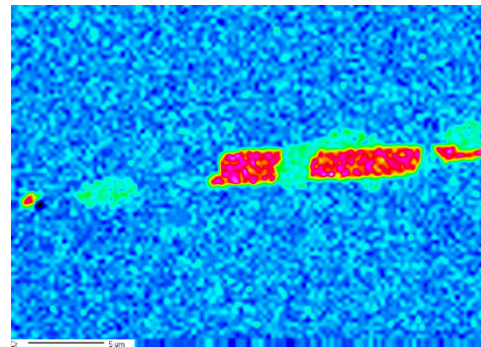
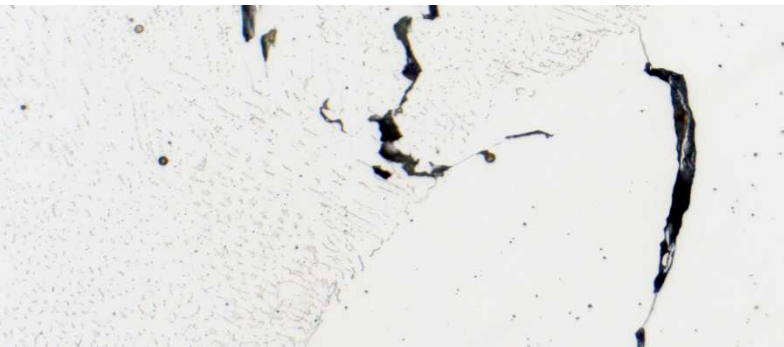


Assessing the Impact of Boron Micro-Alloying Additions on the Weldability of 304L Austenitic Stainless Steel

Final Report  
for the  
Sandia National Laboratories  
Contract DE-NA0003525



## Assessing the Impact of Boron Micro-Alloying Additions on the Weldability of 304L Austenitic Stainless Steel

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# 304L Austenitic Stainless Steel Background

- 304L is extensively used in Sandia Components

- Excellent corrosion resistance
- High ductility
- Strength comparable to mild steel
- *Weldable in autogenous processes*

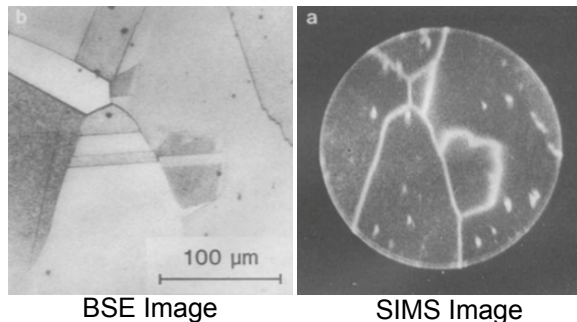


- Autogenous nature of laser welding dictates tightly controlled 304L compositions that solidify as primary ferrite with low impurities

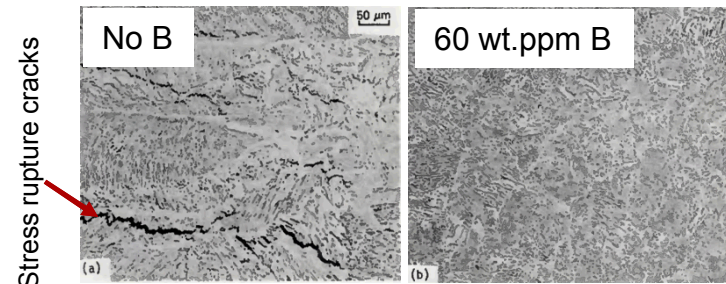
- Sulfur, Phosphorous, and **Boron**

- Micro-alloying additions of B in austenitic stainless steel can be used to tailor grain boundary mobility

Grain boundary B segregation in 316L with **40 wt.ppm B**<sup>1</sup>



Creep-life enhanced 308 filler metal<sup>2</sup>



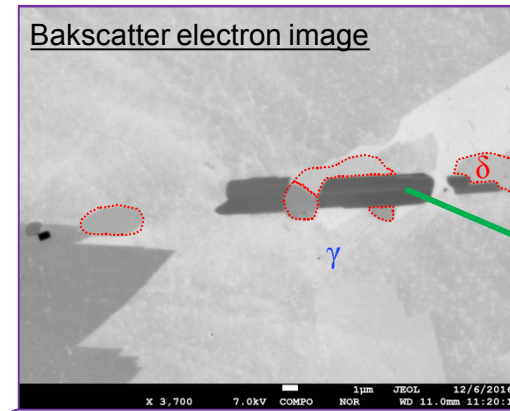
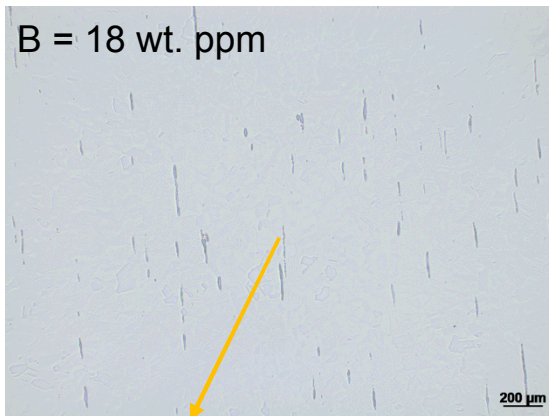
<sup>1</sup> Karlsson, L., et al. Acta Metall. Vol. 36, No.1, 1-12, 1988

<sup>2</sup> Kleuth, R.L., et al., Welding Journal, 65, 1s-7s, 1986

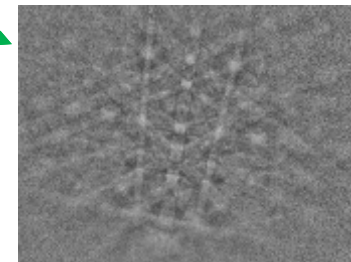
# Why examine boron micro-alloying additions on weldability?:

## Unexpected boron-rich phase discovered in 304L

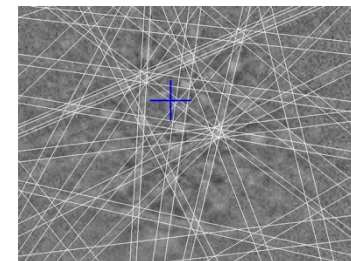
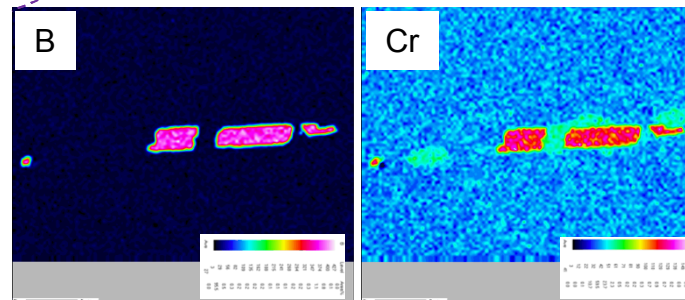
- Microstructural examination of incoming controlled chemistry 304L revealed globular brown/gray phase decorating some ferrite stringers
- Alloy contained near the max. allowable B content of 20 wt.ppm
- Additional characterization confirmed phase is boron-rich and structurally consistent with tetragonal  $M_2B$
- **Concerns raised about potential weldability issues related to the presence of borides**



