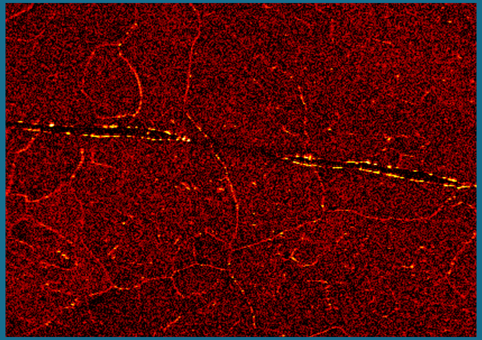
SAND2022-15725C

Sandia National Laboratories

Probing Grain Boundary Segregation in 304L Stainless Steel using Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS)



James A.(Tony) Ohlhausen[1], Erin Barrick[2], Jeffrey Rodelas[2], Donald Susan[2], Charlie Robino[2], Khalid Hattar[3], Jack Herrmann[2], Peter Duran[2]

[1] Materials Characterization & Performance Department

[2] Metallurgy & Materials Joining Department

[3] Nanostructure Physics and Nanosystems Synthesis/Analysis Department

Material, Physical, and Chemical Sciences Center, Sandia National Laboratories, Albuquerque, NM, 87185, USA

Unraveling the composition of Complex Systems with SIMS
AVS 68, Thursday, November 10, 2022, Room 320

U.S. DEPARTMENT OF ENERGY NNSA

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Austenitic Stainless Steels

- Predominantly austenite phase (FCC)
  - Non-magnetic
  - ANSI 200 and 300 series
  - Good welding properties
  - Corrosion resistant (high Cr content)
  - High ductility

- **304SS** is the most used alloy globally
  - Kitchen equipment and appliances
  - Storage Tanks
  - Water piping
  - Auto moldings and trim

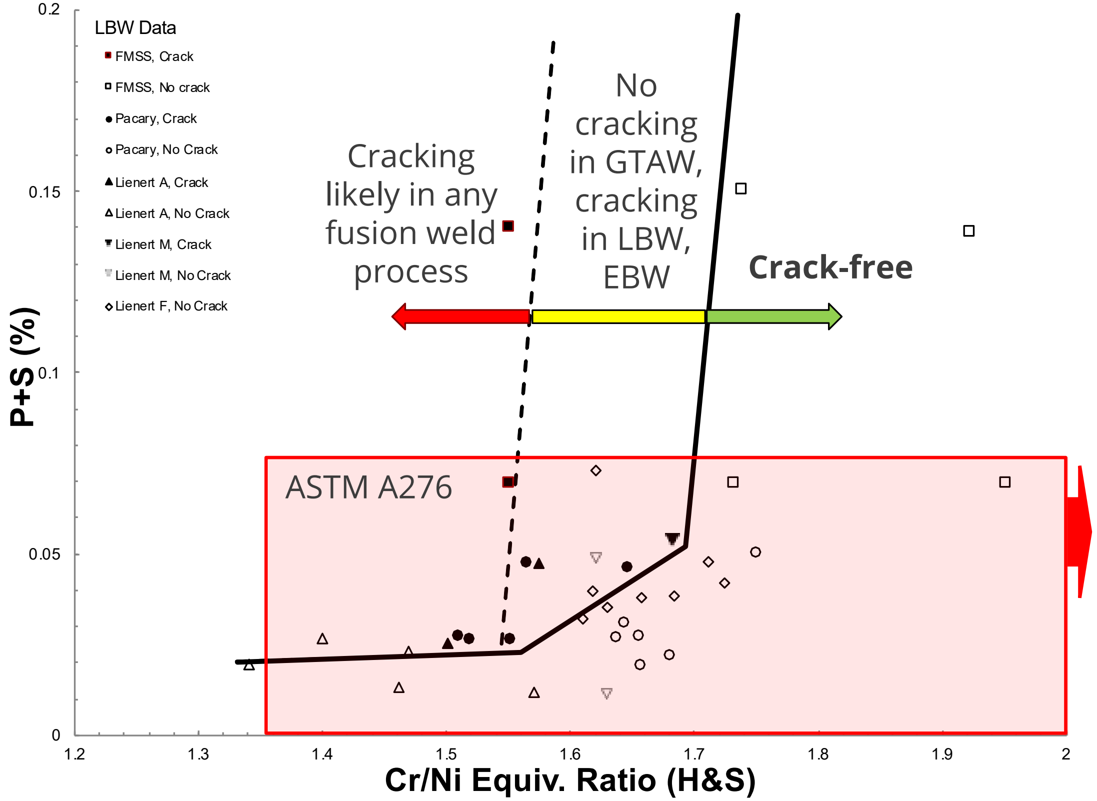
https://www.azom.com/article.aspx?ArticleID=965

https://bergsen.com/316-vs-304-stainless-steel/

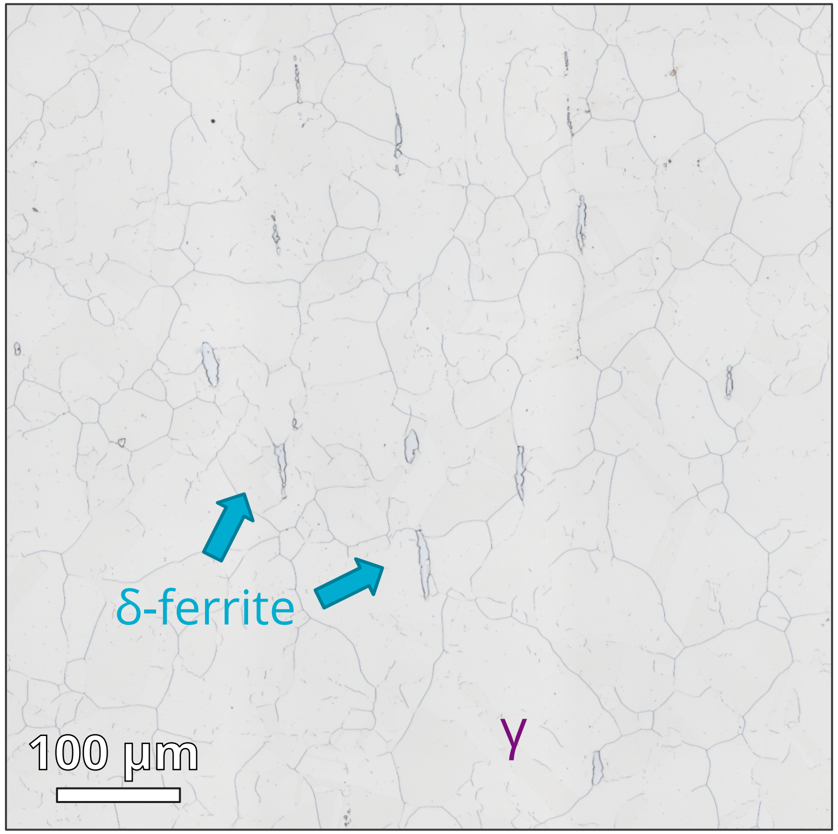
304L Stainless Steel

- Most commonly selected austenitic stainless steel
- Concern with laser welding – **solidification cracking**
  - Tight restriction for impurity elements
  - Highly controlled $(Cr/Ni)_{eq}$
  - Secondary remelting (vacuum arc remelting, VAR)

