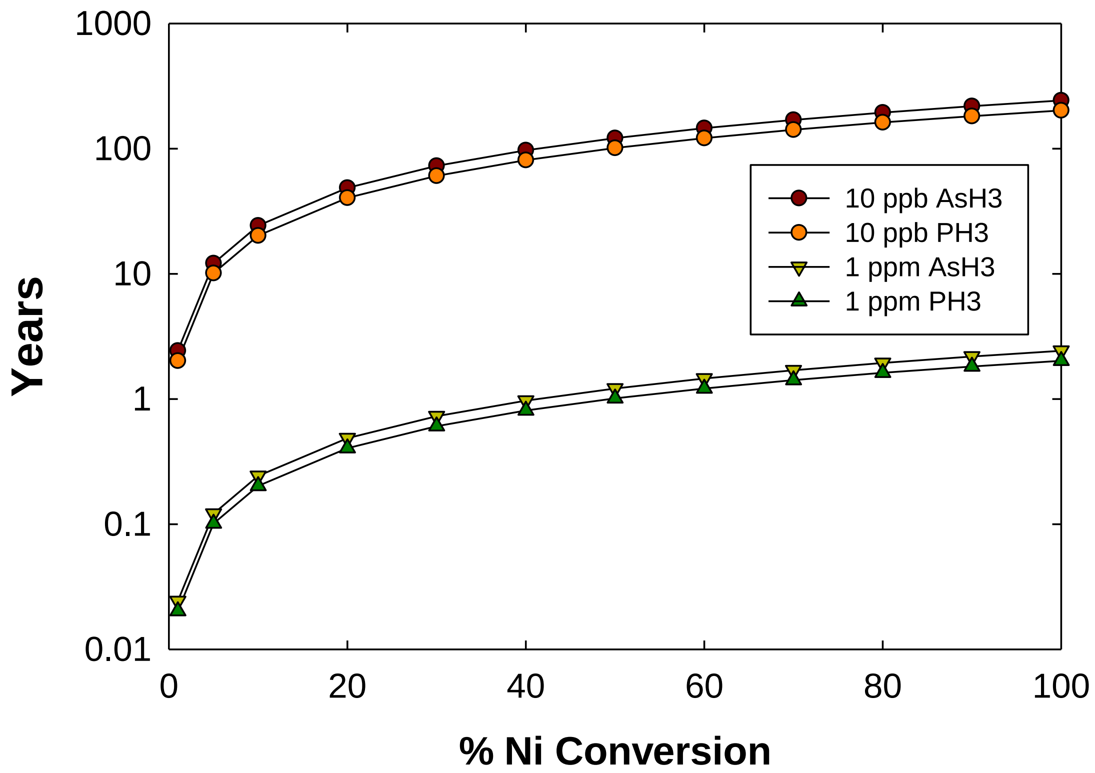



ic Northwest
NATIONAL LABORATORY
y Battelle Since 1965

# Effect of contaminant level on conversion rate

- Expect lower rate of reaction as contaminant level decreases due to lower 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: $Ni_5As_2$




Pacific Northwest NATIONAL LABORATORY

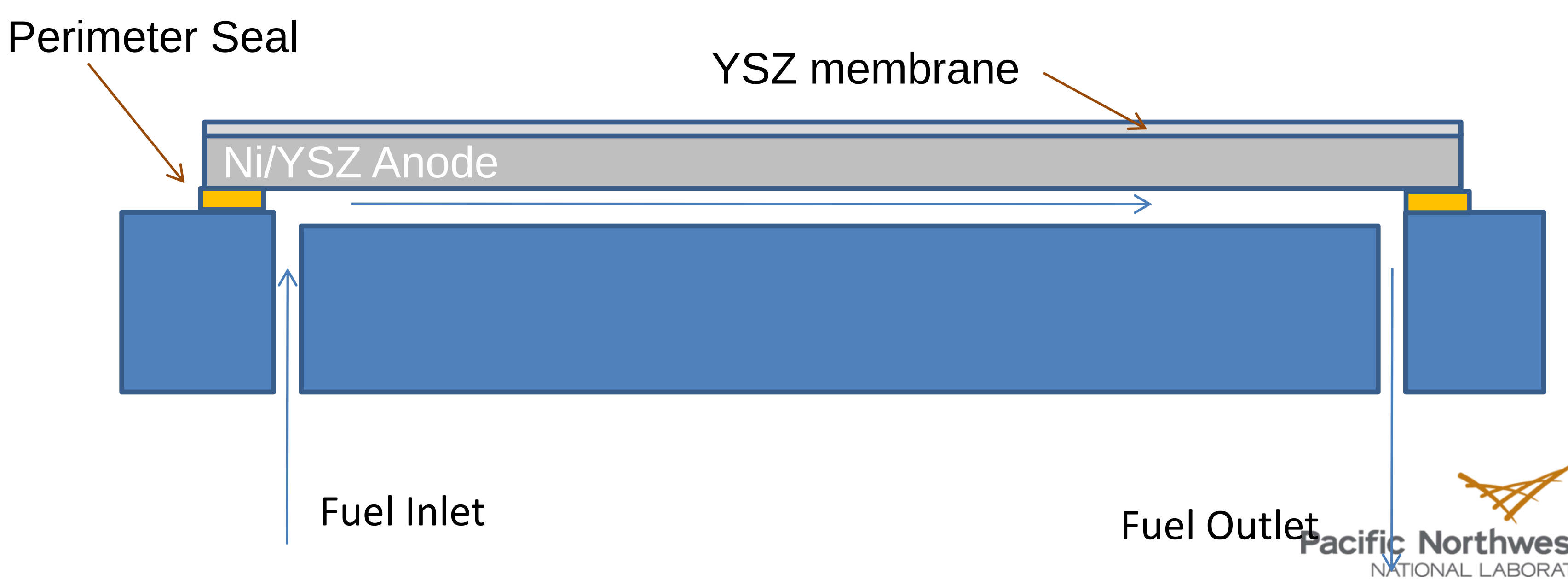
*Proudly Operated by* Battelle *Since 1965*

# Objective/Approach

- Objective: Study effects of sub-ppm levels of P, As on Ni/YSZ anode chemistry and microstructure
  - Coal gasification cleanup may reduce P, As levels to the level of ~10 ppb.
- Previous studies verified substantial reaction phase formation at ppm levels. Do the nature and extent of anode/contaminant interactions change as contaminant concentration decreases below 1 ppm?
- Approach:
  - Perform “flow-by” reaction tests over a range of contaminant levels (between 10 ppb and 1 ppm)
  - Adjust test time to deliver equivalent total dosage for all tests (concentration x time = constant)
  - Use surface and cross-section electron microscope analyses of tested samples to assess relationships between contaminant type, contaminant level, dosing time, and secondary phase formation

# “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: $AsH_3$ and/or $PH_3$
- Temperature: 700, 800ºC




Not to scale

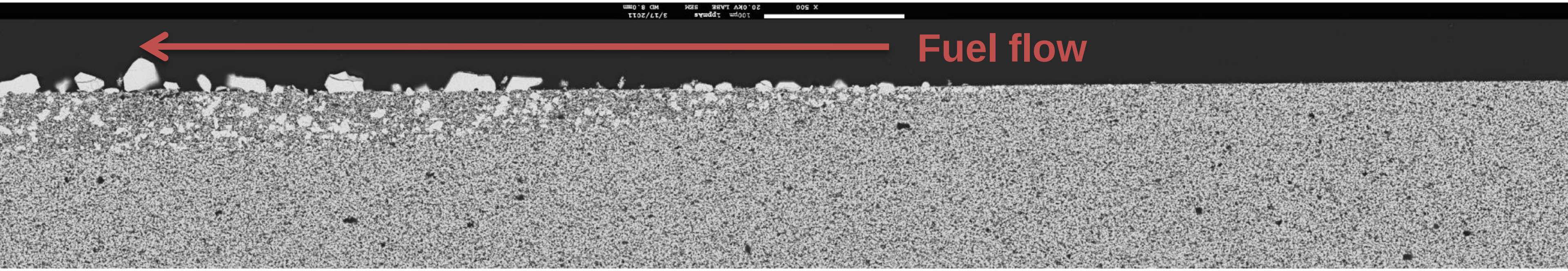
# Experimental parameters

- Perform tests over a range of contaminant levels (between 10 ppb and 1 ppm)
  - Equivalent total dosage of contaminant (dosing rate x time = Constant)

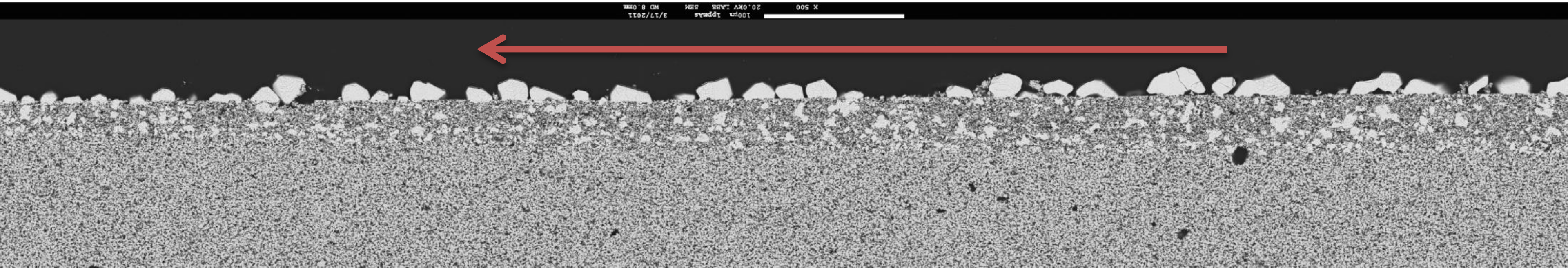
| Concentration | Time (h) | Total Moles Supplied |
|---|---|---|
| 1.00 ppm | 50 | $2.68 \times 10^{-5}$ |
| 0.50 ppm | 100 | $2.68 \times 10^{-5}$ |
| 0.10 ppm (100 ppb) | 500 | $2.68 \times 10^{-5}$ |
| 0.05 ppm (50 ppb) | 1000 | $2.68 \times 10^{-5}$ |
| 0.01 ppm (10 ppb) | 5000 | $2.68 \times 10^{-5}$ |