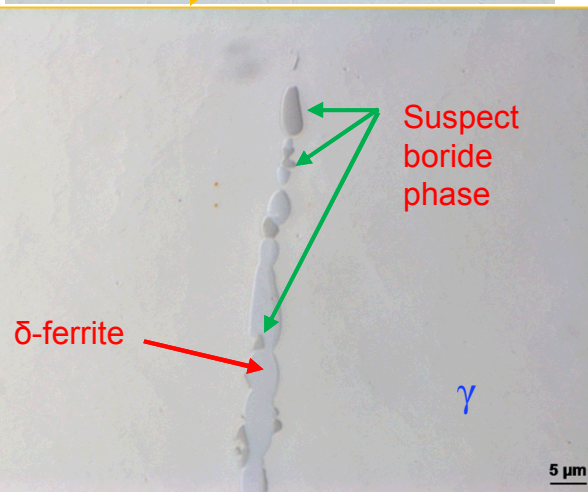
EBSD of Boride



Wavelength Dispersive Spectroscopic Maps



*Kikuchi patterns index as tetragonal  $M_2B$*





# Limited studies exist examining boron effects on 304L laser weldability

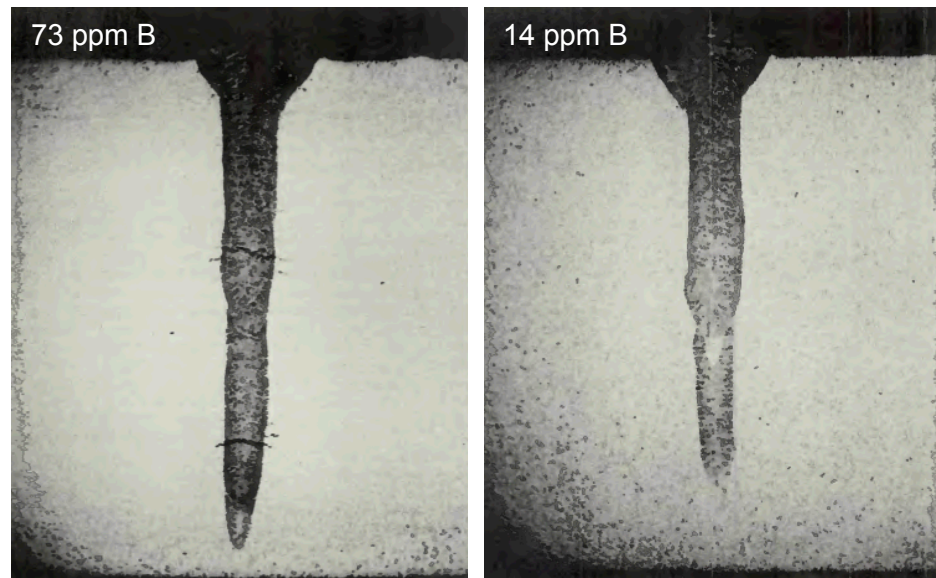
- Effects of boron on HAZ liquation cracking have been well-studied for Ni-base superalloys
- Thomas<sup>1</sup> performed an extensive literature review of the effects of B on HAZ cracking in austenitic stainless steels; however, data is largely based on arc weldability for non-‘L’ or stabilized grades
- Lippold<sup>2</sup> examined solidification crack susceptibility in pulsed laser welds on 304L compositions with B content up to 24 wt. ppm; however, effect of B on HAZ cracking susceptibility was not the focus of the work

Inconel 718 HAZ liquation cracks; 43 ppm B



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

Electron beam welding of A286



Books, J.A. and Krenzer, R.W. Welding Journal, June, 242s-245s, 1974

<sup>1</sup>. Thomas, R.D., Welding Journal, December, 355s-368s, 1984

<sup>2</sup>. Lippold, J.C., Welding Journal, June, 129s-139s, 1994



# Controlled-B 304L heats produced to study micro-alloying effects on weldability

- Boron content from 19 to 340 wt.ppm examined
- Small (20 lb.) vacuum induction melted (VIM) heats produced with compositions targeted to be similar to heat originally observed containing Cr<sub>2</sub>B
- All alloys examined have low S + P impurity levels combined with high (Cr/Ni)<sub>eq</sub> ratios expected to solidify as primary ferrite during laser welding

Sample	304L - <b>19B</b> (VAR)	304L - <b>36B</b> (VIM)	304L - <b>96B</b> (VIM)	304L - <b>340B</b> (VIM)
	wt.%			
<b>B</b>	<b>0.0019</b>	<b>0.0036</b>	<b>0.0096</b>	<b>0.0340</b>
C	0.021	<0.001	<0.001	0.003
Cr	19.45	18.84	18.94	19.01
Cu	0.11	0.13	0.13	0.14
Mn	1.42	1.54	1.52	1.50
Mo	0.09	0.12	0.11	0.09
Ni	10.24	10.26	10.10	10.32
N	0.010	0.006	0.005	0.008
P	0.019	<0.005	<0.005	<0.005
Si	0.63	0.60	0.60	0.57
S	0.001	0.002	0.003	0.003
Cr/Ni <sub>eq</sub> *	<b>1.80</b>	<b>1.82</b>	<b>1.84</b>	<b>1.80</b>

Production-scale melt  
hot worked into 4" bar



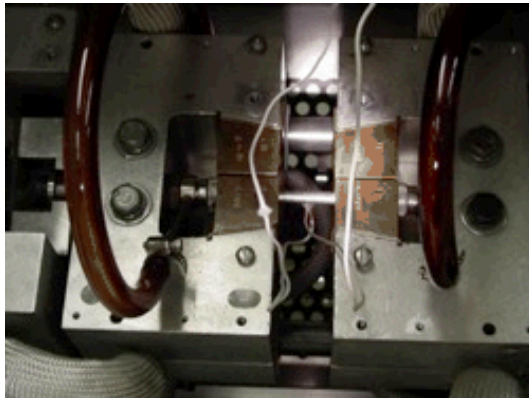
~20 lb. VIM 304L ingots.  
Ingots hot rolled into 1" bar,  
annealed 1100°C/1hr.