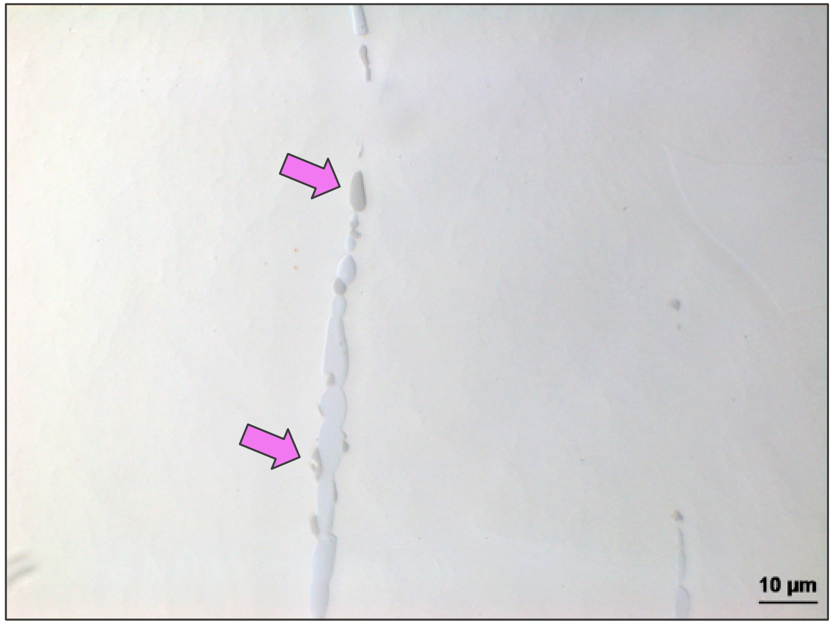
Modified Suutala Weldability Diagram

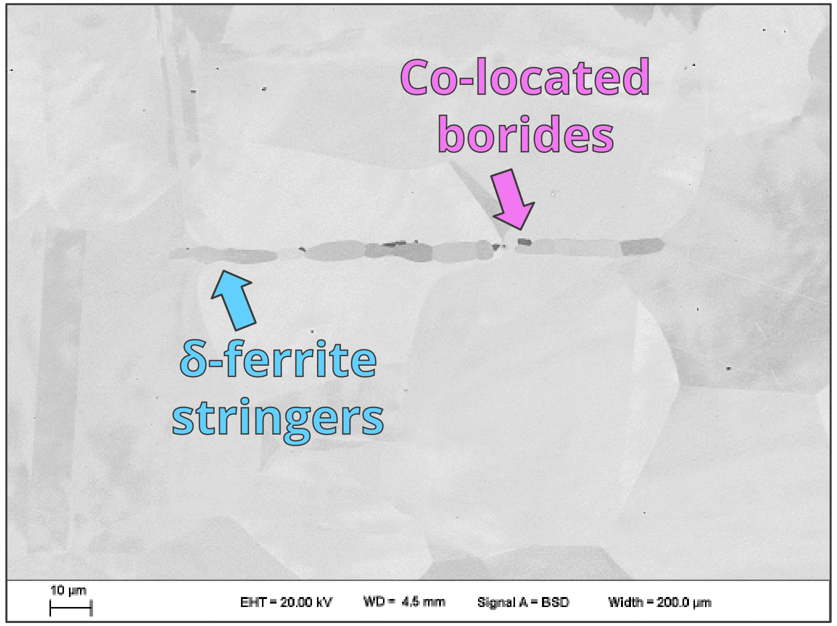


Typical 304L Microstructure

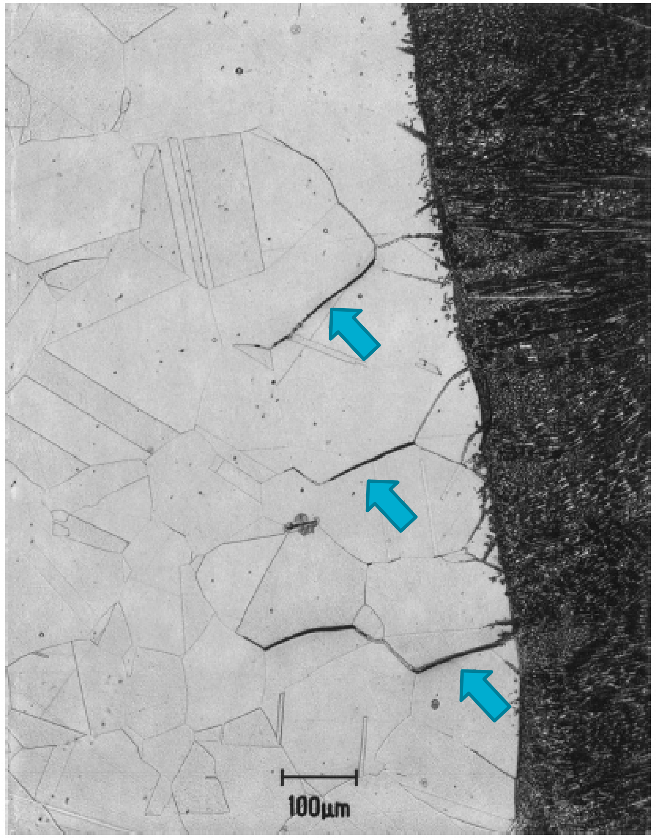


Borides identified in microstructure; raises liquation cracking concern





Inconel 718 Heat Affected Zone liquation cracks; 43 ppm B

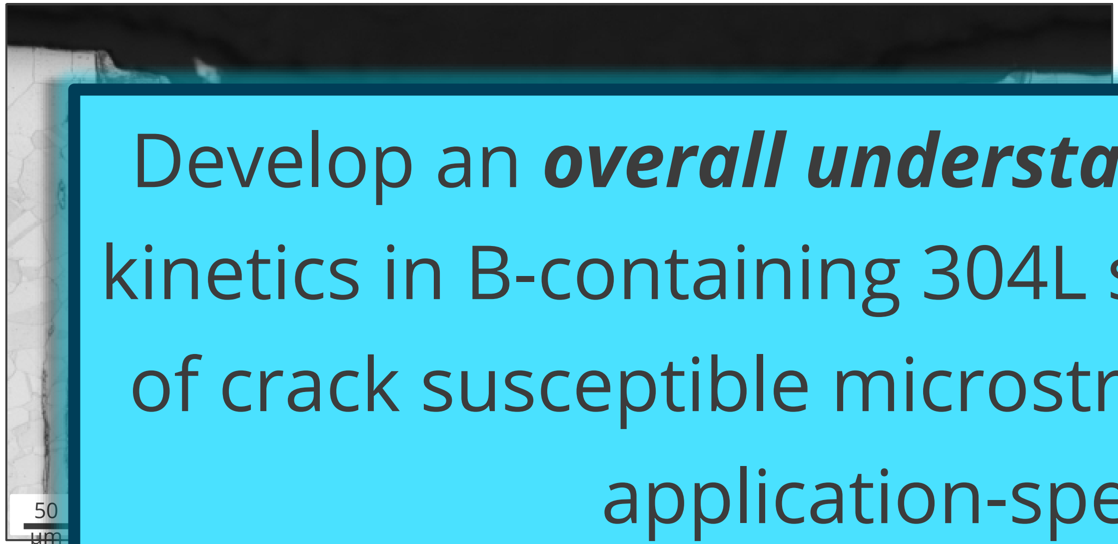


Chen, W., et al. Met Mat Trans: A, Volume 32A, April 2001, 931-939.

Cr-rich borides observed along δ-ferrite stringers for boron concentrations as low as 10-20 wt ppm!

Liquation cracking identified in heat-treated B-containing 304L

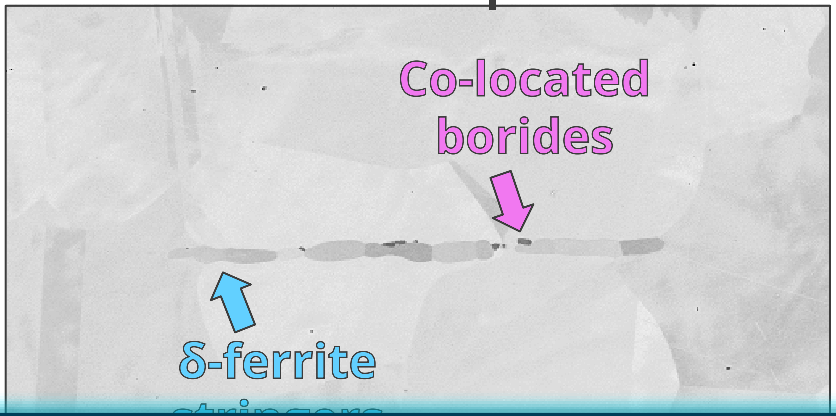
Laser welds on 304L with ~20 wt.ppm B

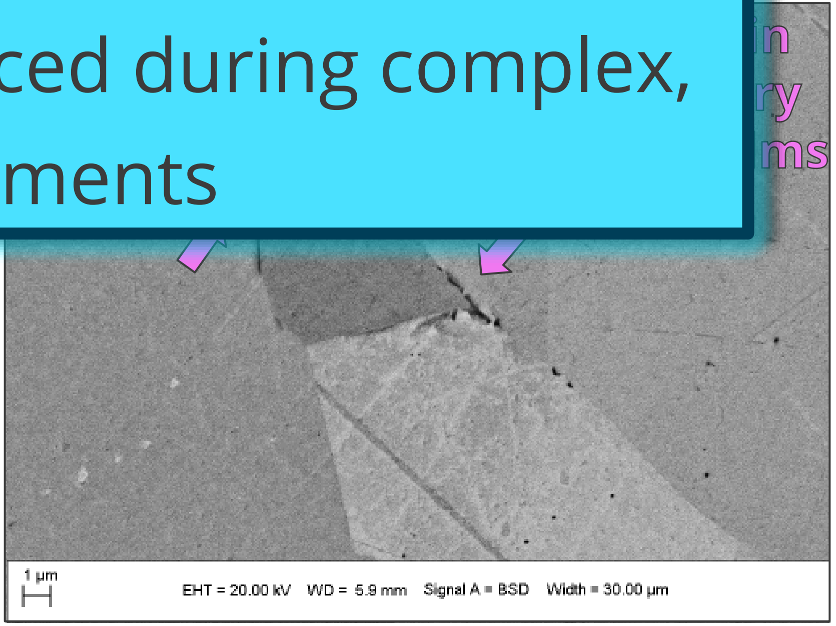


304L part (not brazed)

Brazed 304L part

As-received microstructure – not crack susceptible

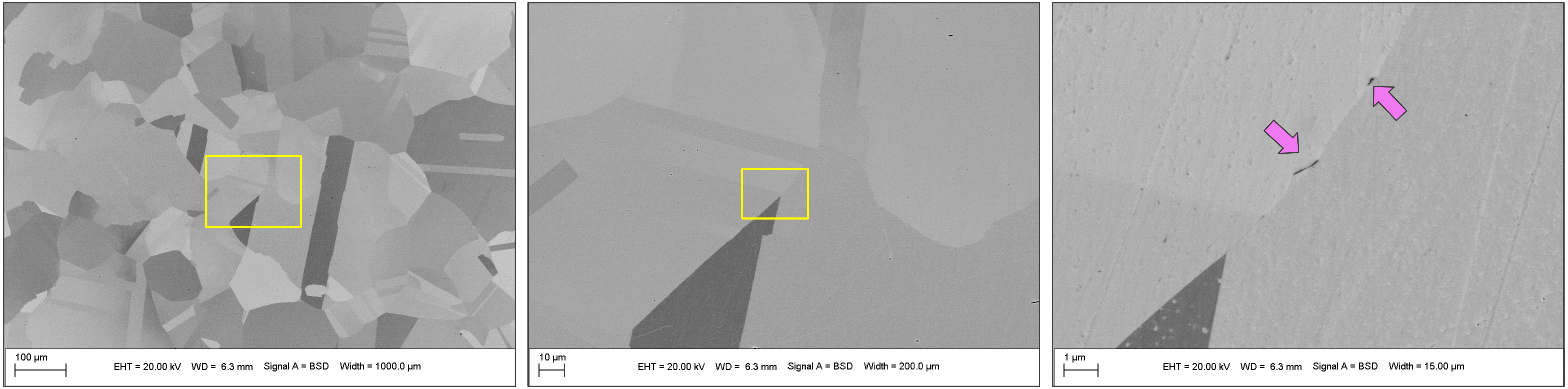




Develop an ***overall understanding*** of the phase transformation kinetics in B-containing 304L stainless steel to enable predictions of crack susceptible microstructures produced during complex, application-specific heat treatments

Fundamental kinetics of microstructural evolution as a function of heat treatment not understood

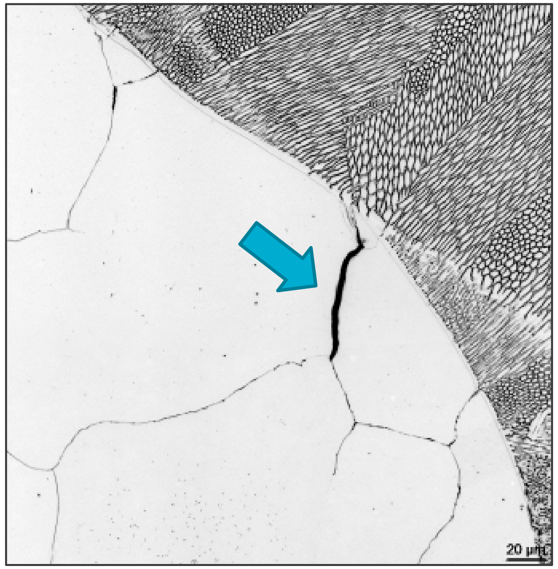
Identification of borides on γ/γ grain boundaries is challenging



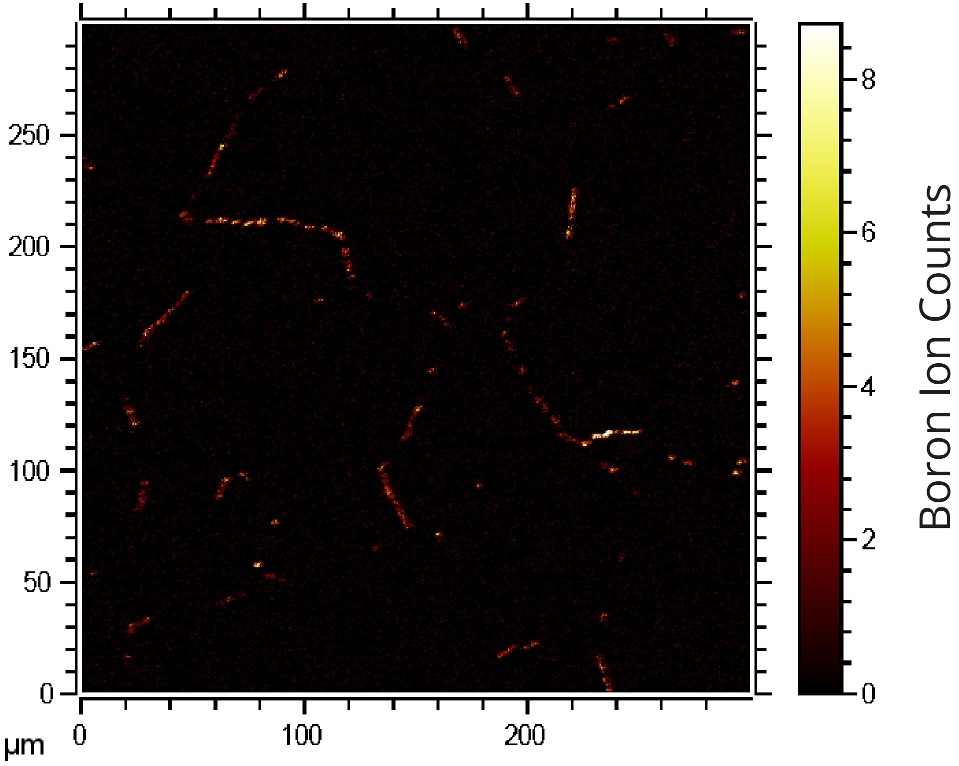
Other characterization techniques present similar challenges (e.g. WDS, TEM, etc.)