# Experimental Results

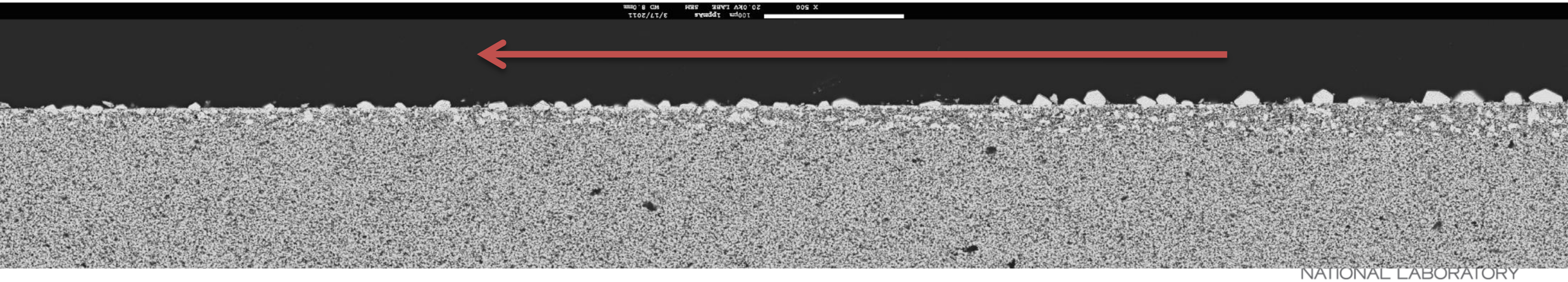
# 50 h, 1 ppm $AsH_3$ in simulated coal gas, 800ºC




- Region 1 (inlet)