# Assessing Weld HAZ susceptibility: Approach

- Assessing boron micro-alloying effects on HAZ liquation cracking susceptibility will utilize both simulative weldability testing and autogenous weld trials

#1:

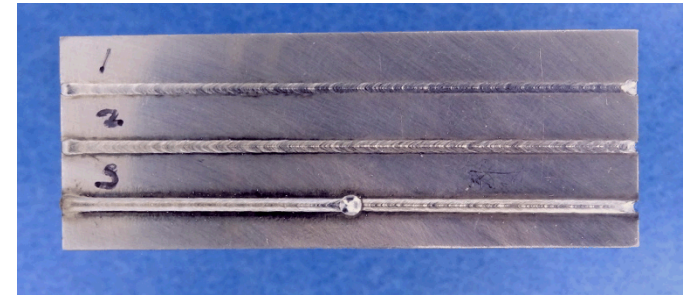
Evaluation of elevated temperature ductility



Gleeble Thermomechanical Simulator

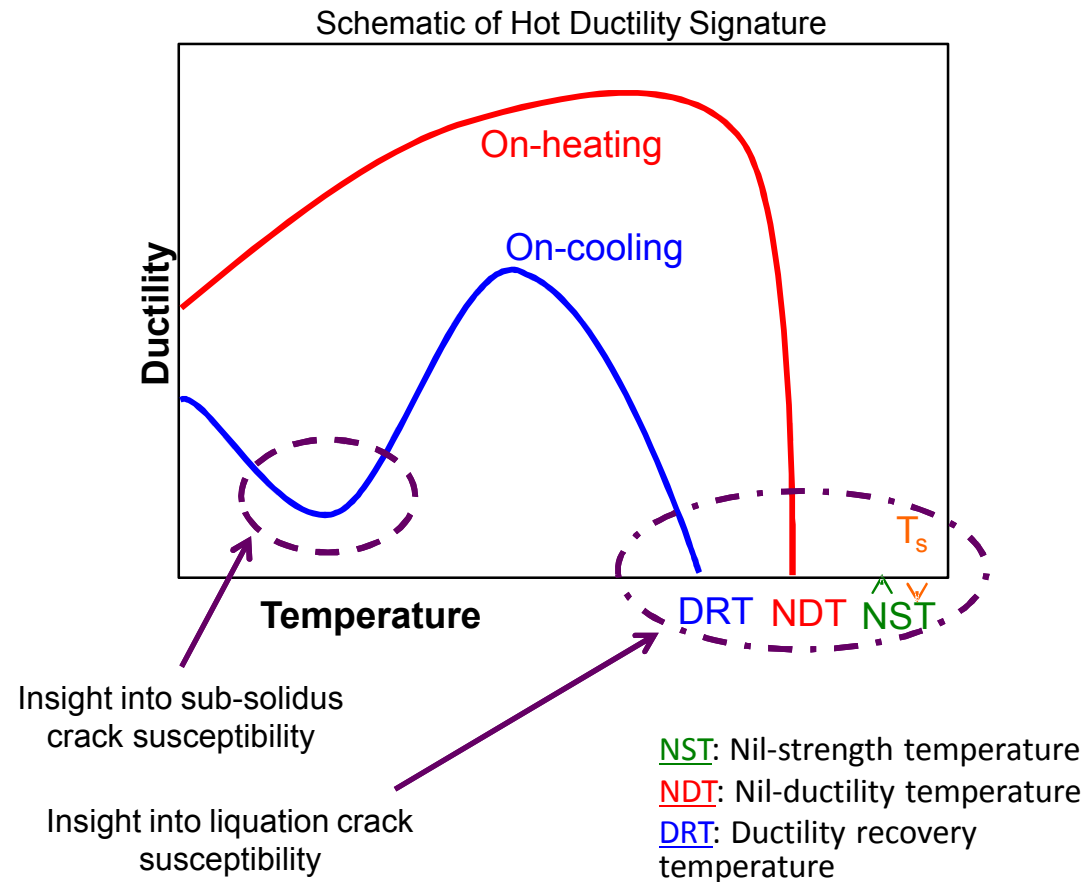
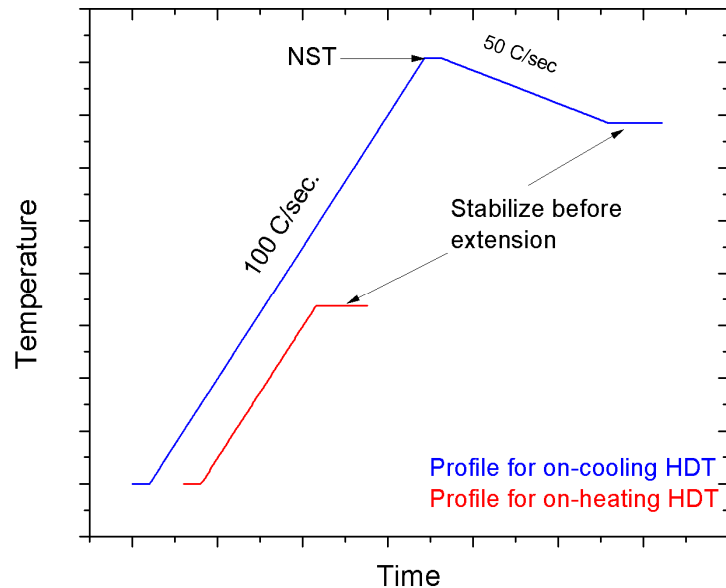
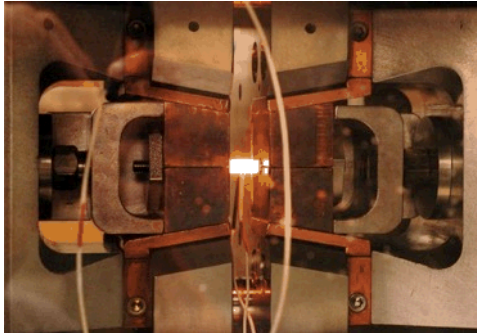
#2:

Autogenous GTA and laser welds



# Gleeble Hot Ductility Test

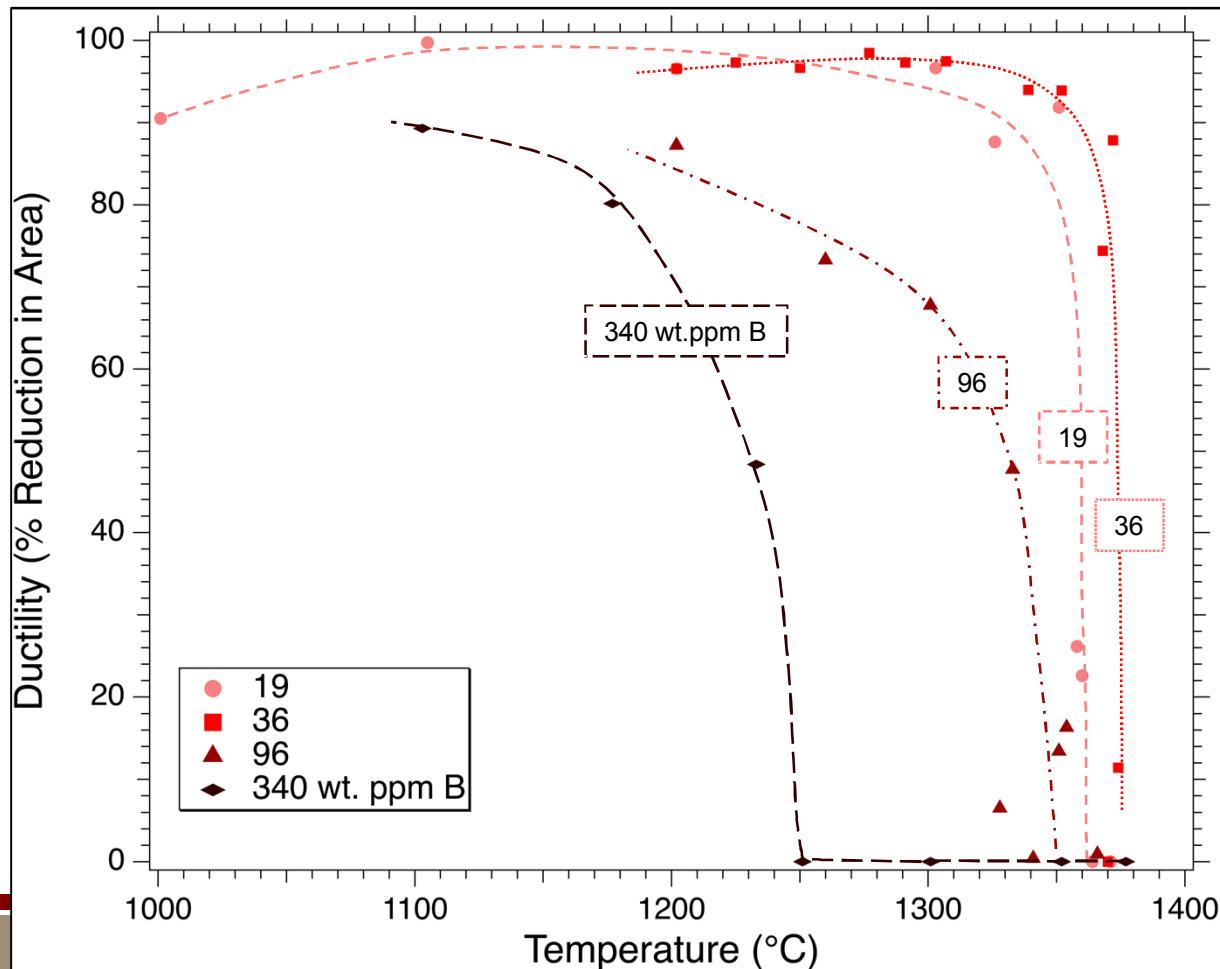
- High-temperature ductility response of material provides insight into material weldability
- HAZ cracking generally associated with exhaustion of available ductility





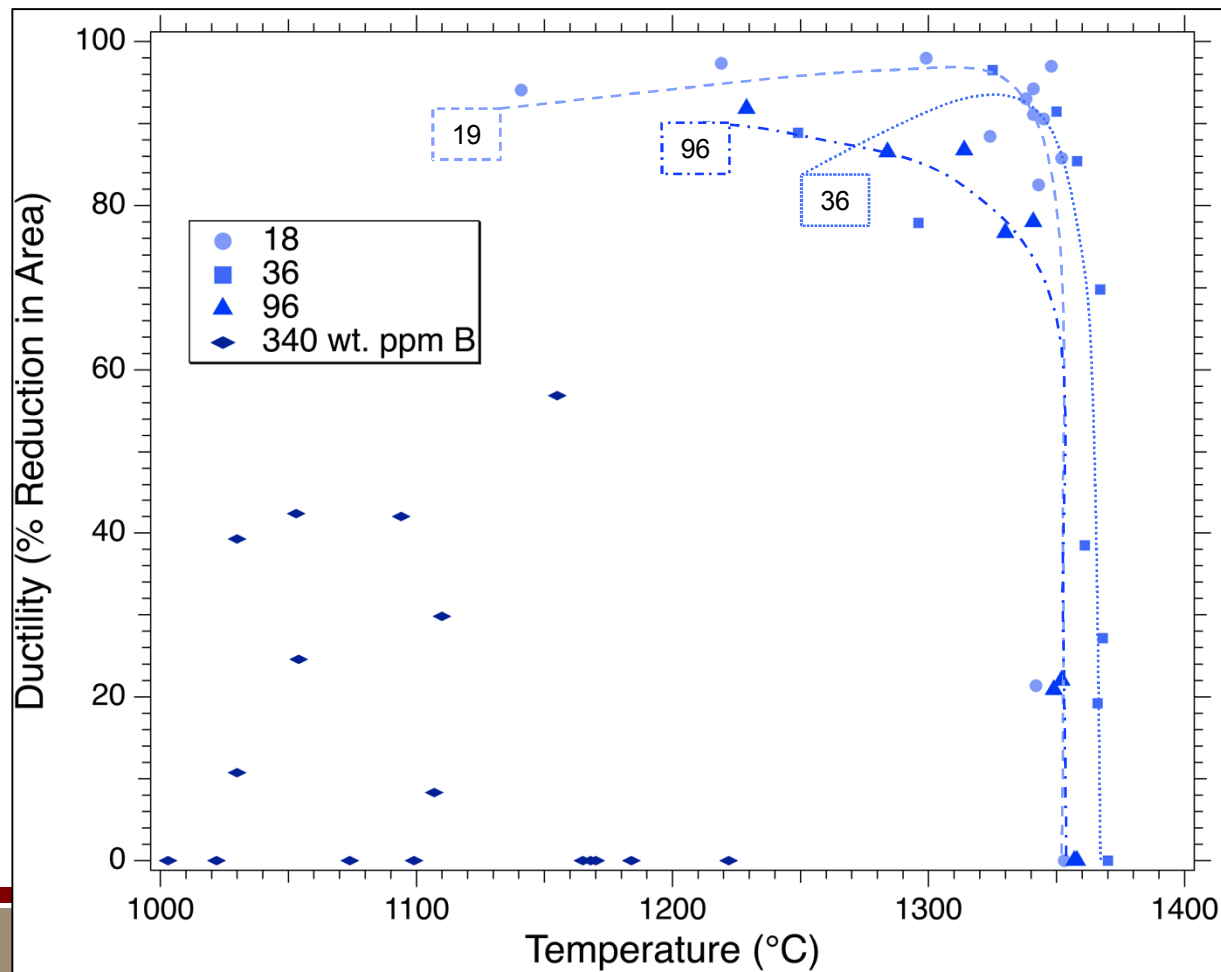
# On-heating ductility signature

- Ductility decreases precipitously for B contents  $\leq 96$  wt. ppm around 1350C; with the 96 wt.ppm B condition exhibiting a wider temperature range over which ductility decreases
- Highest B condition (340 wt.ppm) demonstrated nil-ductility temperature (NDT) approximately 100C lower than other conditions