ToF-SIMS enables boron location identification

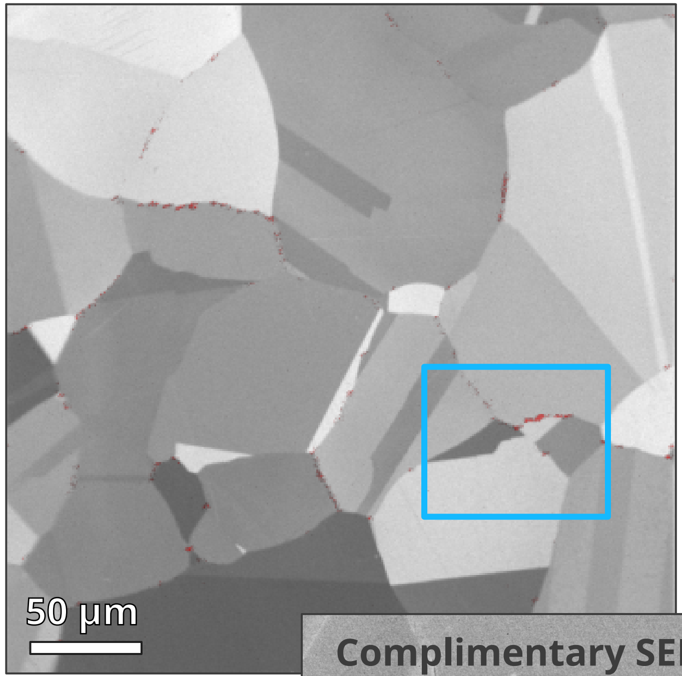
Benefits:
- Sensitivity
- Elemental Specificity
- Image Area
- Resolution
- Acquisition time

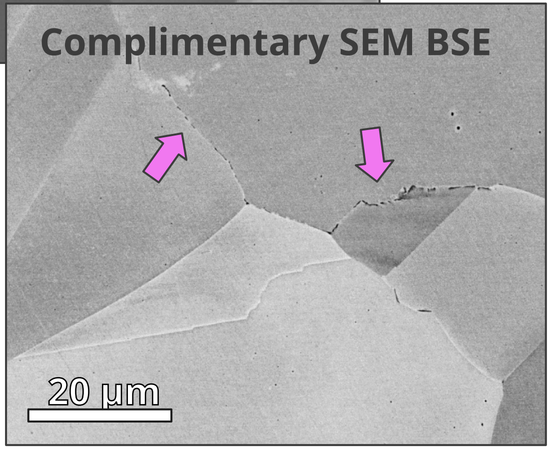


ToF-SIMS Boron Map



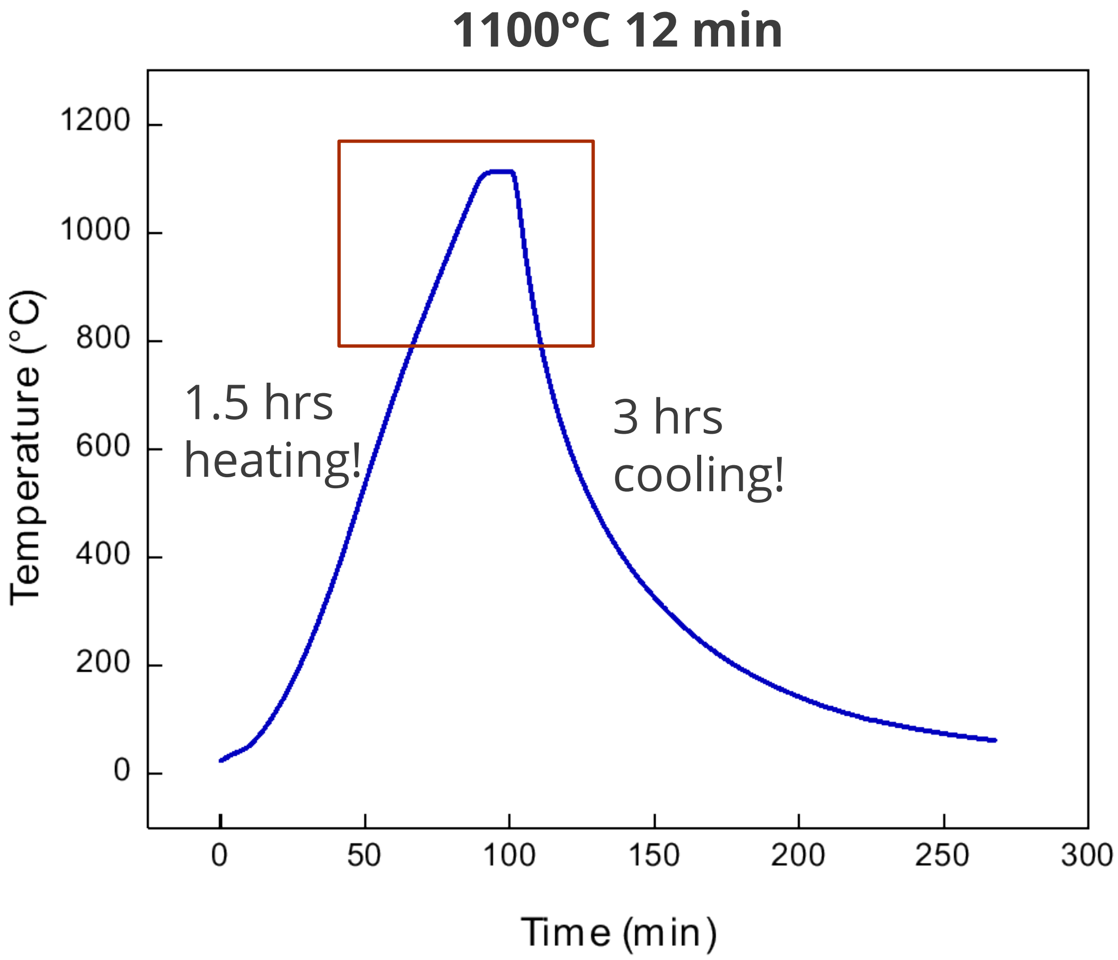
Overlaid B Map and SIMS Secondary Electron (SE) Image

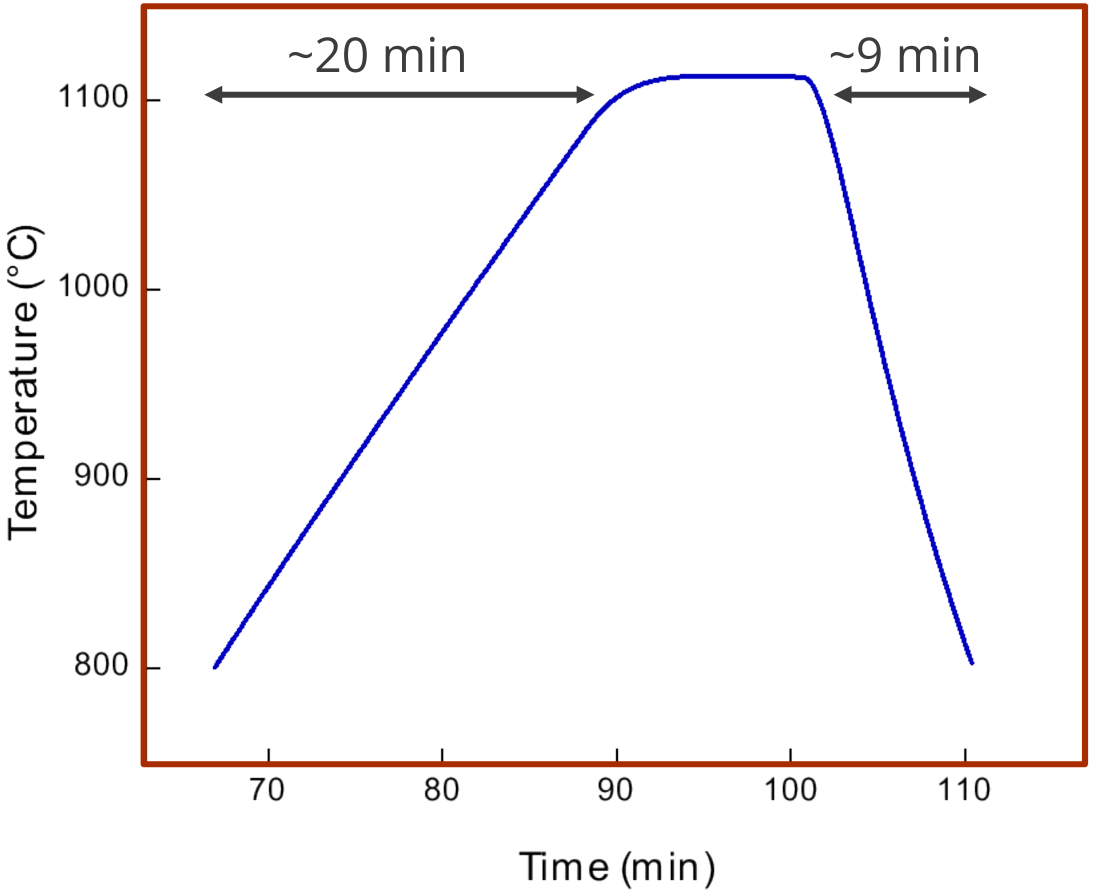




Evaluated microstructure of a crack-susceptible furnace heat treatment condition

Problem: Previous weldability trials were conducted with furnace heat treatments



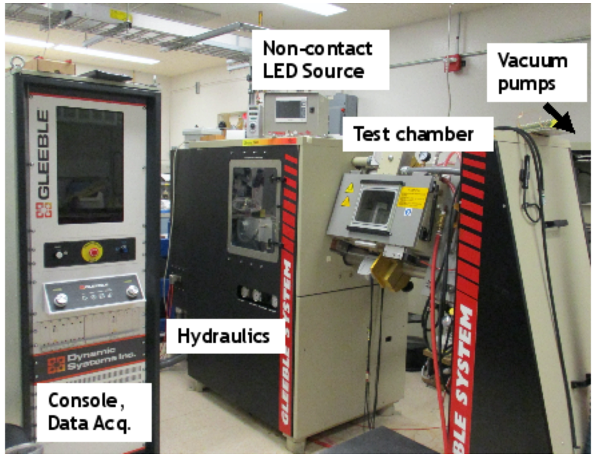


Furnace profiles were selected to replicate part-specific heat treatments

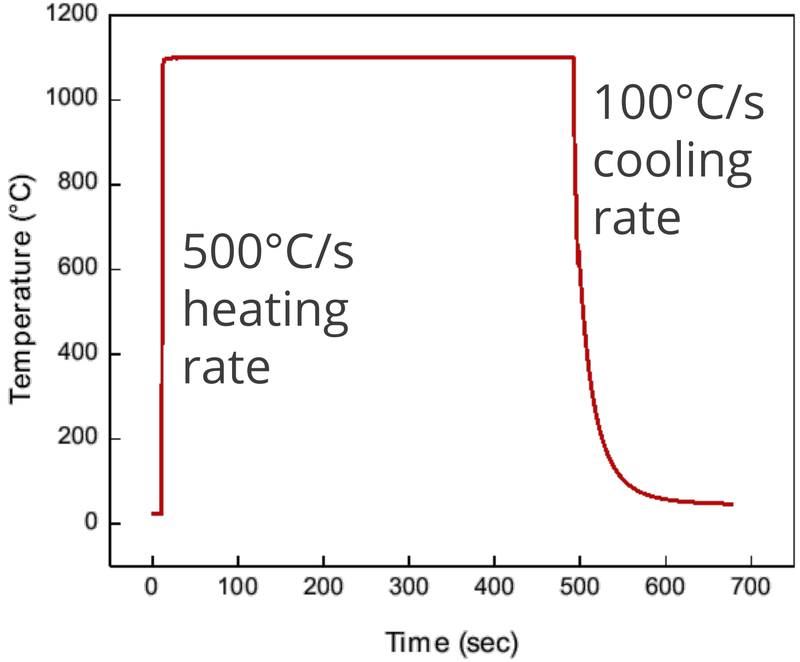
Solution: Utilize Gleeble for Isothermal Heat Treatments