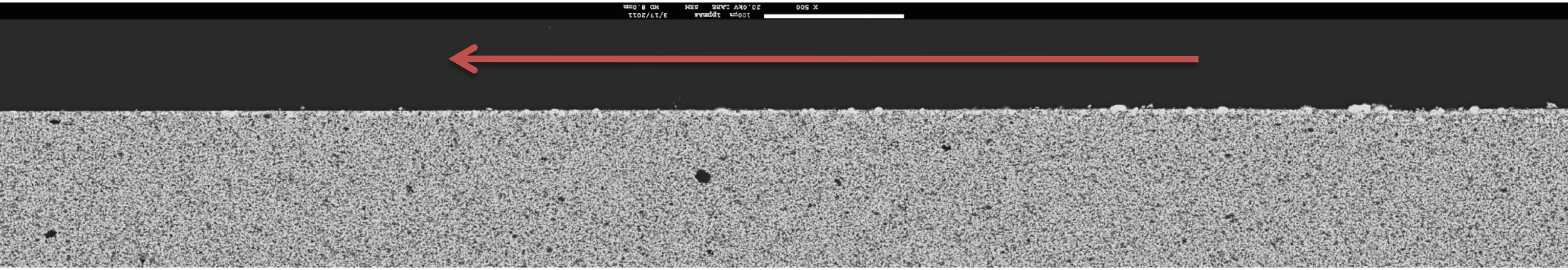


- Region 2



- Region 3

# 50 h, 1 ppm $AsH_3$ in simulated coal gas, 800ºC



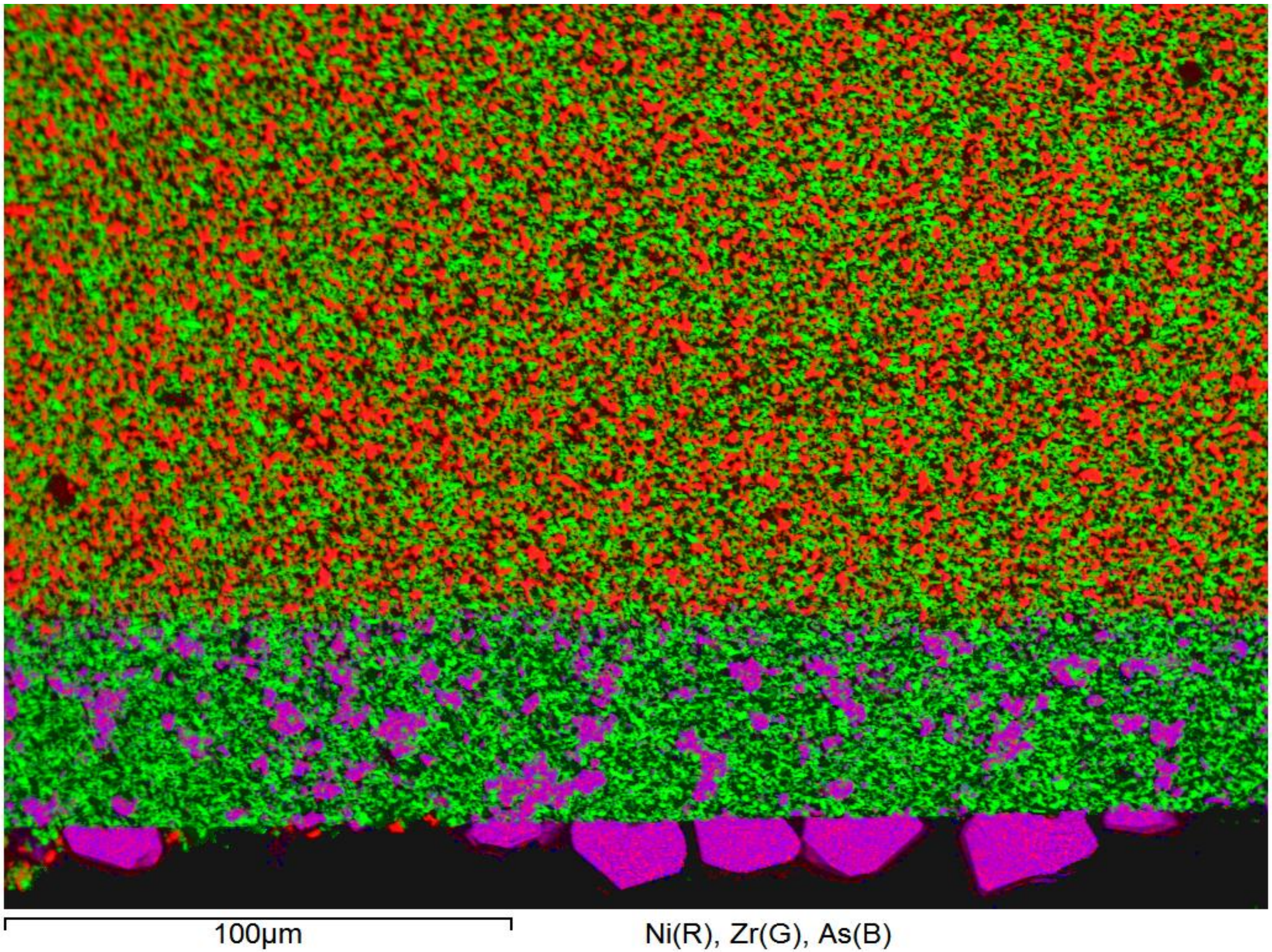
- Region 4

- Region 5

Pacific Northwest
NATIONAL LABORATORY

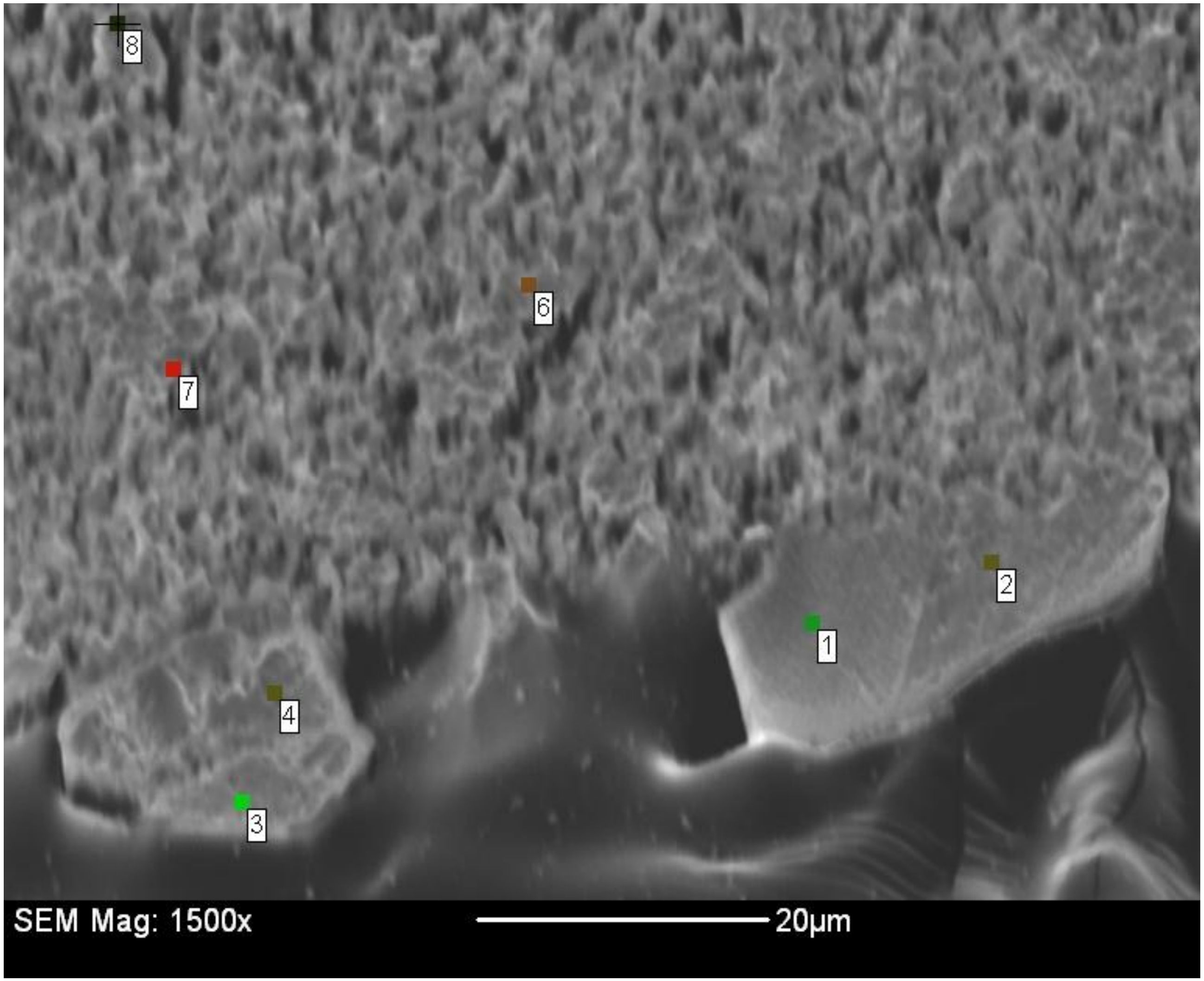
*Proudly Operated by* Battelle *Since 1965*

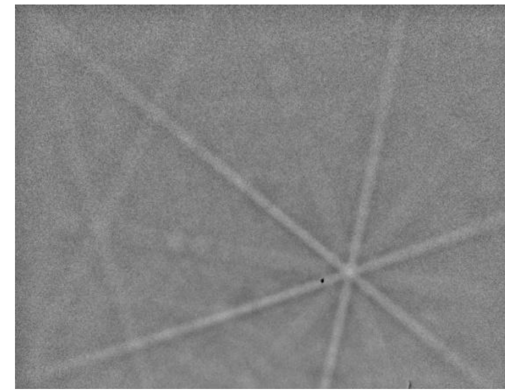
# 50 h, 1 ppm $AsH_3$ in simulated coal gas, 800ºC: EDS Analysis