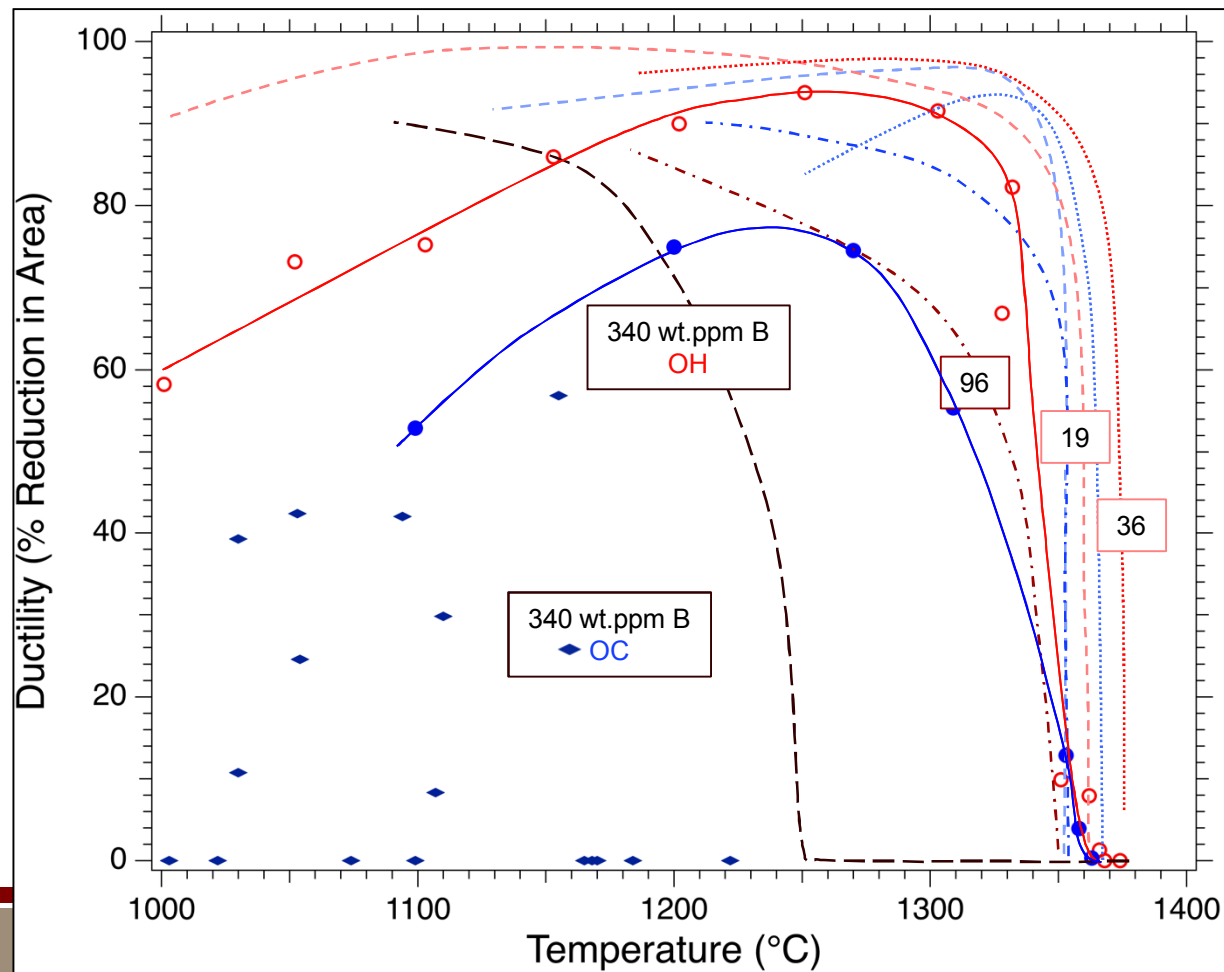
# On-cooling ductility signature

- 19, 36, and 96 wt.ppm B specimens exhibited rapid ductility recovery on-cooling
- 340 wt.ppm B condition exhibits ductility recovery 200+°C lower than other condition evaluated
- Longitudinal cross sections near fracture for 340 ppm needed to better understand ductility variability



# Hot ductility testing does not indicate liquation cracking risk for 304L with < 100 wt.ppm boron

- Boron-containing 304L with < 100 wt.ppm B shows similar ductility signature as commercial ASTM A276 304L with no B micro-alloying addition

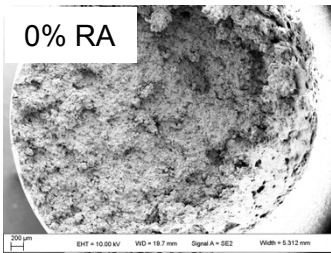




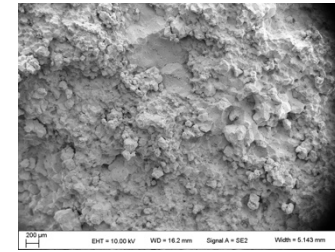
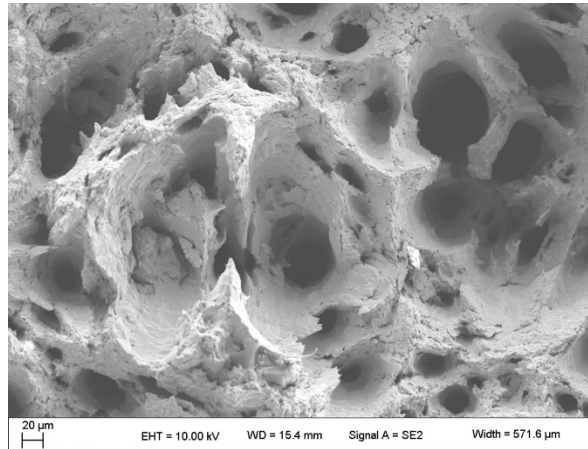
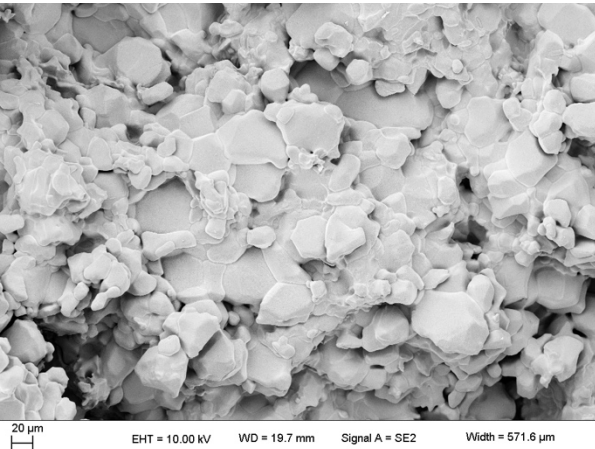
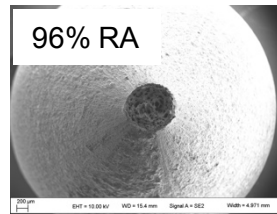
# Fractographic Examination of Hot Ductility Specimens

- At test temperatures explored, ductility loss is associated with intergranular fracture due to the formation of liquid films