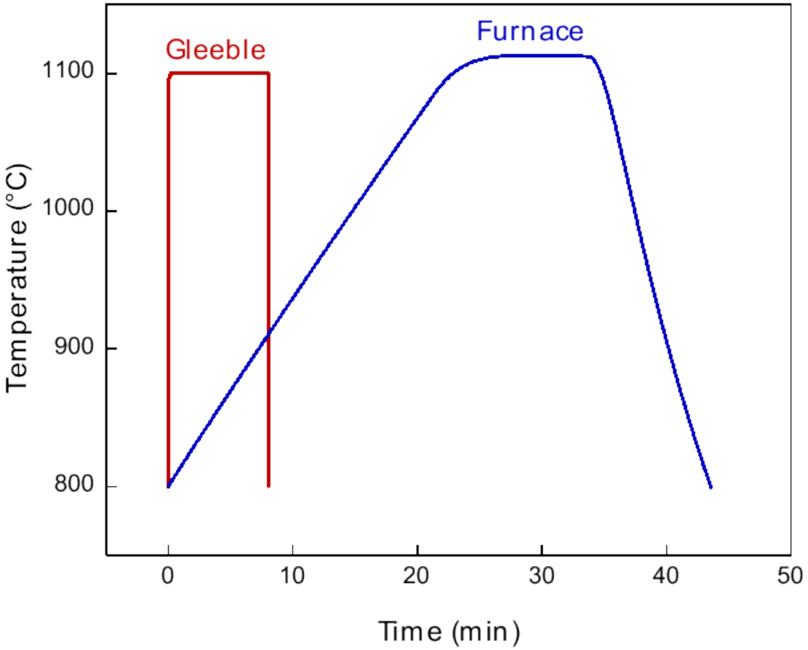
Rapid heating and cooling rates to restrict phase transformations to a single temperature

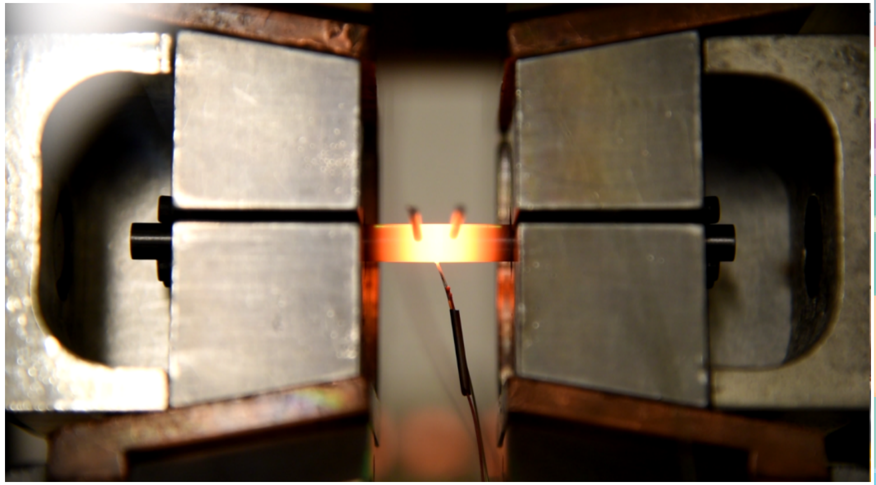
Temperatures: 1000°C, 1100°C, 1200°C, 1300°C
Hold Times: 1 min, 8 min, 32 min, 64 min
Utilized 304L composition with **16 wt ppm B**



1100°C 8 min







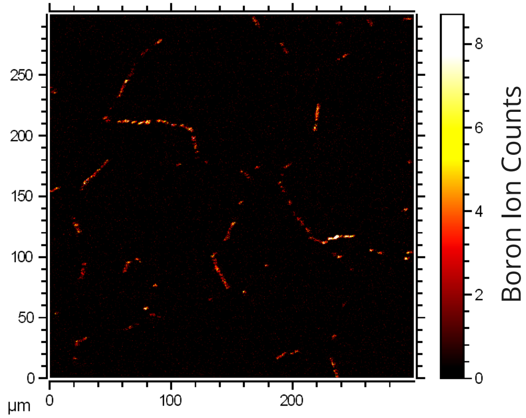
Sample Preparation and Analysis Methods Important

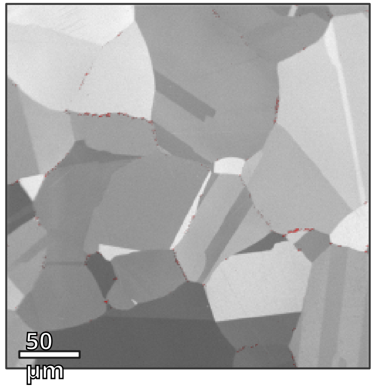
Sample Prep Steps

- Sample Mounting/Polishing
  - Samples mounted in epoxy for polishing – not too much epoxy (outgassing)
  - Polish for EBSD finish– sample finish important (no scratches left)

ToF-SIMS Acquisition Steps (using Ion-TOF ToF-SIMS.5 instrument)

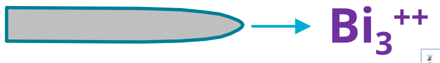
1. Sputter surface with 1kV O_2 to remove surface contamination
   - Can perform crude profile watching hydrocarbon signals drop to zero
2. Acquire Boron Image
   - High spatial resolution imaging mode
   - Neg Secondary Ion Mode
   - Analyze for BO_2^- while sputtering with O_2 (depth profile)
   - Sacrifice bonding information for B sensitivity
   - Must align subsequent frames due to image drift

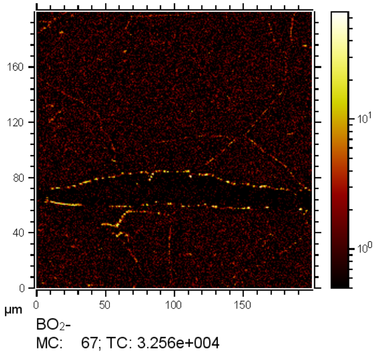


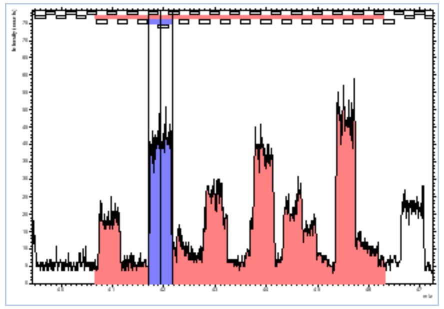


3. Acquire SE Image
   - Same probe except switch to DC mode, secondary electron imaging
   - Many scans to remove oxide and reveal ion/electron contrast

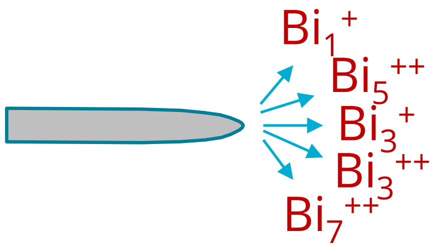
Optimizations enable high sensitivity, large area Boron measurements in ToF-SIMS