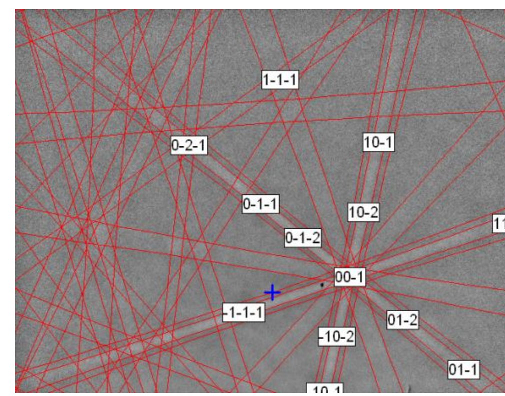



Purple is $Ni_5As_2$ phase

# EBSD Analysis confirmed surface (points 1-4) and bulk reaction phase (point 8) to be $Ni_5As_2$



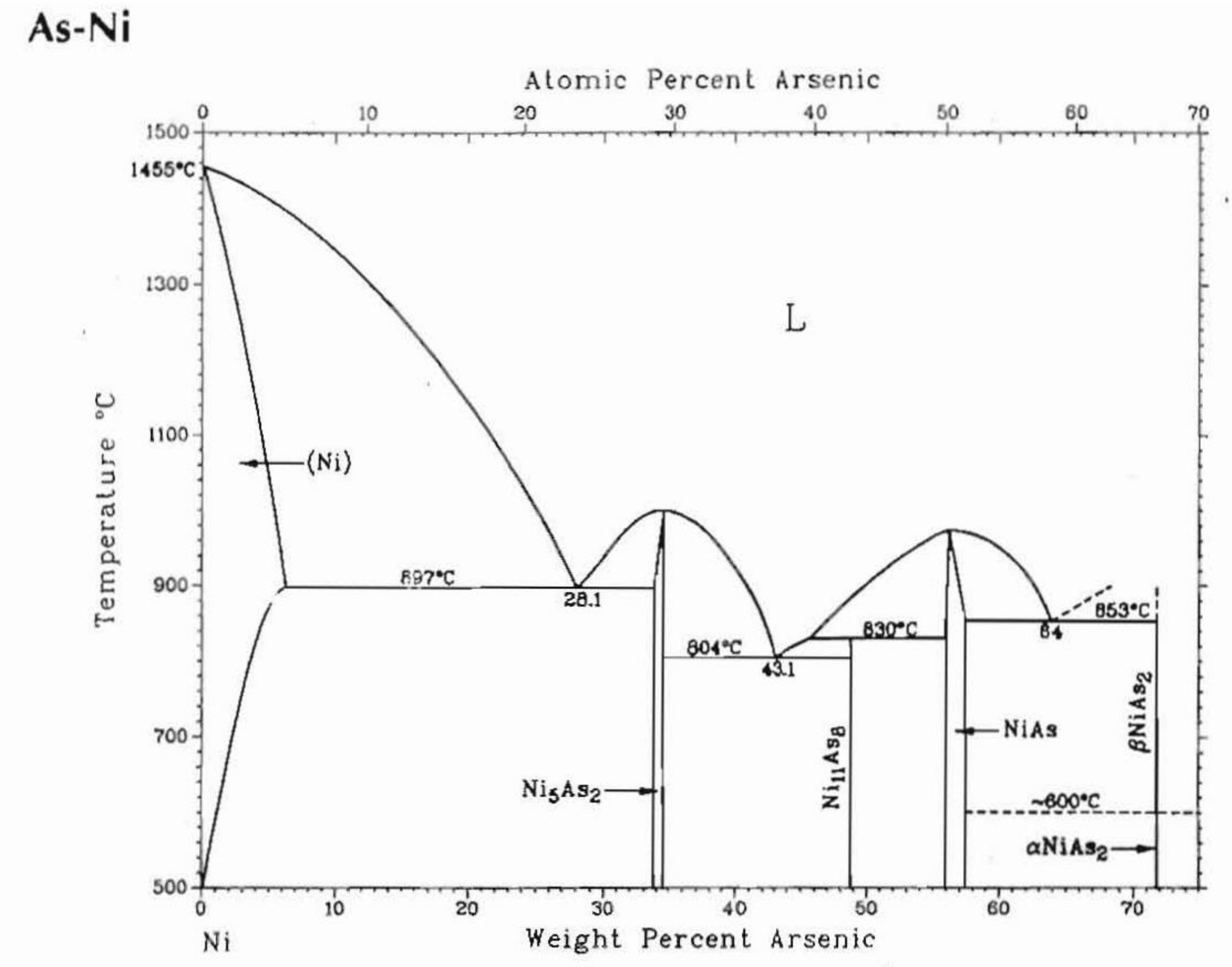






$Ni_5As_2$

Points 6,7 are YSZ

# Arsenic – Nickel Phase Diagram

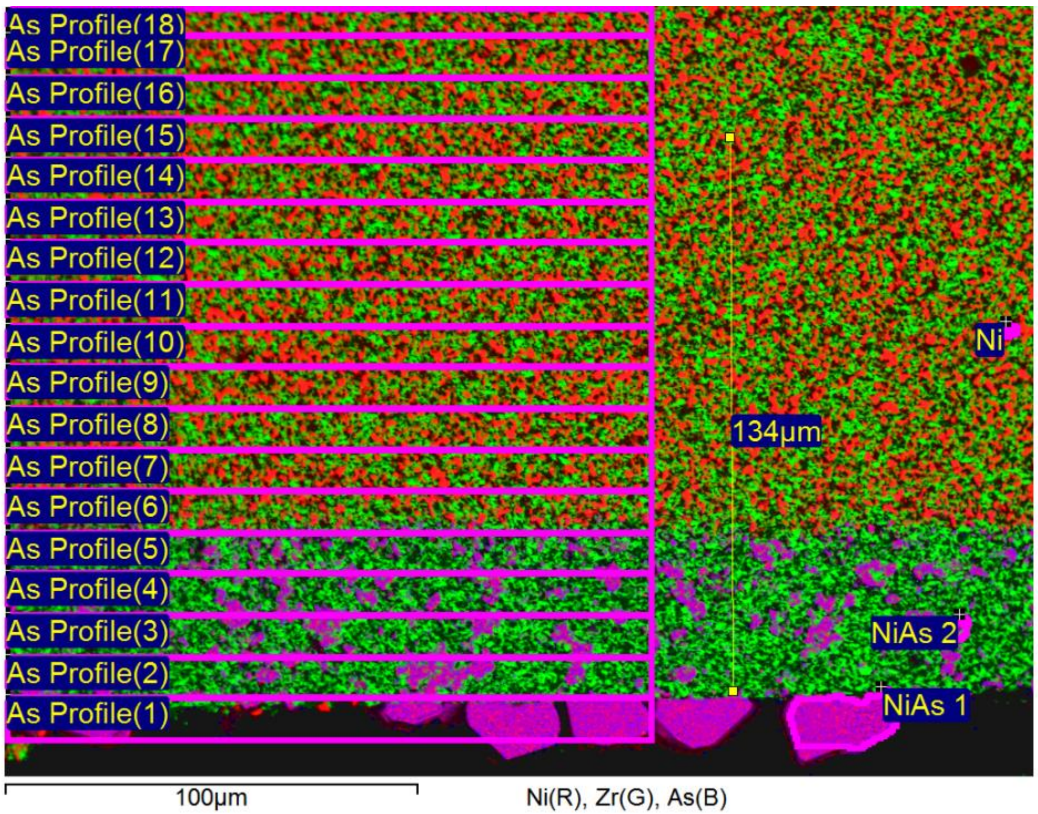



Note eutectics at 897 and 804ºC



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

# 50 h, 1 ppm $AsH_3$ in simulated coal gas, 800ºC: EDS area concentration profiles

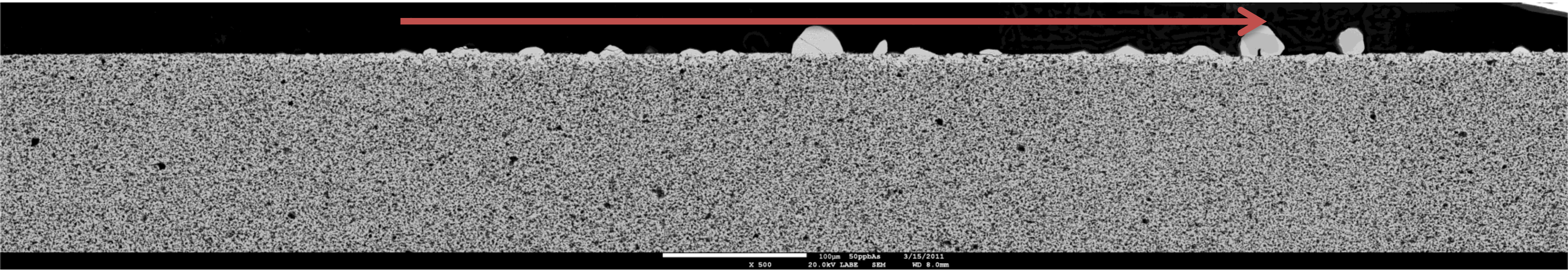



Profile height = 10µm

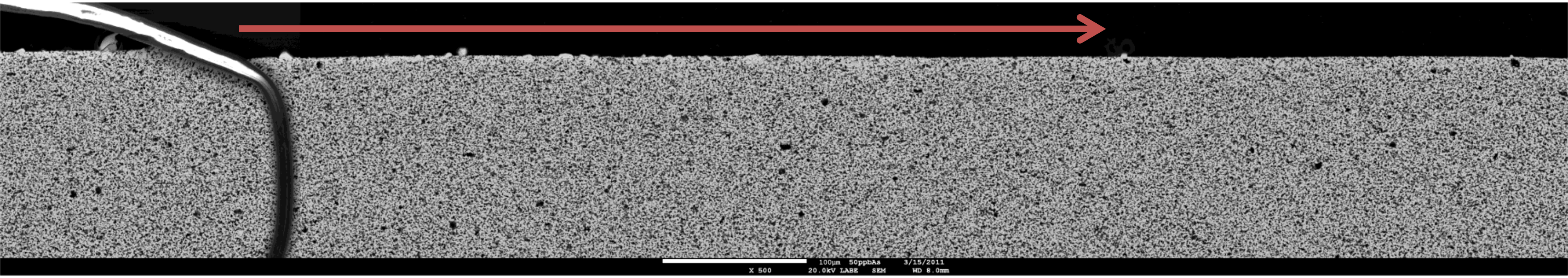
| *Spectrum* | *O* | *Ni* | ***As*** | *Y* | *Zr* |
|---|---|---|---|---|---|
| As Profile(18) | 37.56 | 43.02 | **0** | 1.18 | 18.24 |
| As Profile(17) | 39.75 | 40.19 | **0** | 1.37 | 18.69 |
| As Profile(16) | 41.09 | 38.54 | **0** | 1.32 | 19.05 |
| As Profile(15) | 39.93 | 40.04 | **0.07** | 1.32 | 18.65 |
| As Profile(14) | 40.81 | 38.66 | **0.08** | 1.35 | 19.09 |
| As Profile(13) | 40.69 | 38.85 | **0** | 1.38 | 19.08 |
| As Profile(12) | 40.42 | 39 | **0.07** | 1.37 | 19.14 |
| As Profile(11) | 39.2 | 40.8 | **0** | 1.28 | 18.72 |
| As Profile(10) | 38.68 | 41.65 | **0.1** | 1.24 | 18.33 |
| As Profile(9) | 39.03 | 41.14 | **0.11** | 1.26 | 18.46 |
| As Profile(8) | 40.11 | 39.6 | **0.11** | 1.37 | 18.81 |
| As Profile(7) | 40.1 | 39.49 | **0.52** | 1.29 | 18.61 |
| As Profile(6) | 41.61 | 35.71 | **2.28** | 1.34 | 19.06 |
| As Profile(5) | 48.77 | 22.32 | **6.1** | 1.47 | 21.35 |
| As Profile(4) | 49.48 | 20.91 | **6.21** | 1.61 | 21.78 |
| As Profile(3) | 51.74 | 18.74 | **5.39** | 1.64 | 22.49 |
| As Profile(2) | 52.65 | 17.66 | **5.05** | 1.7 | 22.94 |
| As Profile(1) | 24.78 | 46.87 | **15.3** | 0.74 | 12.31 |

All results in atomic%

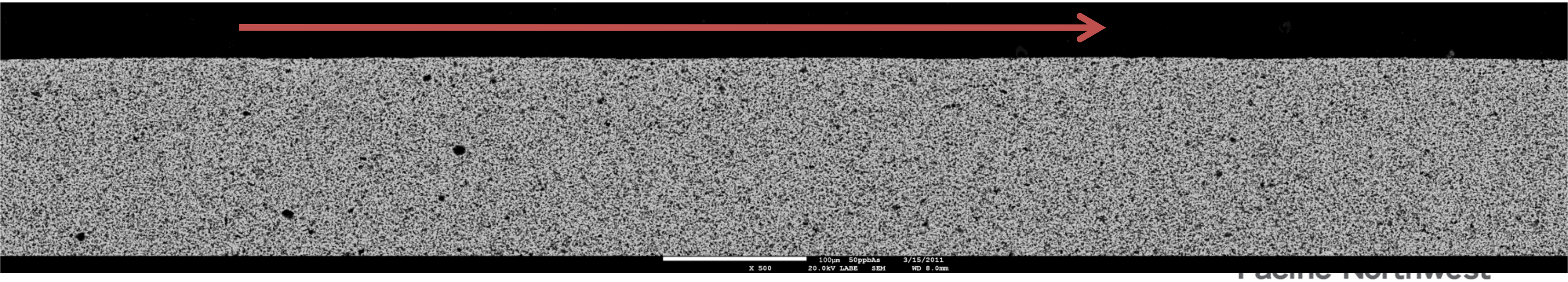
# 1000 h, 0.05 ppm $AsH_3$ in simulated coal gas, 800ºC




- Region 1 (inlet)