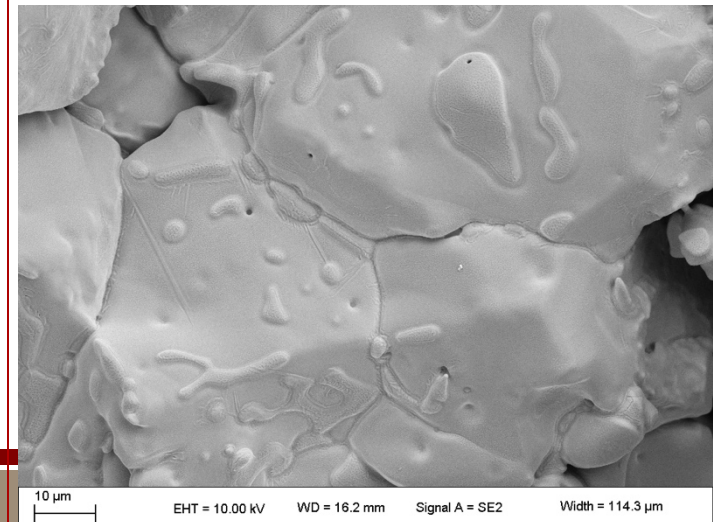
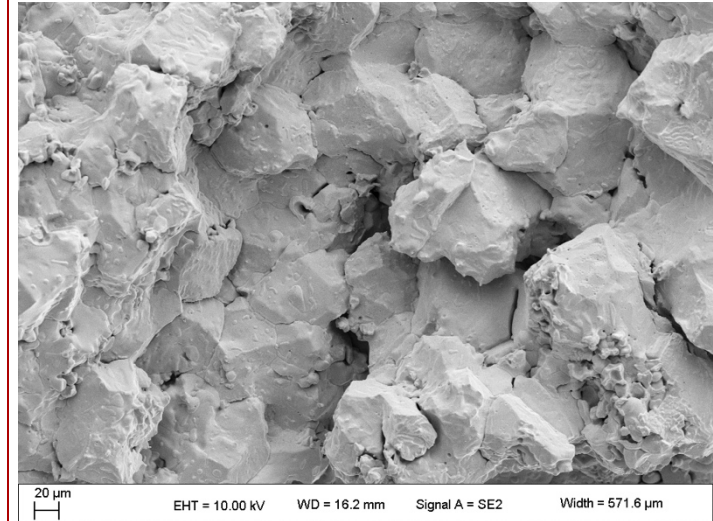
19 ppm B; 1353°C OC



19 ppm B; 1348°C OC

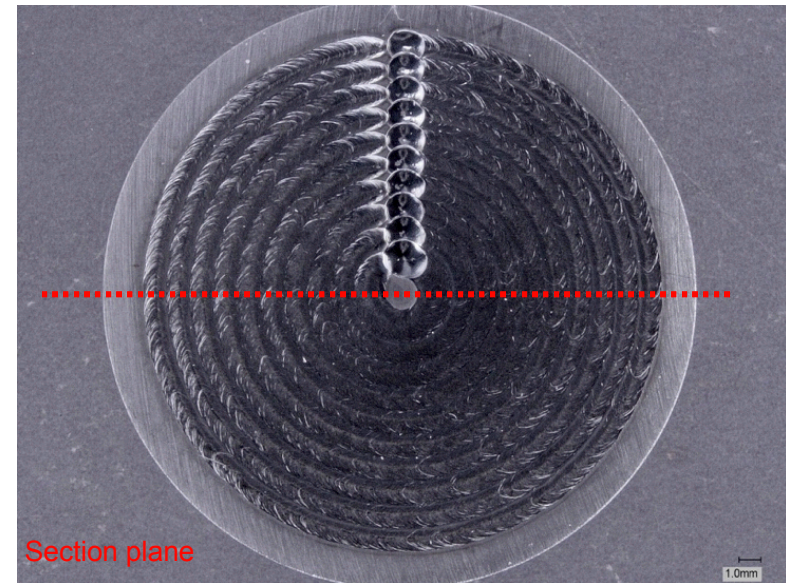


340 ppm B  
1184°C OC  
0% RA



# Autogenous Weld Trials

- Continuous wave laser weld parameters
  - 600 W average power; 33.8 mm/sec. [80 in./min.]
  - 18 J/mm linear heat input
  - 8.8 ms beam interaction time
  
- GTA weld parameters
  - 100 A; 11.1 V DCEN
  - 1.6 mm/sec travel speed
  - 720 J/mm linear heat input

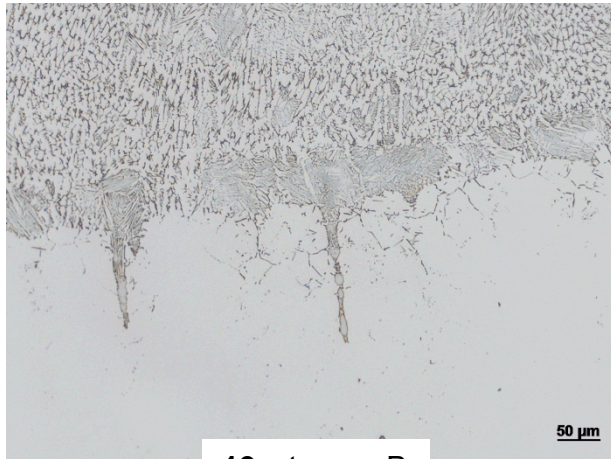


Laser welds produced in concentric pattern allowing each pass to cool to room temperature

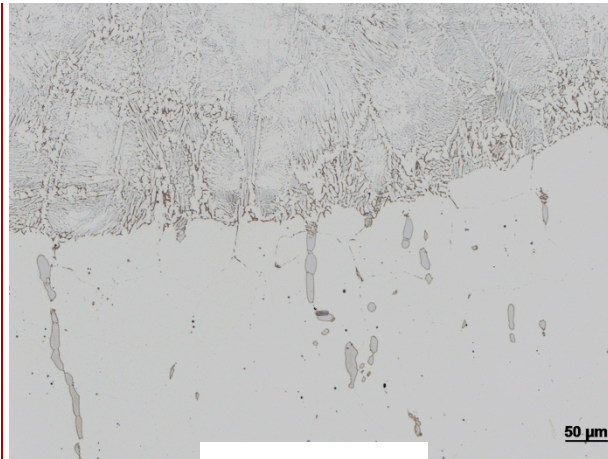


# GTA Welds: Light optical microscopy

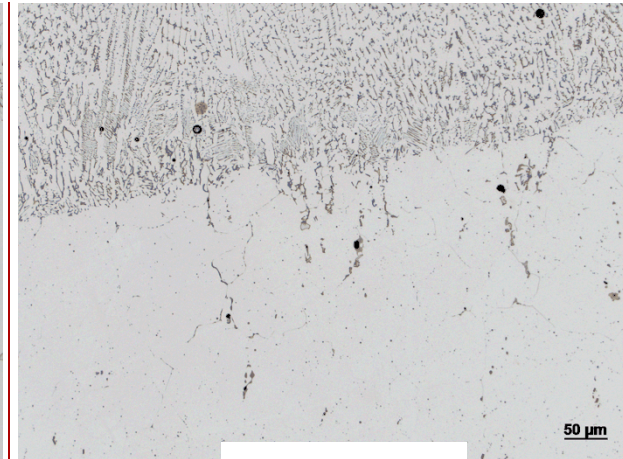
- Near fusion boundary HAZ liquation cracks only observed in highest B content condition
- Examination of autogenous GTA weld samples exhibits similar trend predicted by Gleeble hot ductility