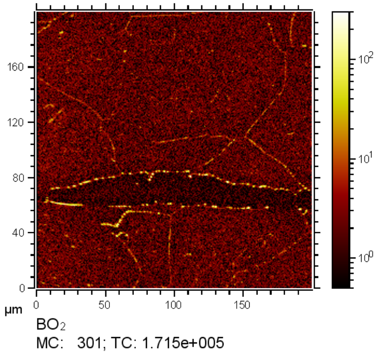






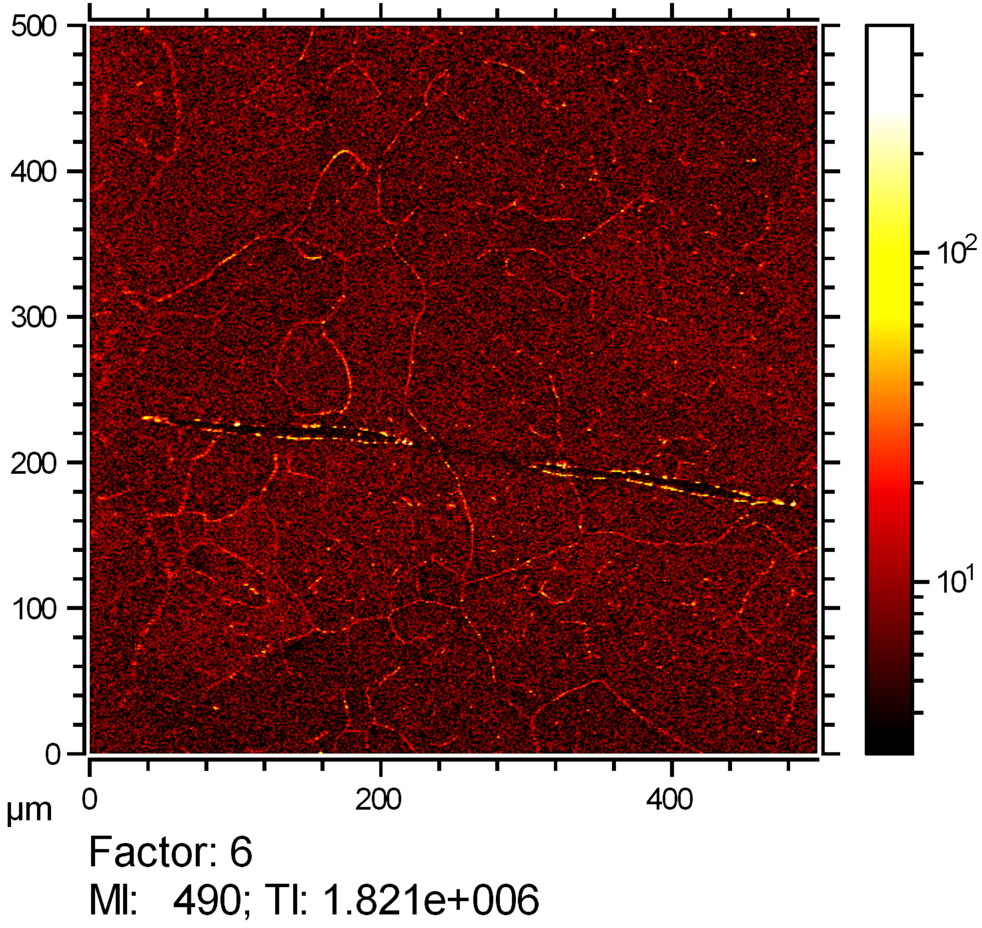
~5X Sensitivity





Max: 67 counts
Total: 3.3E+4 Counts

Max: 301 counts
Total: 1.7E5 counts

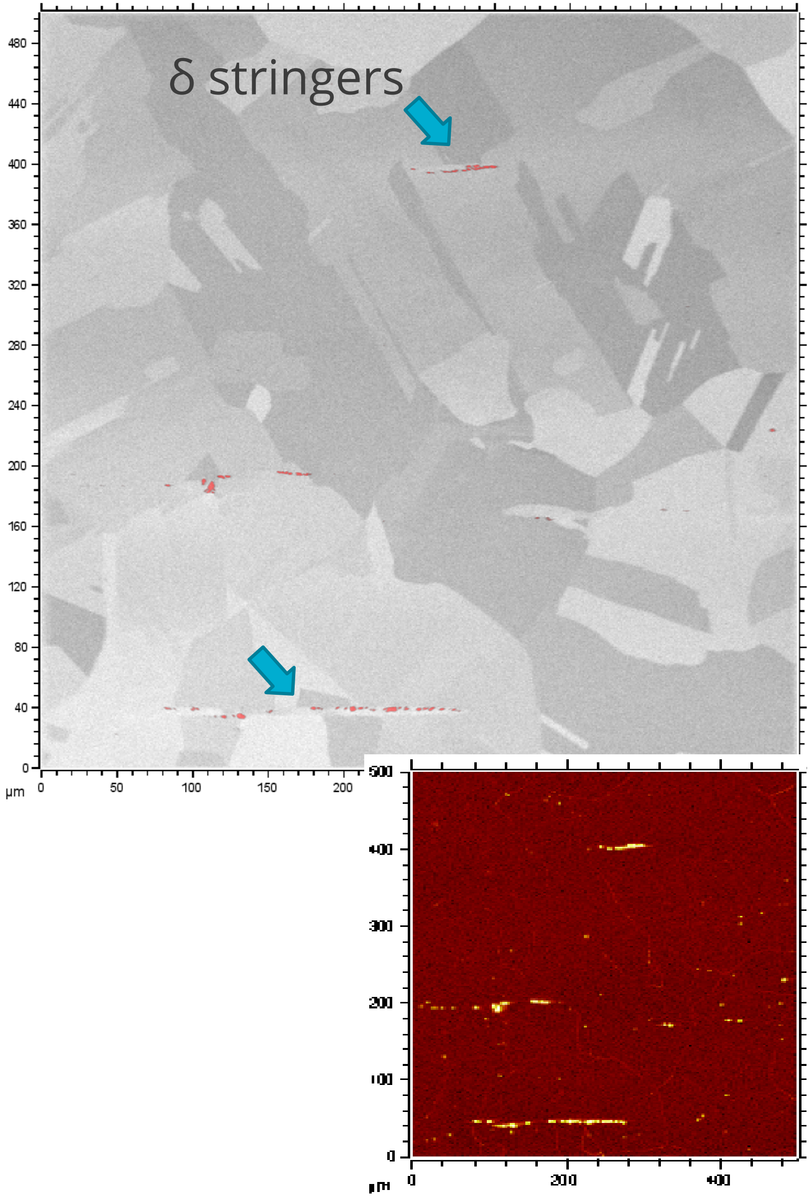


9.8hr acquisition

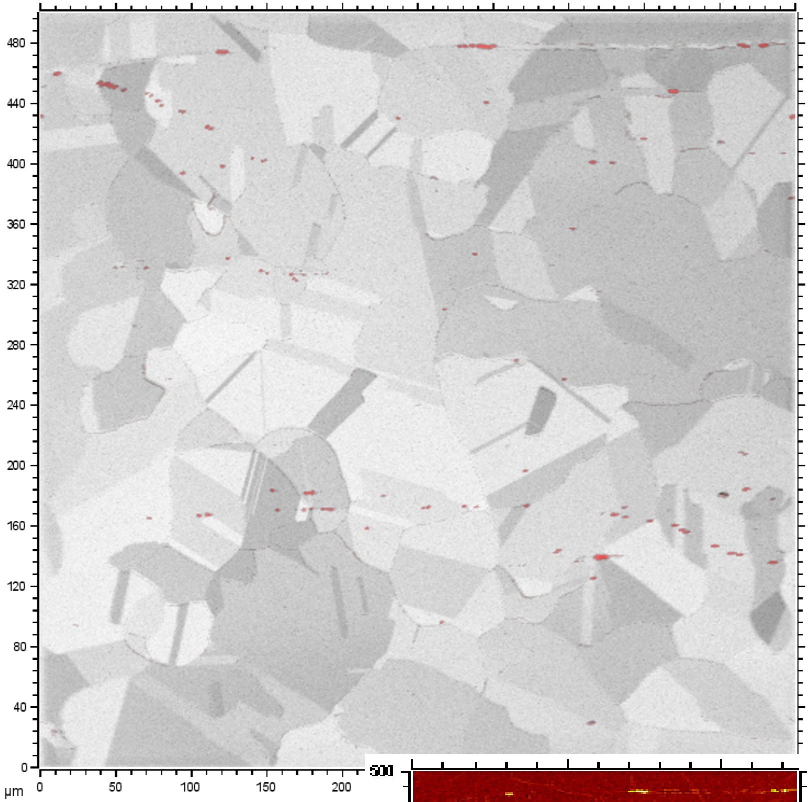
- Use multivariate analysis to separate complex signatures
- Ultralow detection limits
- Large area scan (500μmx500μm)

Boride dissolution occurs between 1000°C and 1100°C

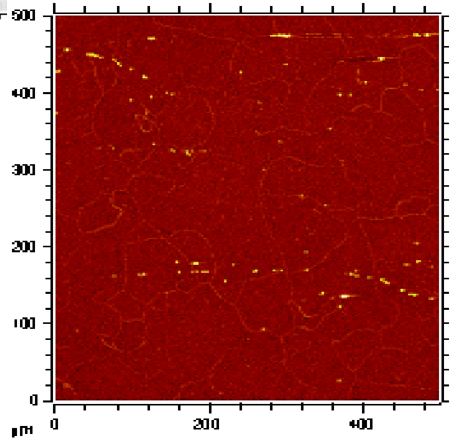
As-Received



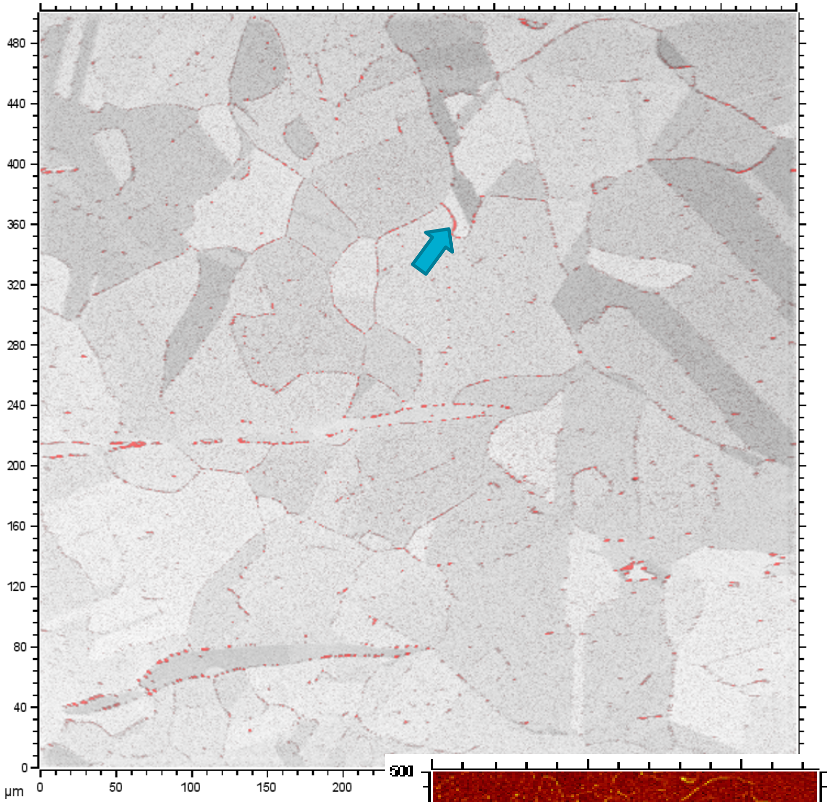
1000°C 32 min



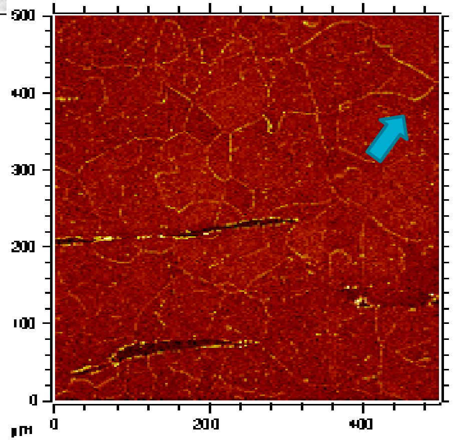
Little (if any) observable changes between as-received and 1000°C 32 min