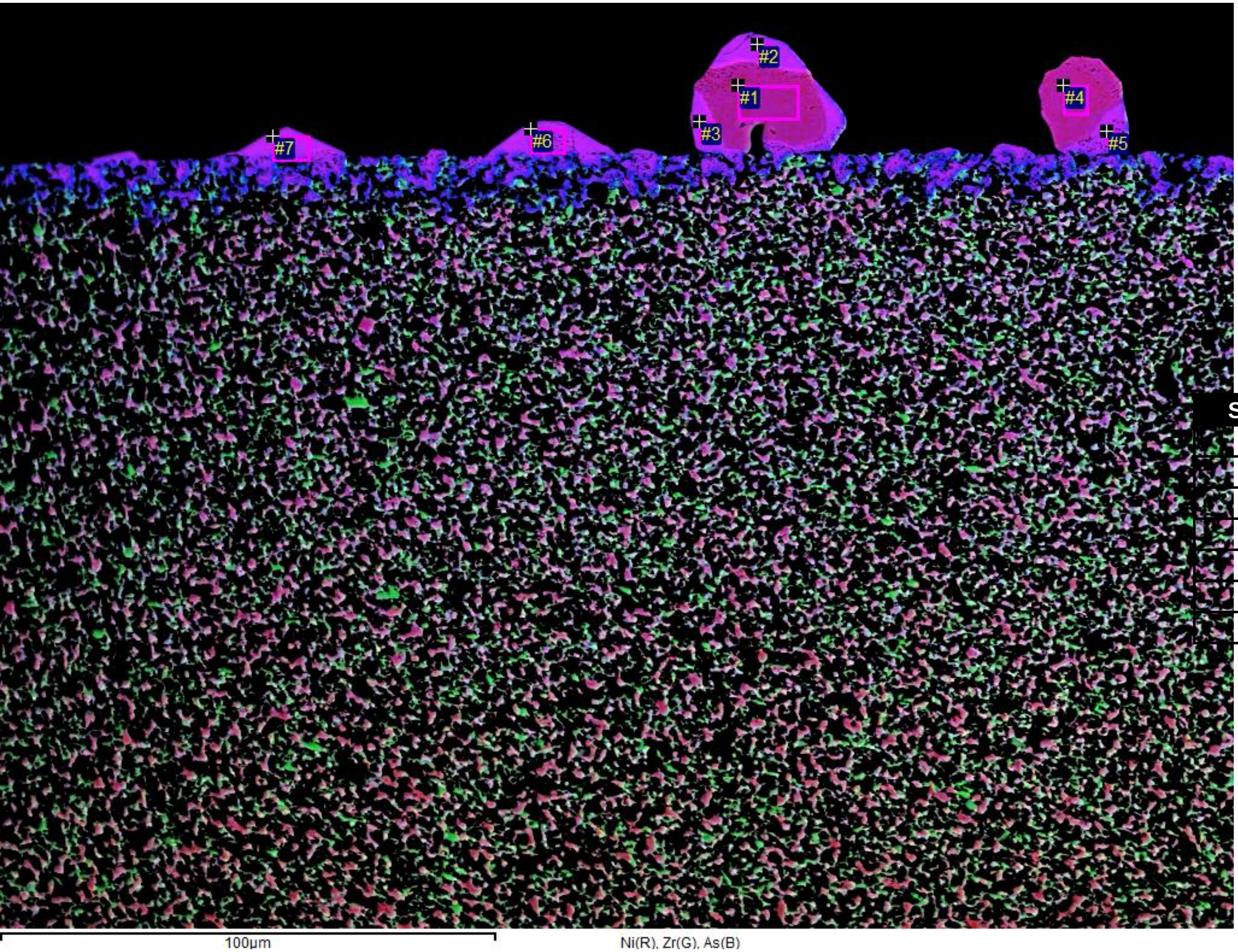



- Region 2




- Region 3

# 1000 h, 0.05 ppm $AsH_3$ in simulated coal gas, 800ºC



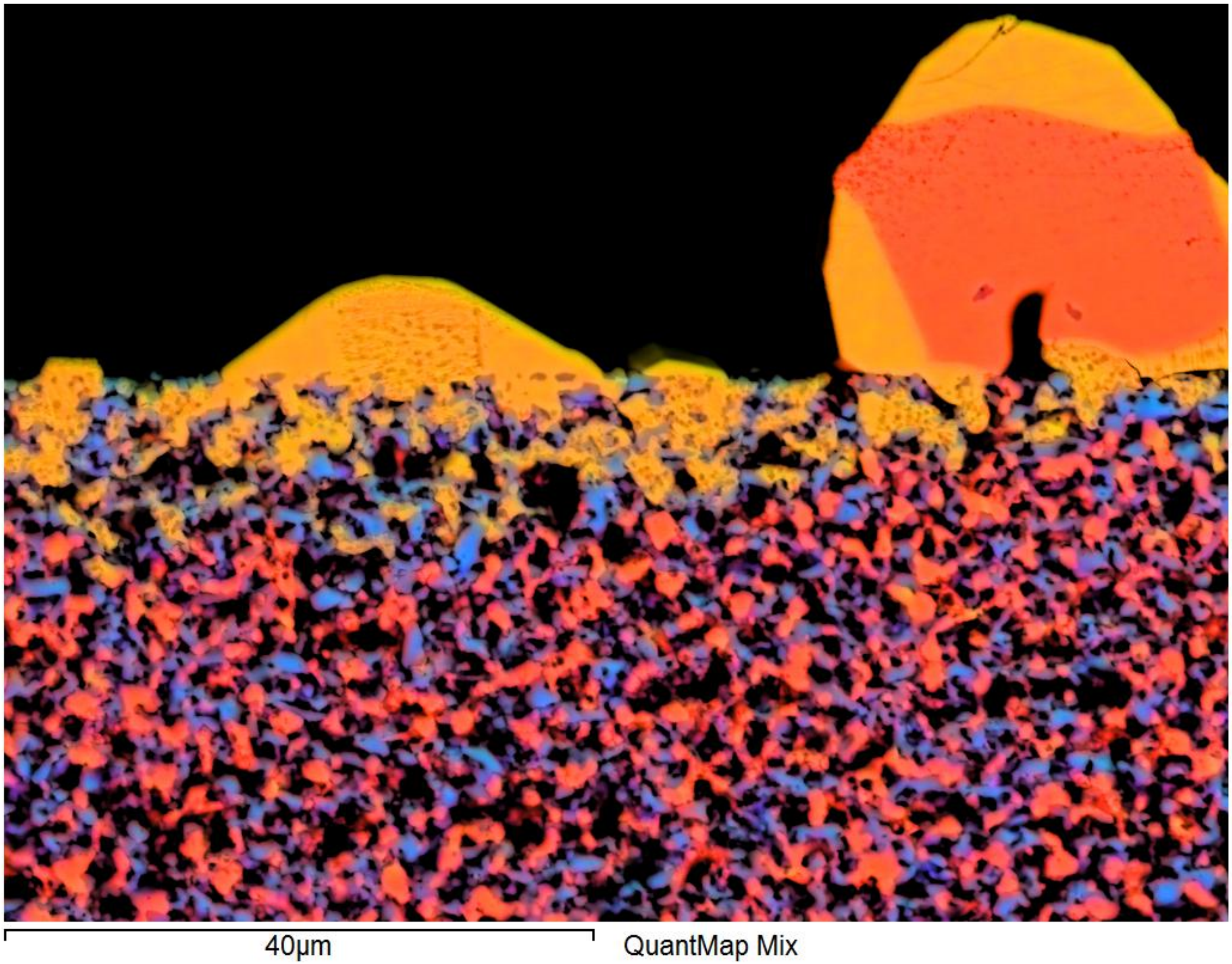

| Spectrum | O | Ni | As | Y | Zr |
|---|---|---|---|---|---|
| #1 | 2.42 | 89.41 | 8.16 | 0.00 | 0.00 |
| #2 | 0.00 | 71.47 | 28.53 | 0.00 | 0.00 |
| #3 | 0.00 | 71.64 | 28.36 | 0.00 | 0.00 |
| #4 | 2.77 | 89.85 | 7.38 | 0.00 | 0.00 |
| #5 | 7.19 | 67.45 | 25.36 | 0.00 | 0.00 |
| #6 | 0.00 | 73.00 | 27.00 | 0.00 | 0.00 |
| #7 | 3.65 | 68.93 | 25.95 | 0.00 | 1.48 |

**All results in atomic%**

**Points 2,3,5,6,7 are $Ni_5As_2$**

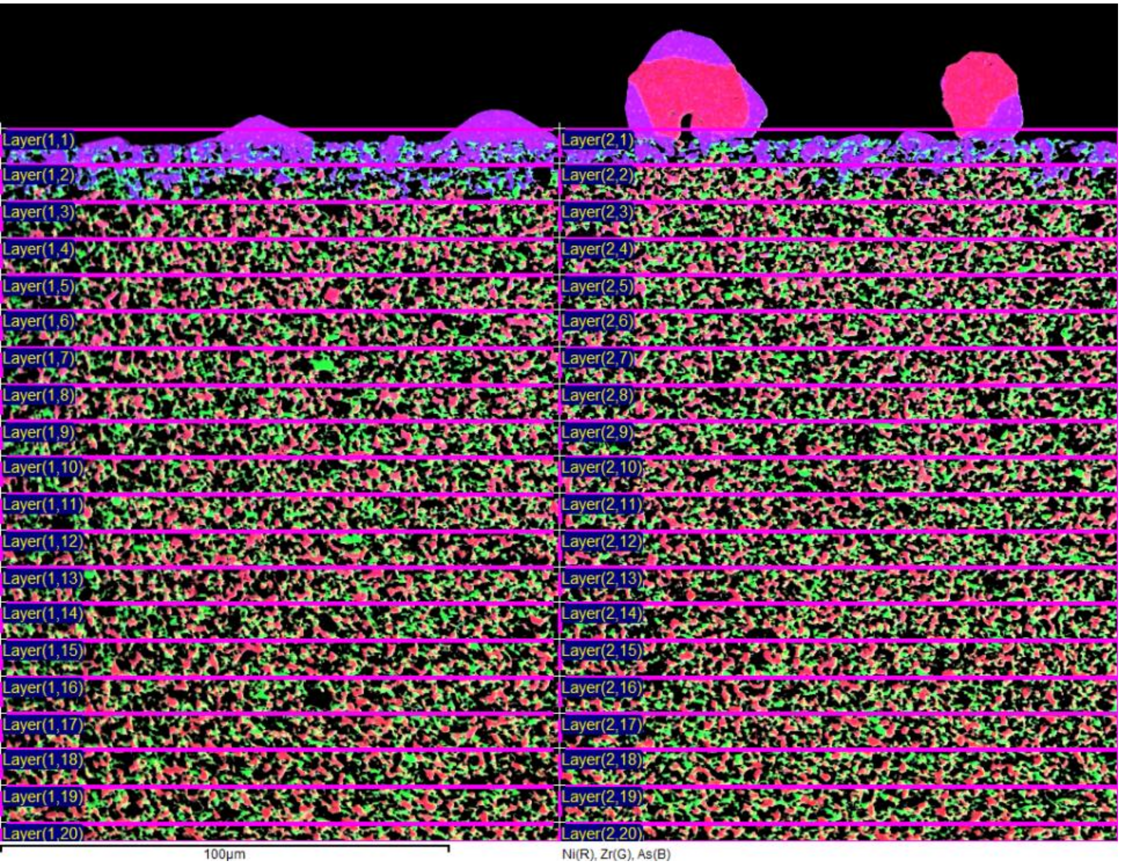
Ni (red); Zr (green); As (blue)