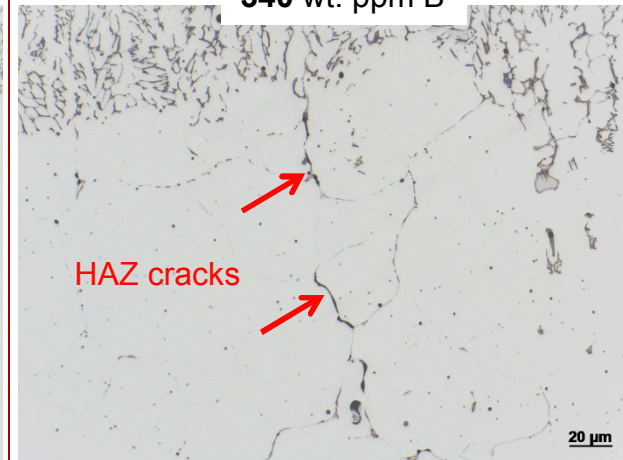
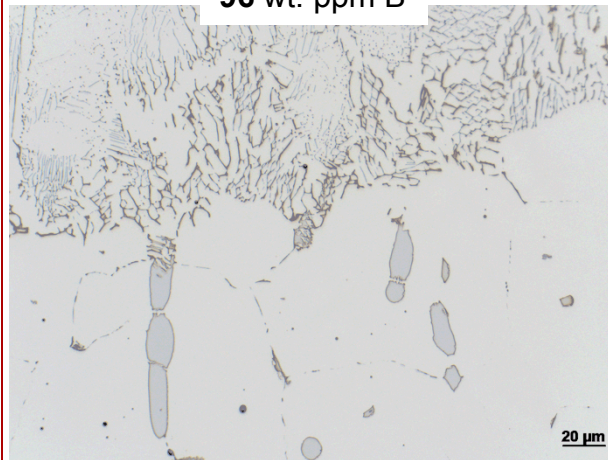
19 wt. ppm B