1100°C 1 min

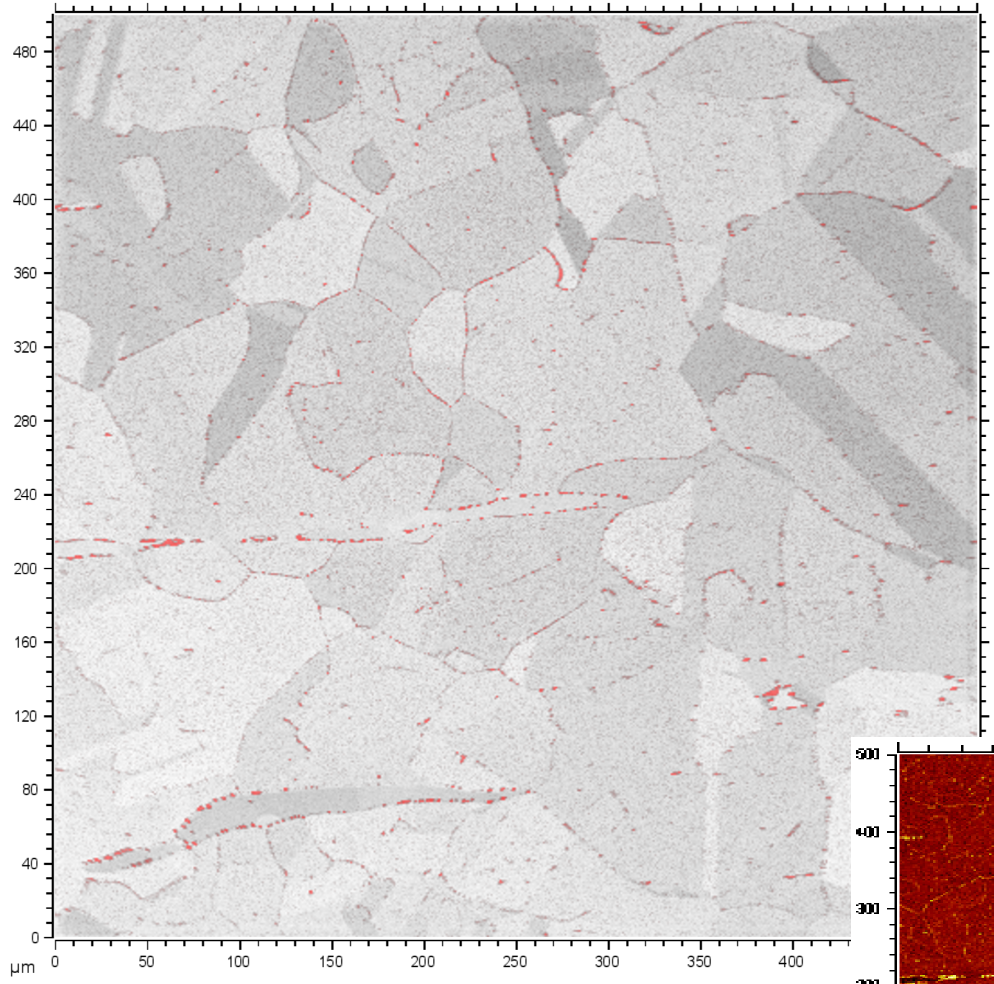


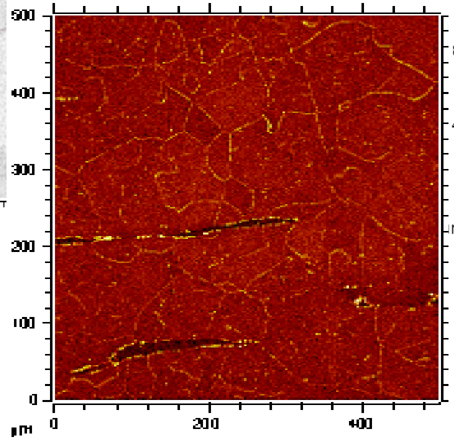
Some boron migration to γ grain boundaries; some remains on δ



Boron diffusion to γ/γ grain boundaries is rapid

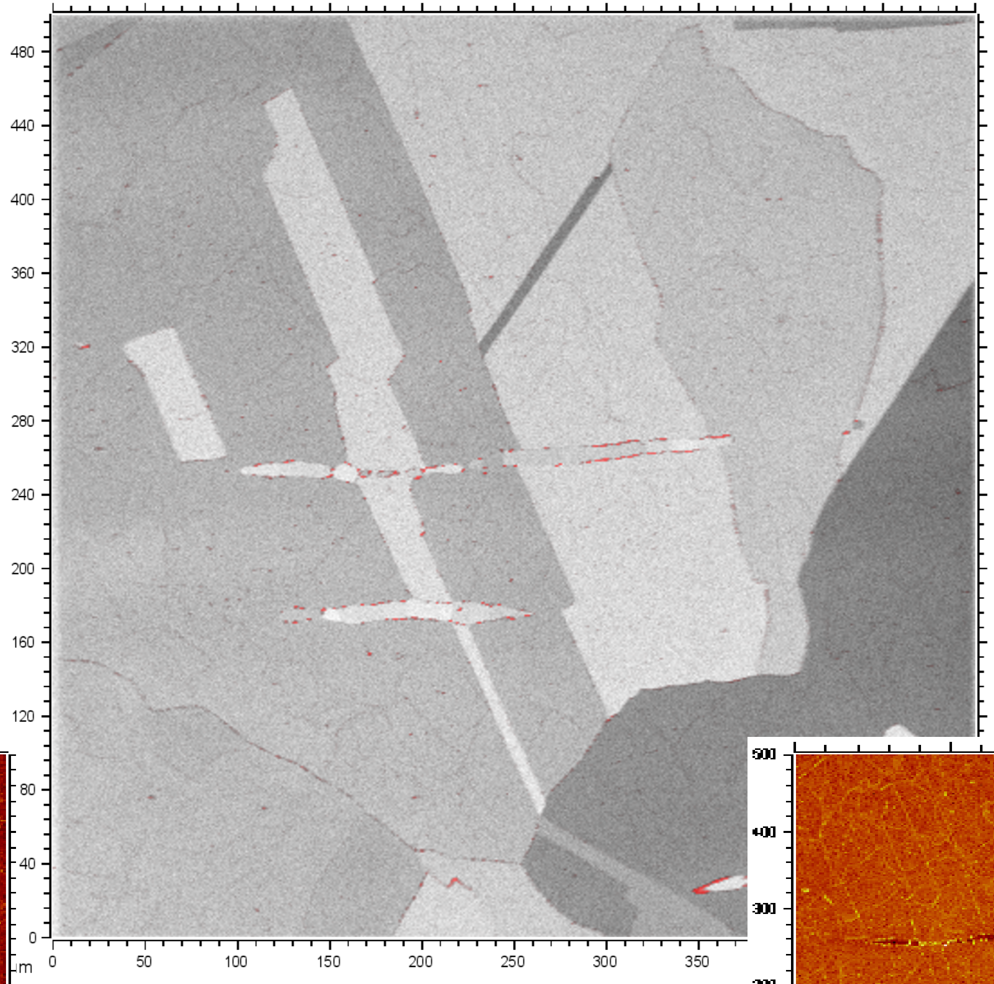
1100°C 1 min

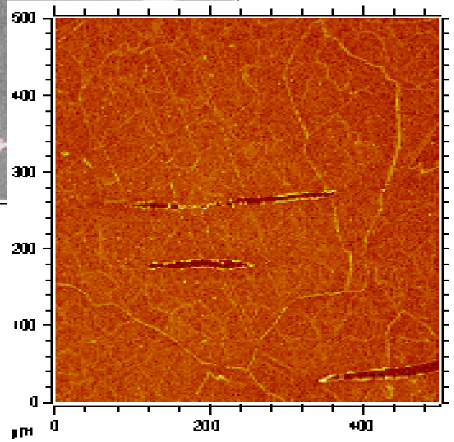




Grain coarsening

1100°C 32 min

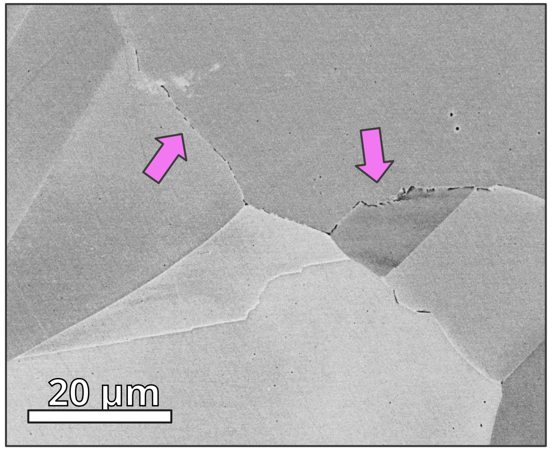


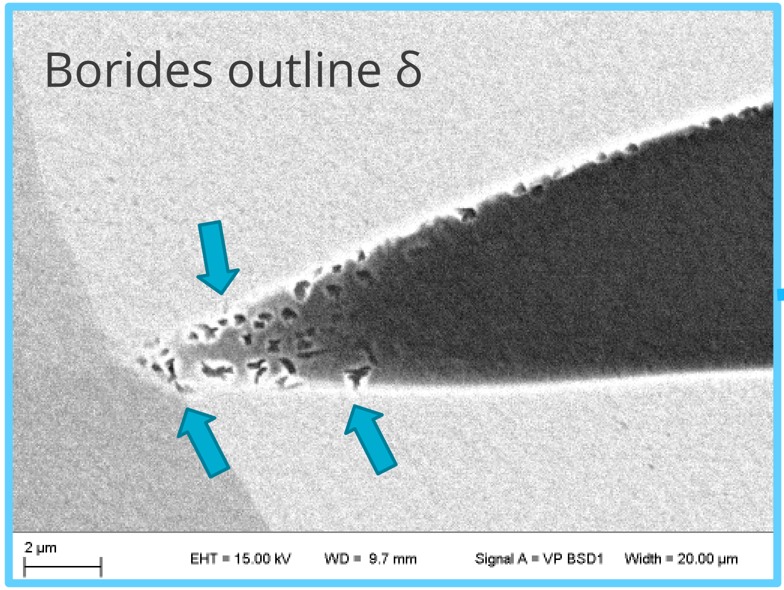


Little (if any) observable changes with additional hold time at 1100°C

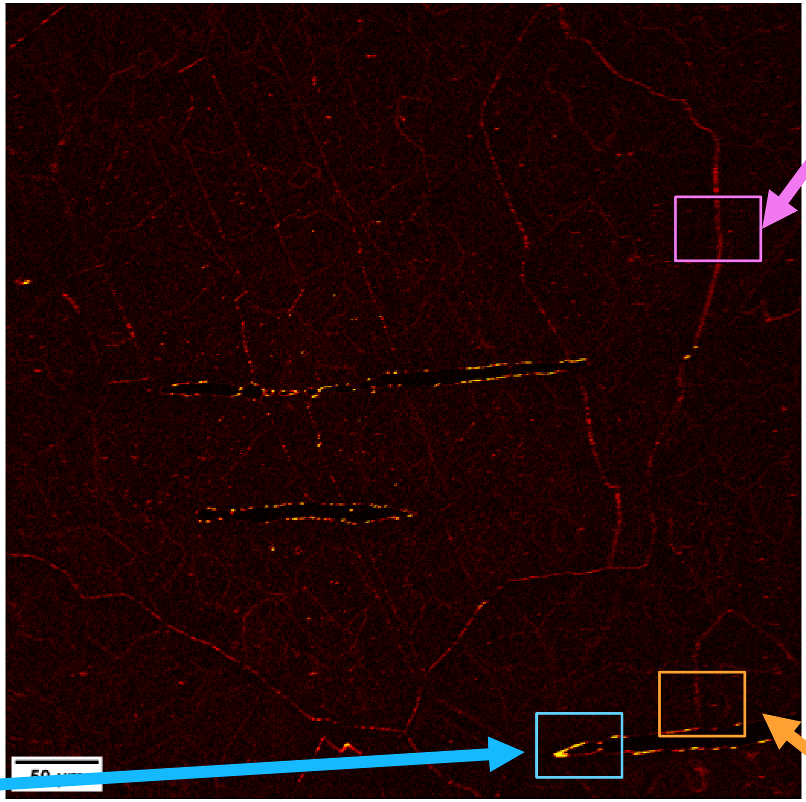
Borides re-precipitate on δ/γ boundaries but not on γ/γ boundaries