# 1000 h, 0.05 ppm $AsH_3$ in simulated coal gas, 800ºC




Yellow orange is $Ni_5As_2$, orange-red is Ni with varying levels of As, blue purple is YSZ

# 1000 h, 0.05 ppm $AsH_3$ in simulated coal gas, 800ºC

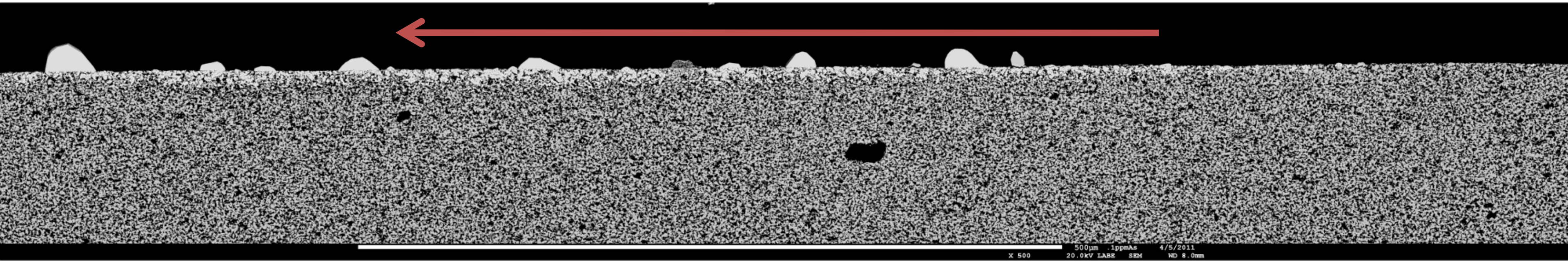



| Spectrum | Ni | As | Y | Zr | O |
|---|---|---|---|---|---|
| Layer 1 | 40.005 | **13.03** | 0.81 | 13.27 | 32.88 |
| Layer 2 | 32.78 | **4.685** | 1.195 | 18.31 | 43.025 |
| Layer 3 | 35.29 | **2.135** | 1.135 | 18.42 | 43.02 |
| Layer 4 | 34.43 | **1.95** | 1.205 | 18.67 | 43.74 |
| Layer 5 | 35.025 | **1.985** | 1.175 | 18.56 | 43.25 |
| Layer 6 | 33.715 | **1.745** | 1.225 | 18.955 | 44.365 |
| Layer 7 | 33.99 | **1.77** | 1.215 | 19 | 44.025 |
| Layer 8 | 34.535 | **1.665** | 1.22 | 18.775 | 43.81 |
| Layer 9 | 33.43 | **1.52** | 1.255 | 19.105 | 44.695 |
| Layer 10 | 34.84 | **1.465** | 1.23 | 18.6 | 43.87 |
| Layer 11 | 35.21 | **1.375** | 1.195 | 18.71 | 43.51 |
| Layer 12 | 36.025 | **1.285** | 1.22 | 18.555 | 42.91 |
| Layer 13 | 36.335 | **1.185** | 1.23 | 18.42 | 42.825 |
| Layer 14 | 34.52 | **0.975** | 1.23 | 18.815 | 44.45 |
| Layer 15 | 37.225 | **0.95** | 1.21 | 18.55 | 42.07 |
| Layer 16 | 36.025 | **0.785** | 1.245 | 18.785 | 43.15 |
| Layer 17 | 37.435 | **0.71** | 1.195 | 18.66 | 41.995 |
| Layer 18 | 36.47 | **0.595** | 1.24 | 18.765 | 42.93 |
| Layer 19 | 35.36 | **0.485** | 1.315 | 19.1 | 43.73 |
| Layer 20 | 39.72 | **0.475** | 1.22 | 17.955 | 40.635 |

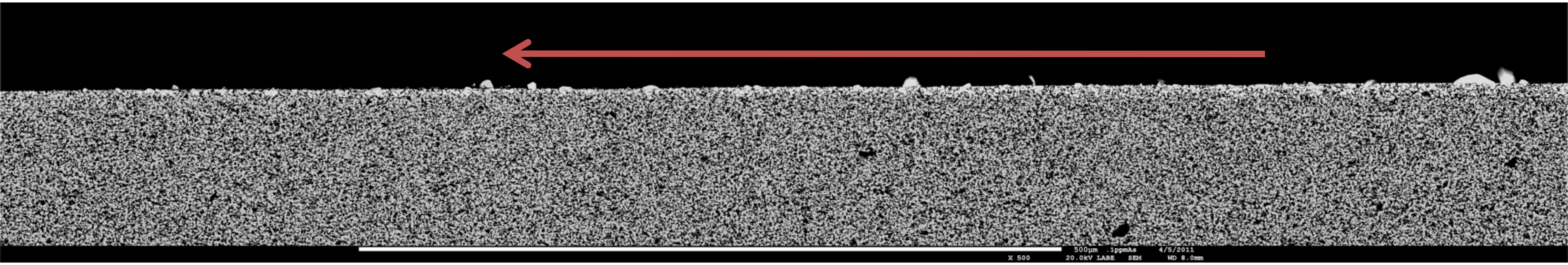
**Average values of both depth profiles.**
All results in atomic%

As is detectable down to ~150 µm below the surface.

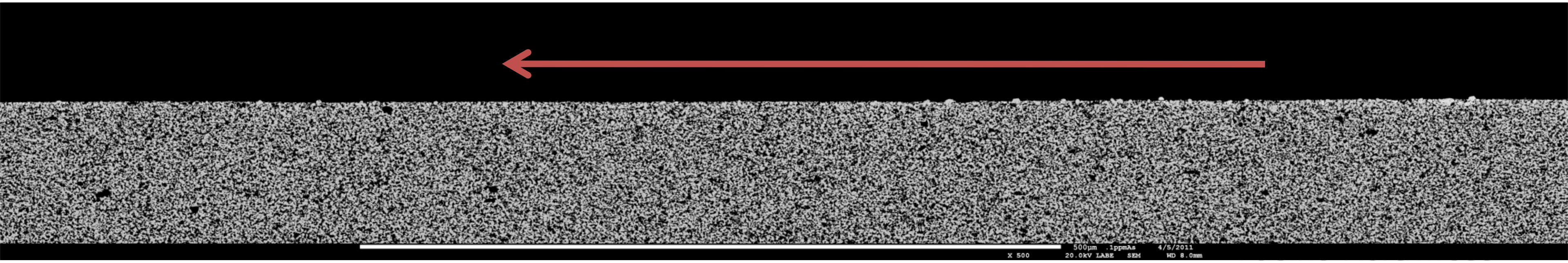
# 500 h, 0.1 ppm $AsH_3$ in simulated coal gas, 800ºC




- Region 1 (inlet)