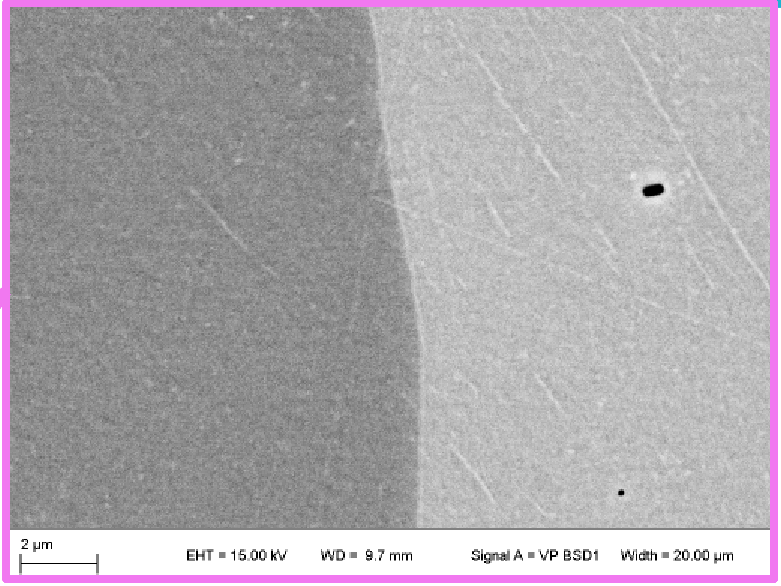
Recall: ability to see borides in SEM



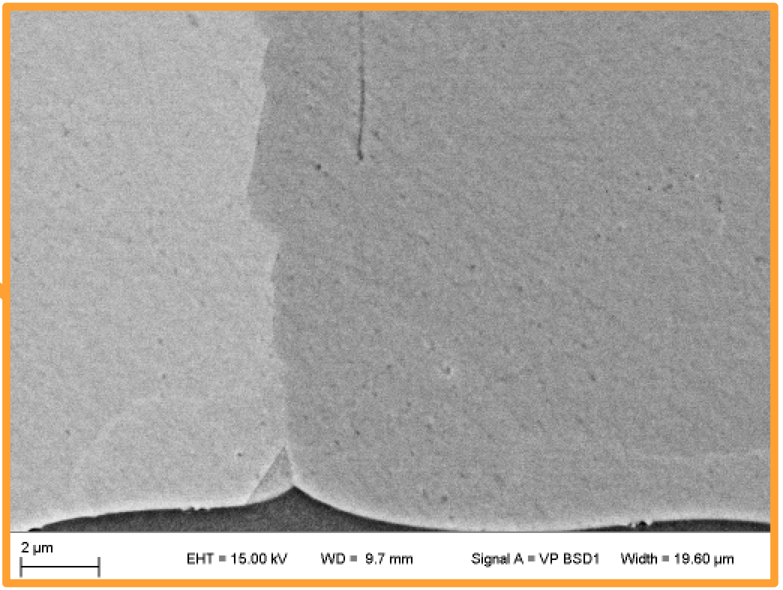


1100°C 32 min





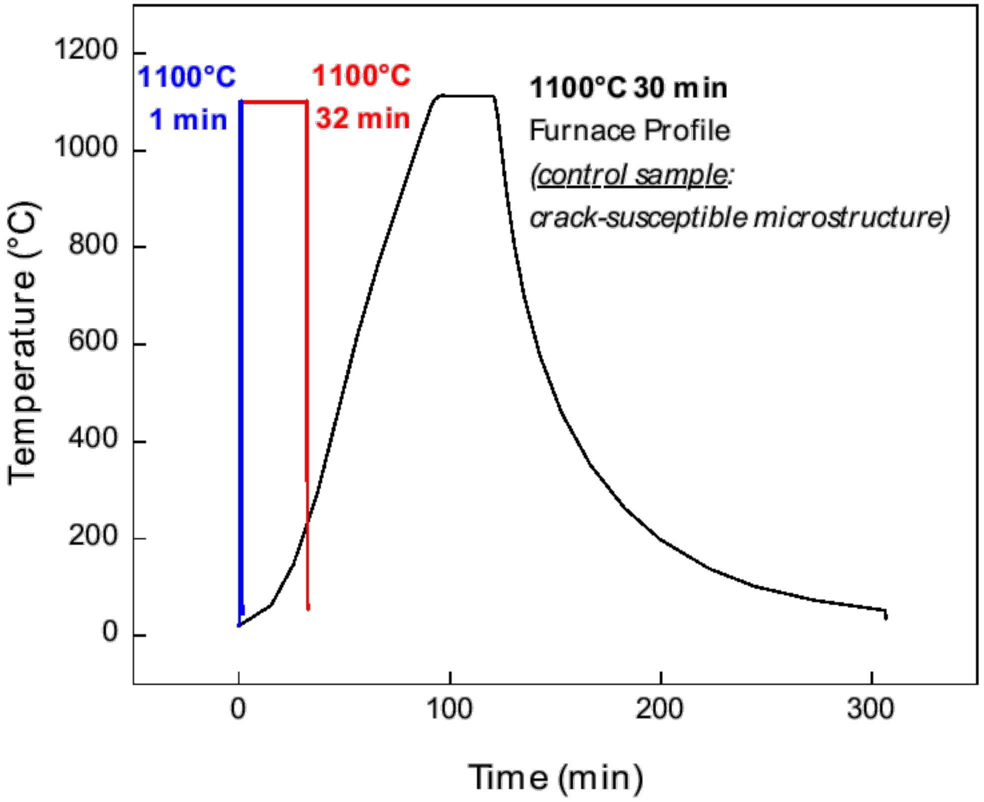
Elemental boron or borides below SEM resolution limit?



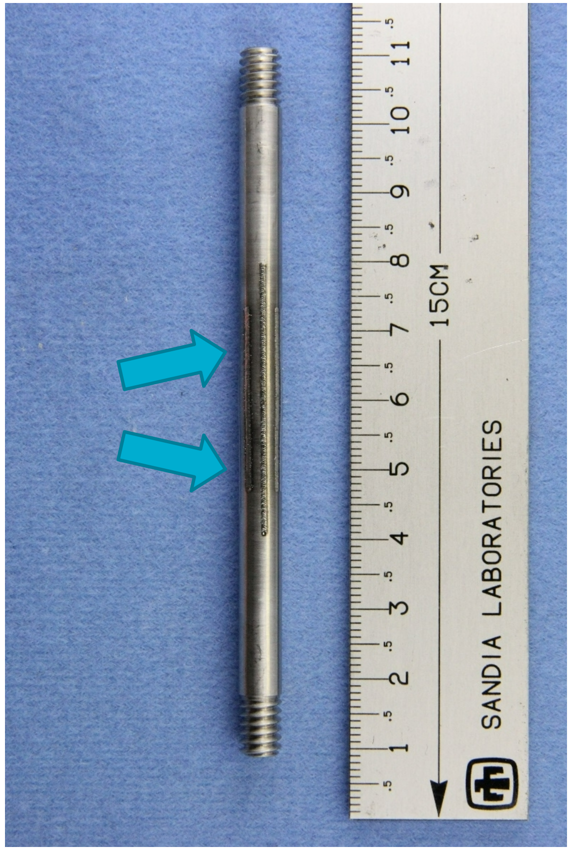
Is this a crack susceptible condition?

Developed test method to correlate phase transformation kinetics to crack-susceptibility

Step 1: Gleeble heat treatments



Step 2: Laser welds directly on Gleeble bars

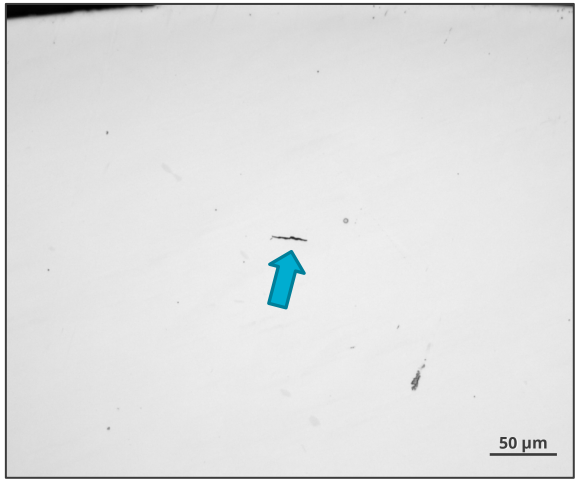


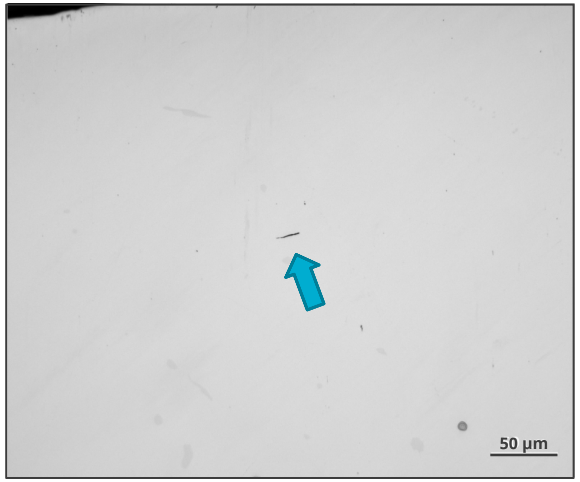
Step 3: Section welds in transverse, scan HAZ for cracks

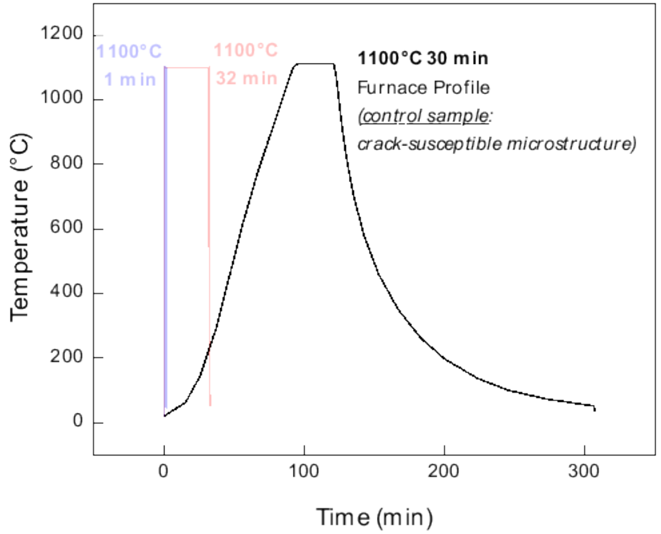
60 weld cross-sections surveyed per Gleeble condition

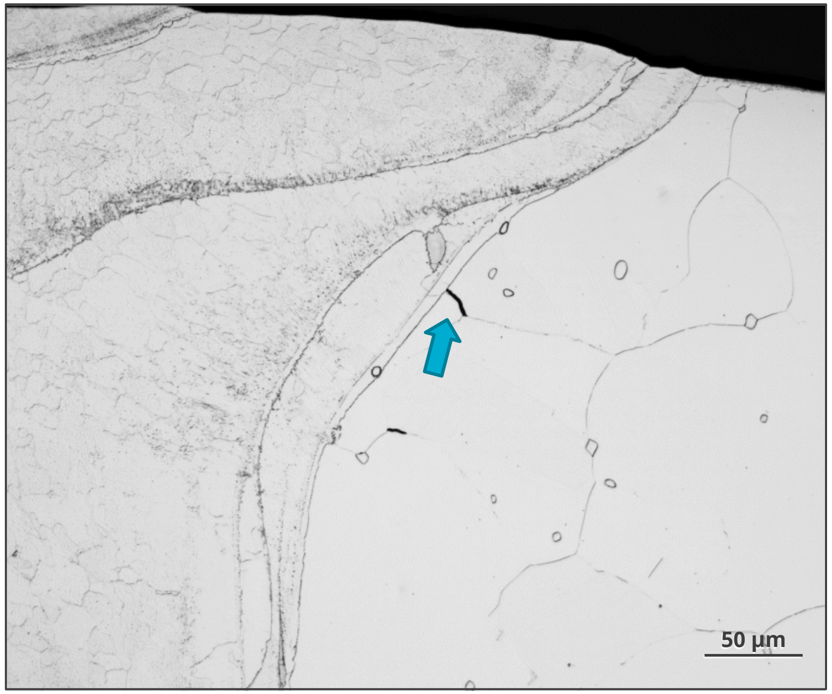
Furnace profile condition is crack-susceptible

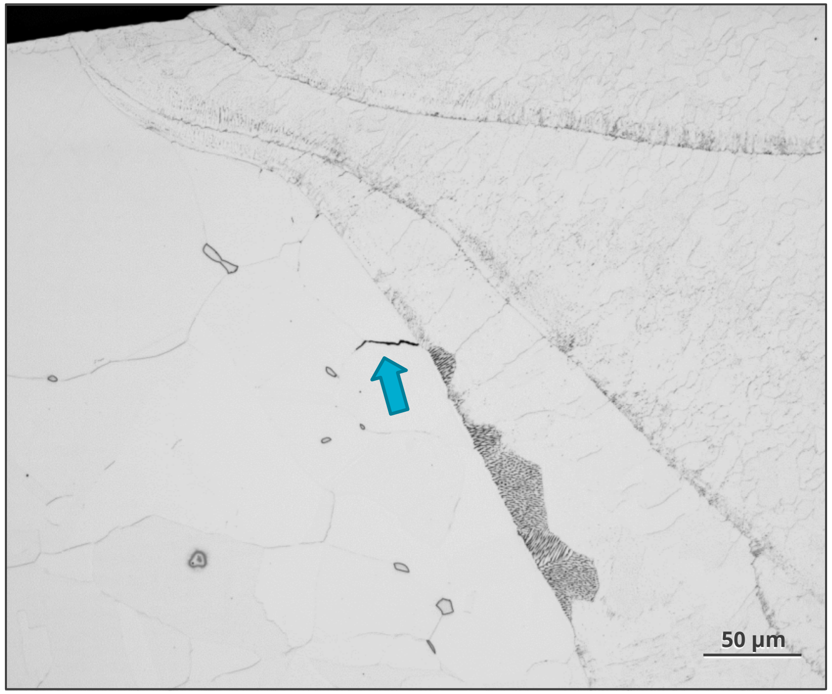
Unambiguous crack determination in as-polished condition

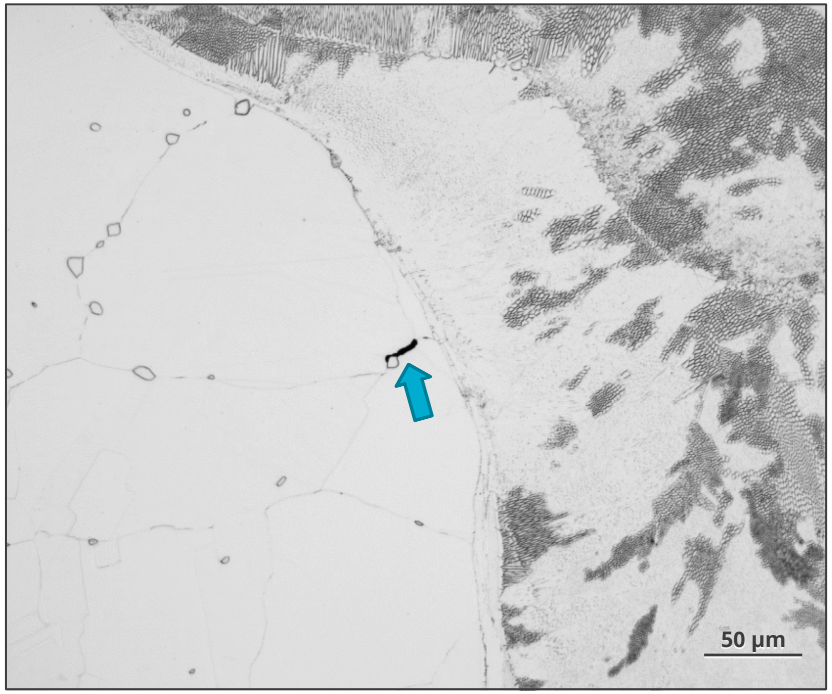




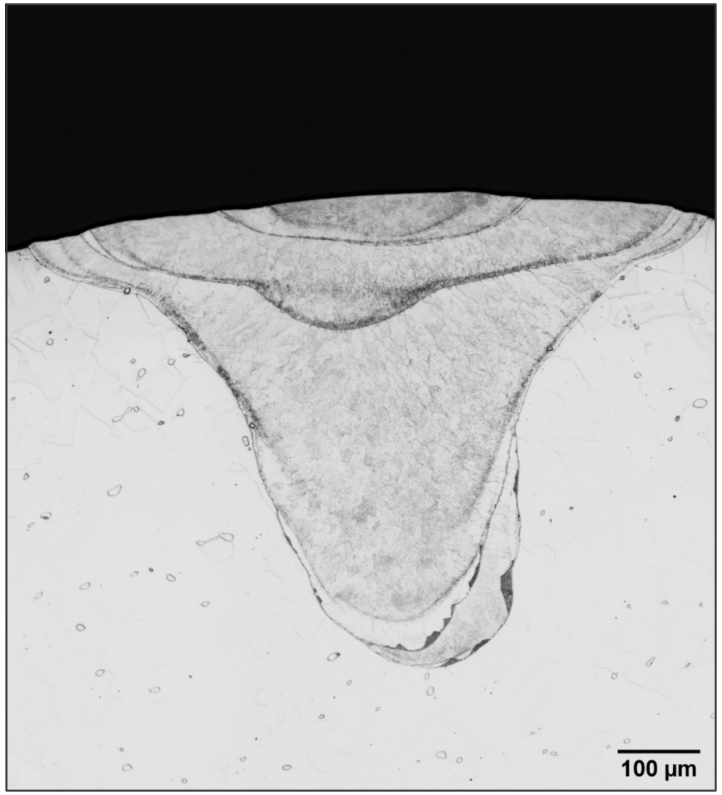




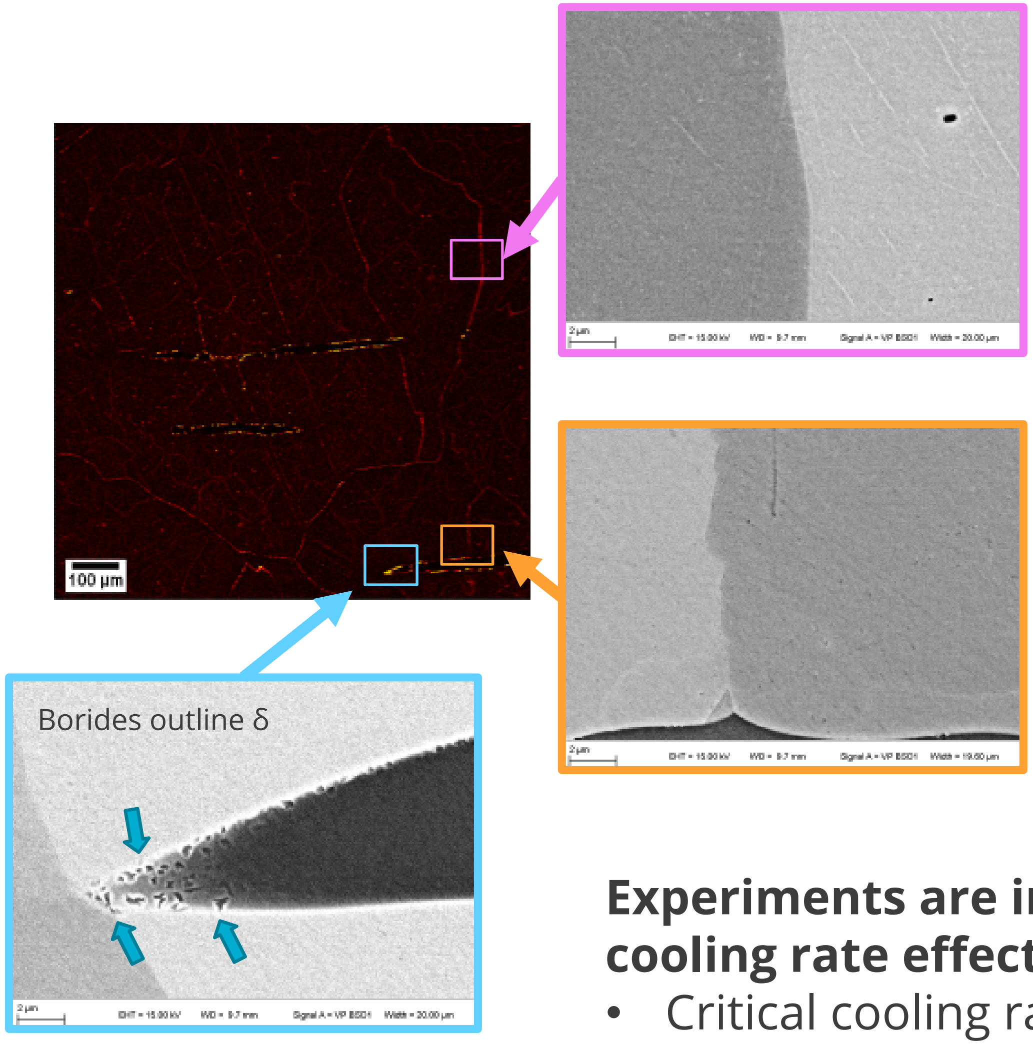


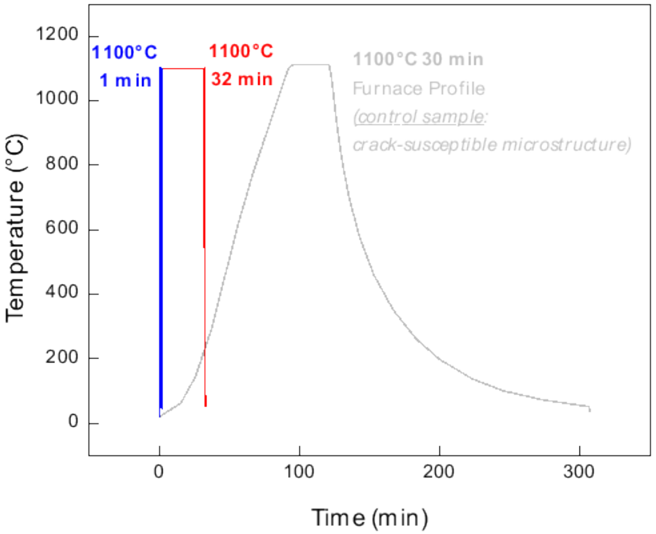


Crack-susceptible microstructure is related to heating/cooling kinetics



No cracks observed in any welds for 1100°C 1 min or 32 min!





Either borides aren't present (elemental boron) or are below resolution limit of SEM (and are small enough to not present a cracking risk)

Experiments are in progress to elucidate cooling rate effects on crack-susceptibility

- Critical cooling rate must be between 100°C/s and 0.5 C/s (furnace profile cooling rate)

Summary

- ToF-SIMS is an enabling technique for imaging Boron, leading to the ability to study grain boundary migration kinetics.
  - Special optimizations enable high resolution, large area analyses in a reasonable amount of time.
- Boride solvus temperature is between 1000°C and 1100°C
  - Subsequent experiments narrowed solvus temperature to 1025-1050° C
- Boron migration to γ grain boundaries is rapid (1 min at 1100°C is sufficient)
- Heat treatments with rapid heating/cooling rates are not crack-susceptible despite evidence of boron diffusion to grain boundaries
  - Cooling rate is significant for generating crack-susceptible microstructures
  - Cooling rate experiments in progress: 10, 1, 0.5, 0.1 °C/s to determine critical cooling rate
- These results begin to form the kinetic framework which will enable predictions of the crack susceptibility of B-containing 304L stainless when subjected to complex, part-specific heat treatments