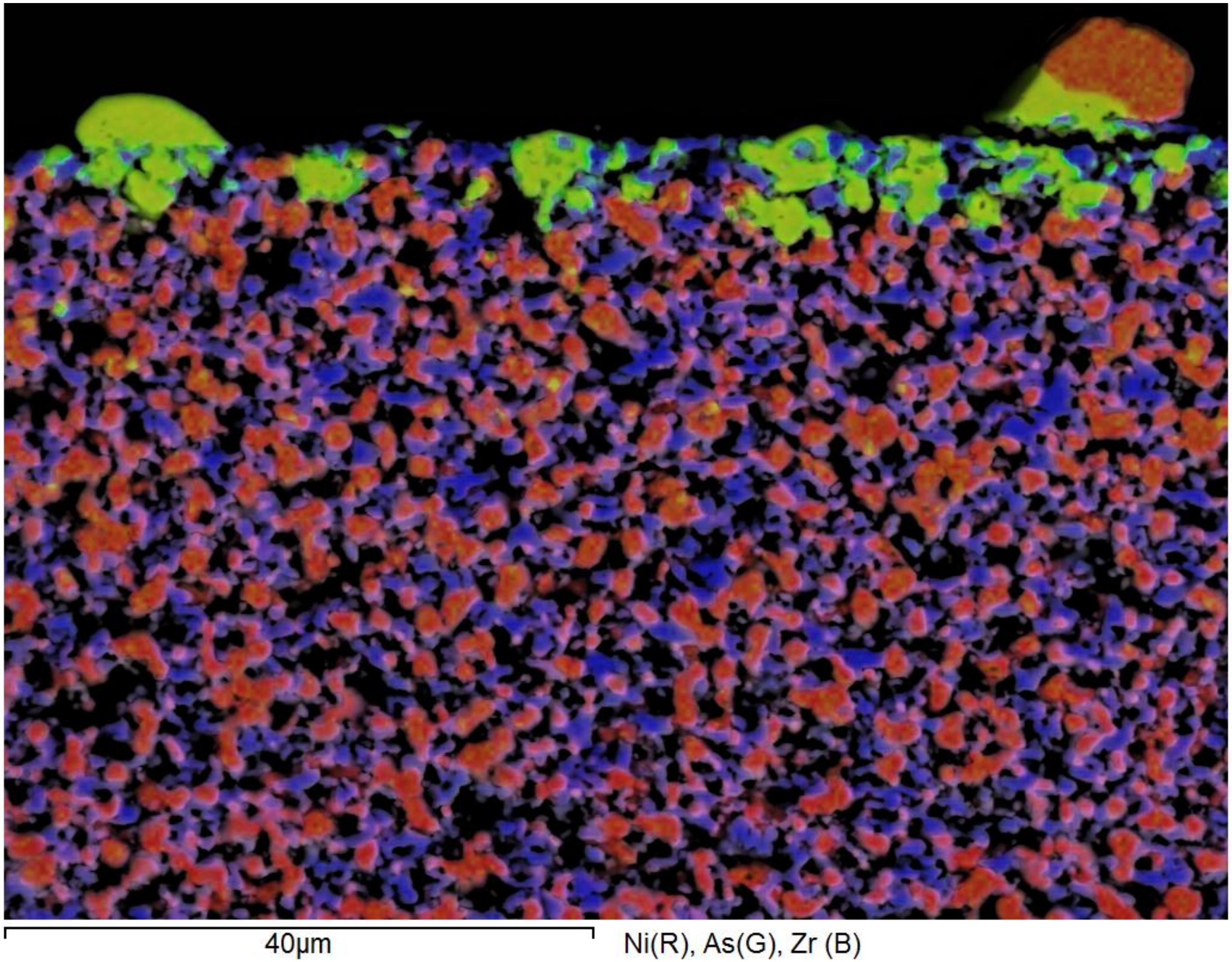



- Region 2



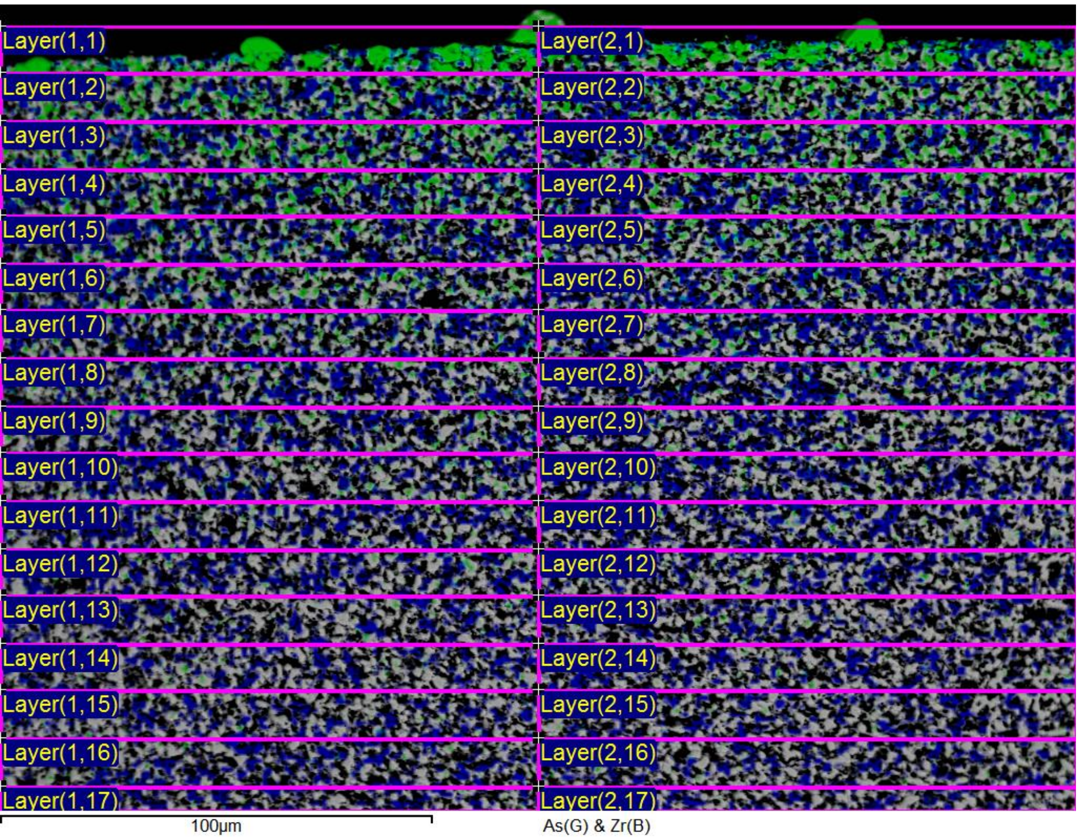

- Region 3

# 500 h, 0.1 ppm $AsH_3$ in simulated coal gas, 800ºC




Green is $Ni_5As_2$, Orange is Ni with levels of As below that of $Ni_5As_2$, purple is YSZ.

# 500 h, 0.1 ppm $AsH_3$ in simulated coal gas, 800ºC



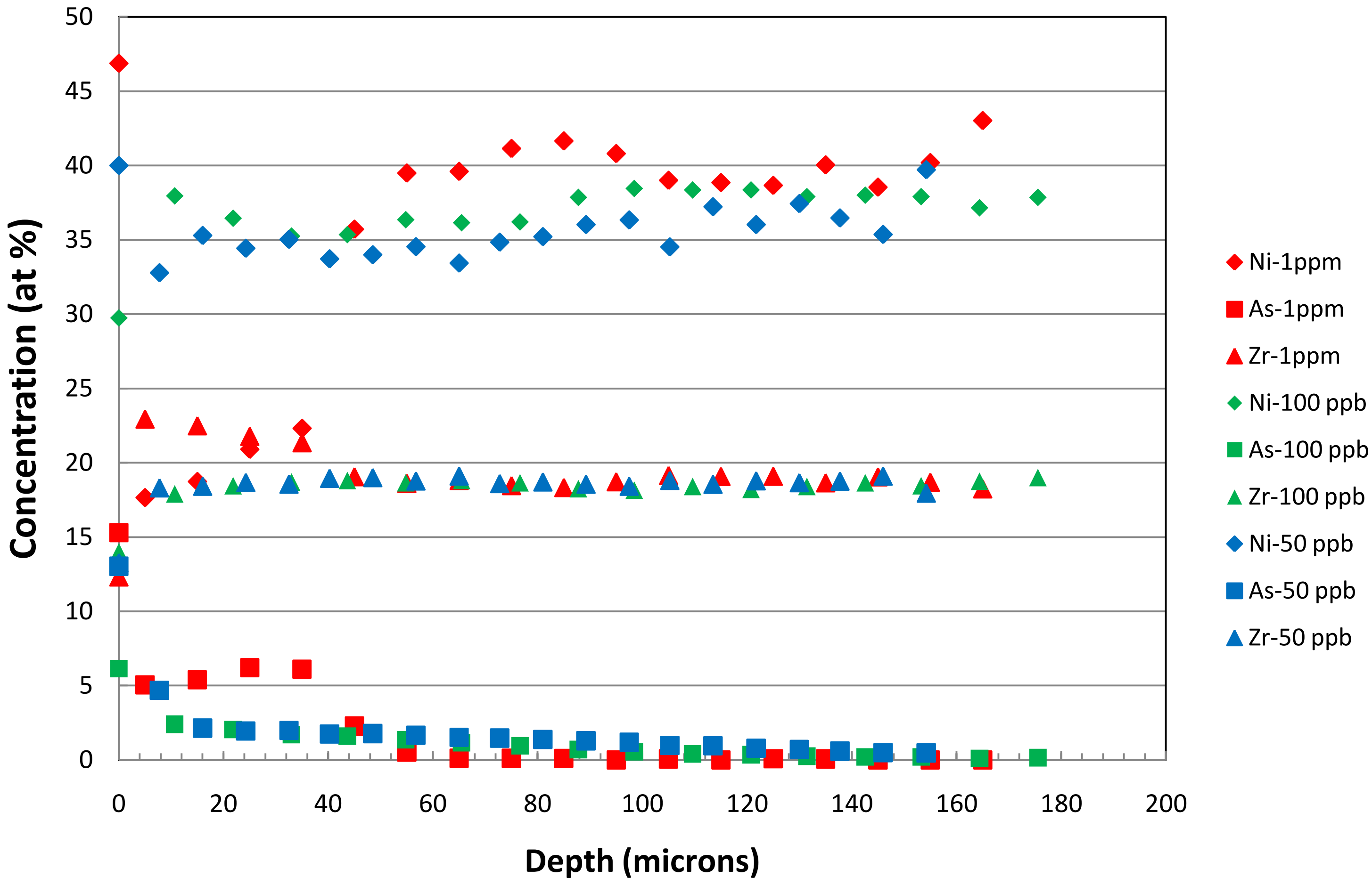

| Spectrum | Ni | **As** | Y | Zr | O |
|---|---|---|---|---|---|
| Layer 1 | 29.75 | **6.15** | 0.95 | 14 | 49.1 |
| Layer 2 | 37.95 | **2.4** | 1.3 | 17.9 | 40.45 |
| Layer 3 | 36.45 | **2.05** | 1.4 | 18.45 | 41.7 |
| Layer 4 | 35.25 | **1.7** | 1.4 | 18.7 | 42.9 |
| Layer 5 | 35.35 | **1.6** | 1.45 | 18.8 | 42.9 |
| Layer 6 | 36.35 | **1.35** | 1.35 | 18.65 | 42.25 |
| Layer 7 | 36.15 | **1.15** | 1.4 | 18.8 | 42.55 |
| Layer 8 | 36.2 | **0.95** | 1.35 | 18.65 | 42.8 |
| Layer 9 | 37.85 | **0.7** | 1.35 | 18.25 | 41.7 |
| Layer 10 | 38.45 | **0.55** | 1.35 | 18.15 | 41.5 |
| Layer 11 | 38.35 | **0.4** | 1.35 | 18.4 | 41.5 |
| Layer 12 | 38.35 | **0.35** | 1.35 | 18.2 | 41.75 |
| Layer 13 | 37.9 | **0.25** | 1.4 | 18.4 | 42 |
| Layer 14 | 38 | **0.2** | 1.45 | 18.65 | 41.75 |
| Layer 15 | 37.9 | **0.2** | 1.45 | 18.45 | 42 |
| Layer 16 | 37.15 | **0.1** | 1.45 | 18.75 | 42.45 |
| Layer 17 | 37.85 | **0.15** | 1.4 | 19 | 41.7 |

**Average values of both depth profiles.**
All results in atomic%

As is detectable down to ~140 µm below the surface.

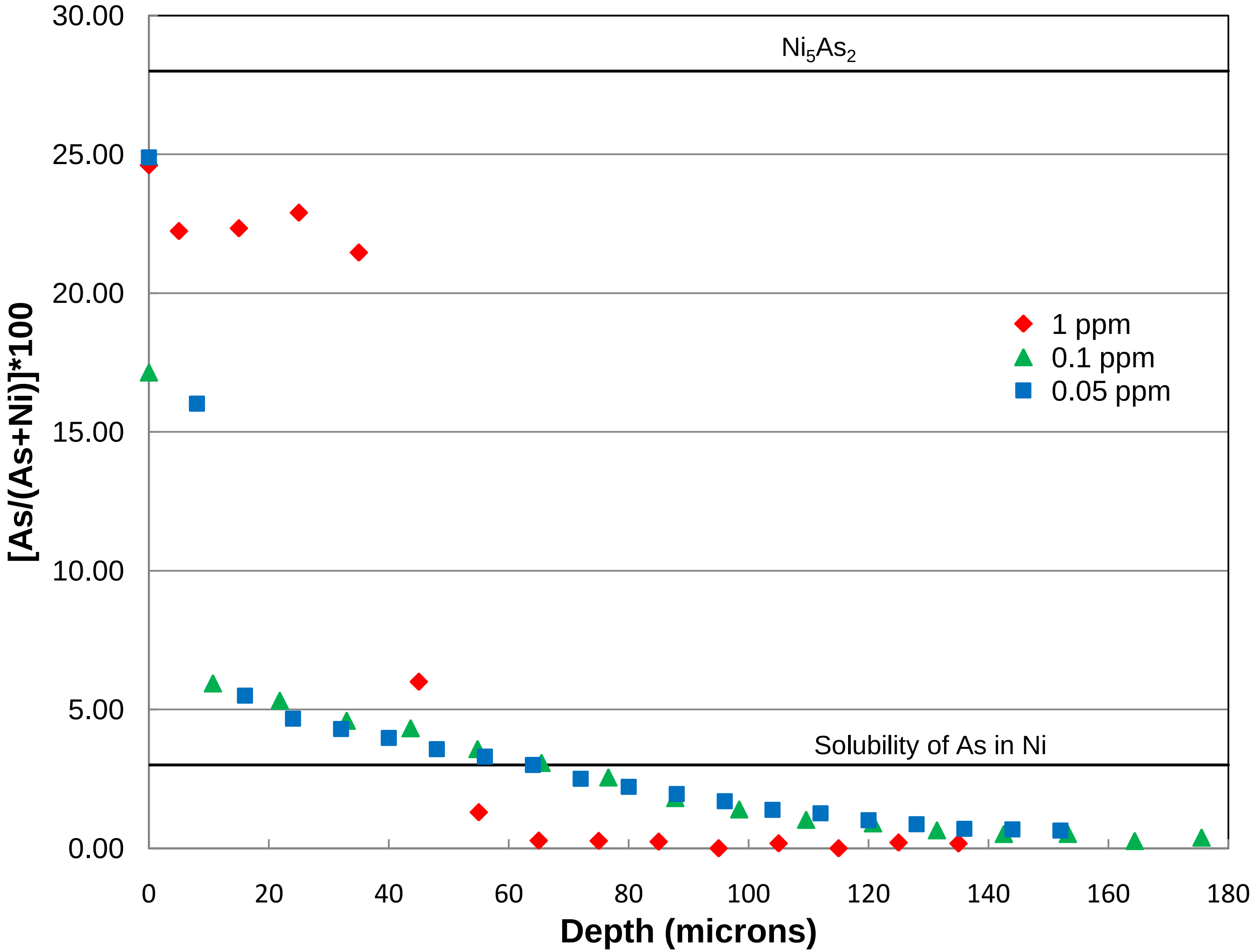
Pacific Northwest
NATIONAL LABORATORY

# Concentration profiles from EDS analyses: Absolute concentration (at%)



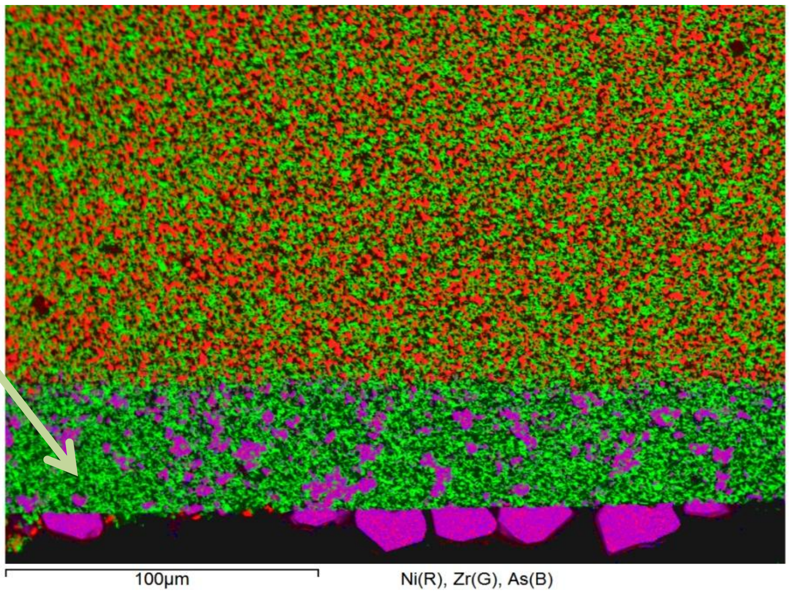

- Extensive arsenide formation zone at 1 ppm; negligible As doping of Ni below arsenide zone; Ni depletion in reaction zone resulted from extensive formation of arsenide above surface of anode
- Narrower arsenide formation zone at 50 or 100 ppb, but extensive region of As-doped Ni below the arsenide zone

# Depth Profile: As / (Ni +As)




Pacific Northwest
NATIONAL LABORATORY

# Length of primary reaction zone as f(concentration/time)




| Test # | Concentration | Time (h) | Approx. Length of "Arsenide zone" |
|---|---|---|---|
| 1 | 1.00 ppm | 50 | 5 mm |
| 2 | 0.50 ppm | 100 | TBD |
| 3 | 0.10 ppm (100 ppb) | 500 | 2 mm |
| 4 | 0.05 ppm (50 ppb) | 1000 | 2 mm |
| 5 | 0.01 ppm (10 ppb) | 5000 | TBD |

# Summary

- Strong interactions occur between Ni-based anodes and P and/or As contaminants in fuel
- These interactions result in formation of secondary phases
  - Nickel phosphide solid phases: e.g., $Ni_3P$, $Ni_5P_2$
  - Nickel arsenide solid phases: e.g., $Ni_5As_2$, $Ni_{11}As_8$
- Arsenide formation ($Ni_5As_2$) was confirmed with As concentrations as low as 50 ppb (in simulated coal gas)
  - Consistent with thermodynamic calculations, which indicate arsenide formation at much lower concentrations (< 1 ppb at 800ºC)
  - Arsenide formation zone occurred in anode surface region near fuel inlet
  - Sharp boundaries were observed between arsenide formation zone and "unreacted" anode below that region
  - However, for [As] = 50 or 100 ppb, substantial As doping of Ni was observed underneath the arsenide formation region

- Implications for SOFC stacks:
  - Interaction zone between anode and arsenic will be concentrated near the fuel gas inlet of the cells, but will, of course, lengthen over time
  - For coal gas fuels cleaned to ppb levels, secondary phase formation is expected, but the low rate of contaminant delivery may significantly reduce degradation rates, and also simplify upstream mitigation

# Future Work

- Complete analysis of results of equivalent dosage tests (As, P, As+P between 10 ppb and 1 ppm) at 700 and 800º
  - Correlate dosing level and time with extent and nature of interactions between anode and contaminant(s)
- Perform variable time reaction tests at a constant contaminant level to evaluate development of reaction zone geometry and composition

# Acknowledgements


- The work summarized in this paper was funded under the U.S. Department of Energy's Solid-State Energy Conversion Alliance (SECA) Core Technology Program
- NETL:  Shailesh Vora, Briggs White, Rin Burke, Travis Shultz, and Joe Stoffa
- PNNL: Clyde Chamberlin and Alan Schemer-Kohrn