96 wt. ppm B

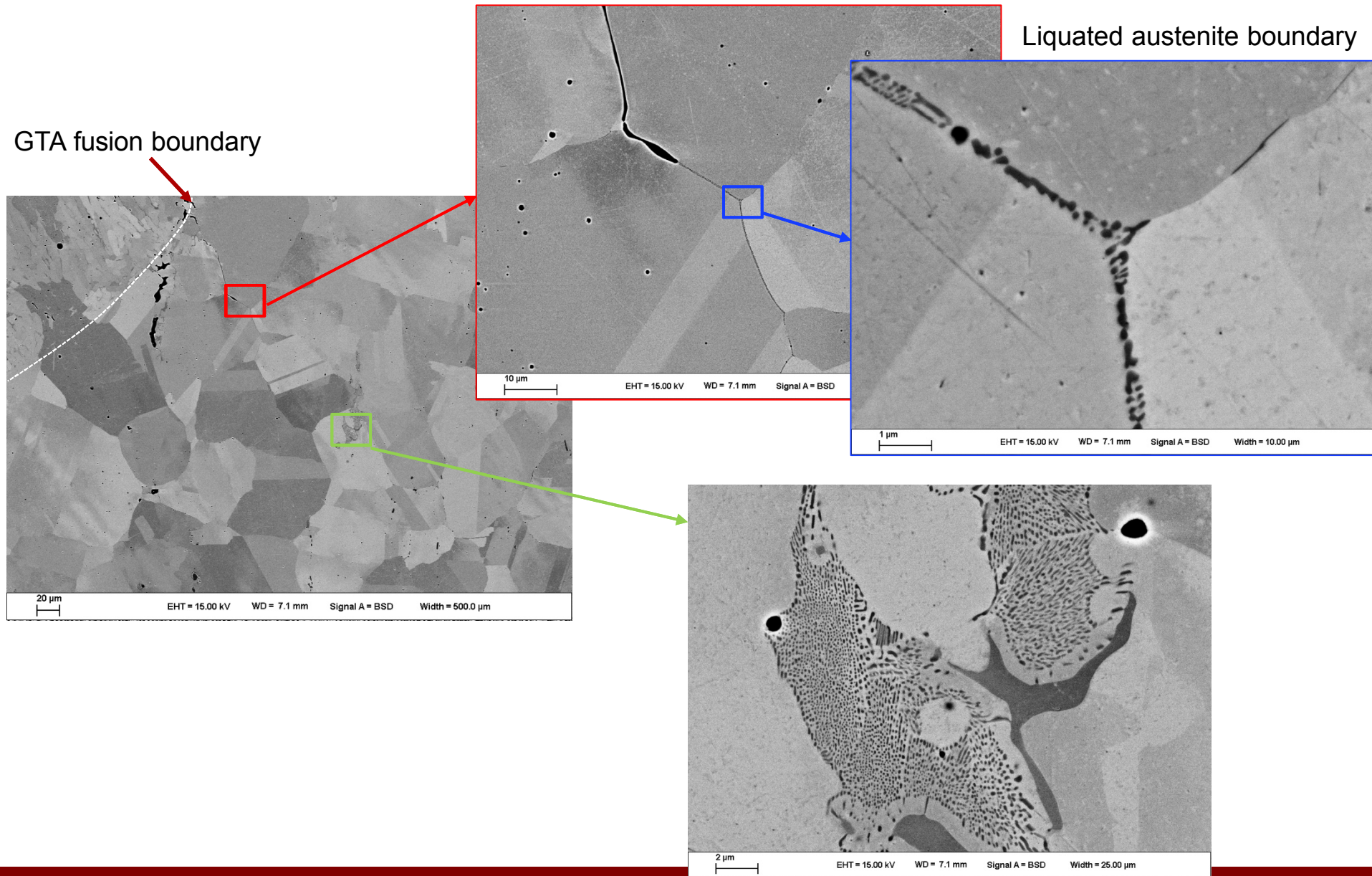


340 wt. ppm B





# GTA Welds: Electron Microscopy

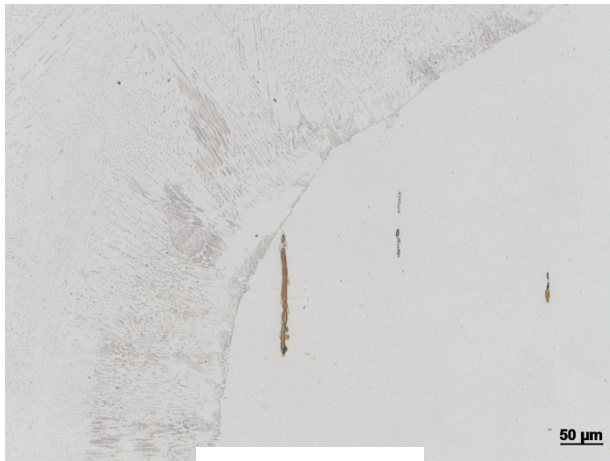


Liquated ferrite stringer

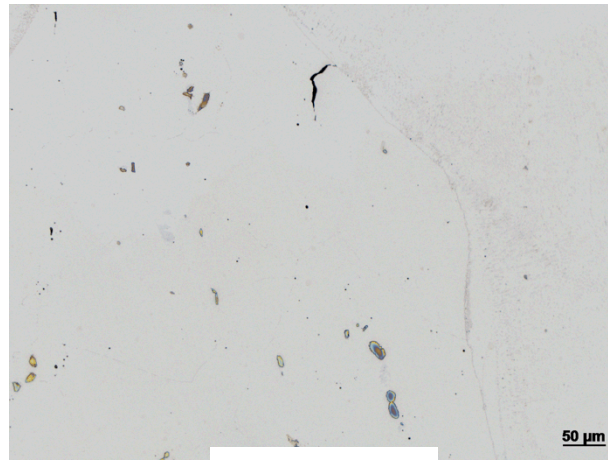


# CW Laser Welds: Light Optical Microscopy

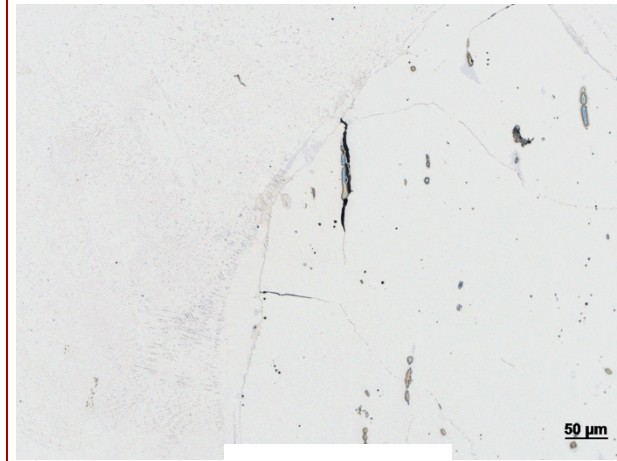
- Intermittent HAZ cracking observed in laser welds at significantly lower B content compared to autogenous GTA welds.



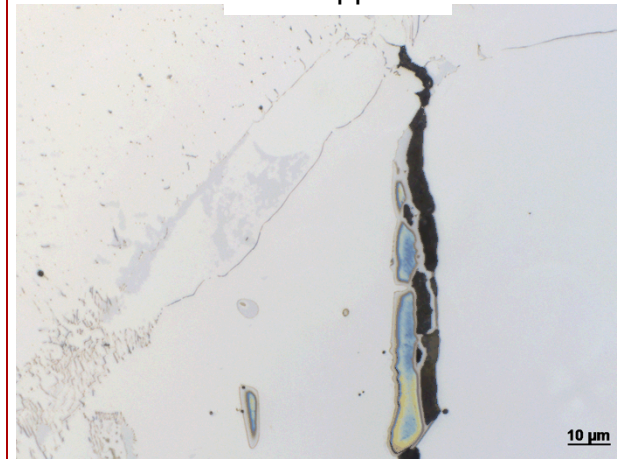
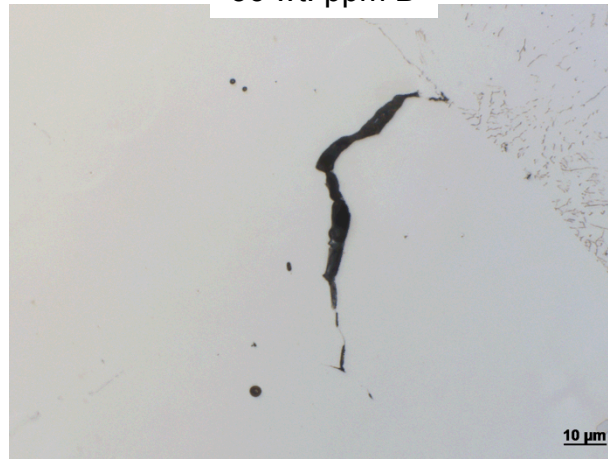
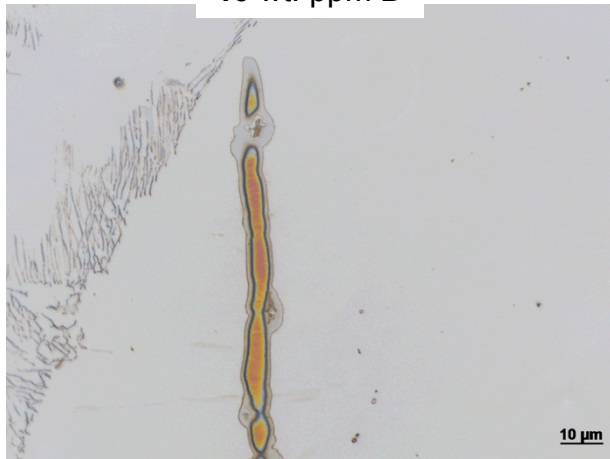
19 wt. ppm B



36 wt. ppm B

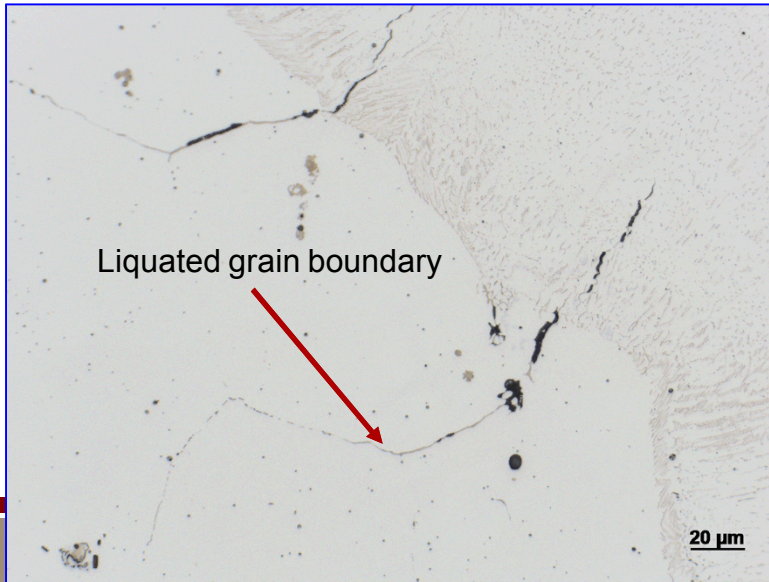
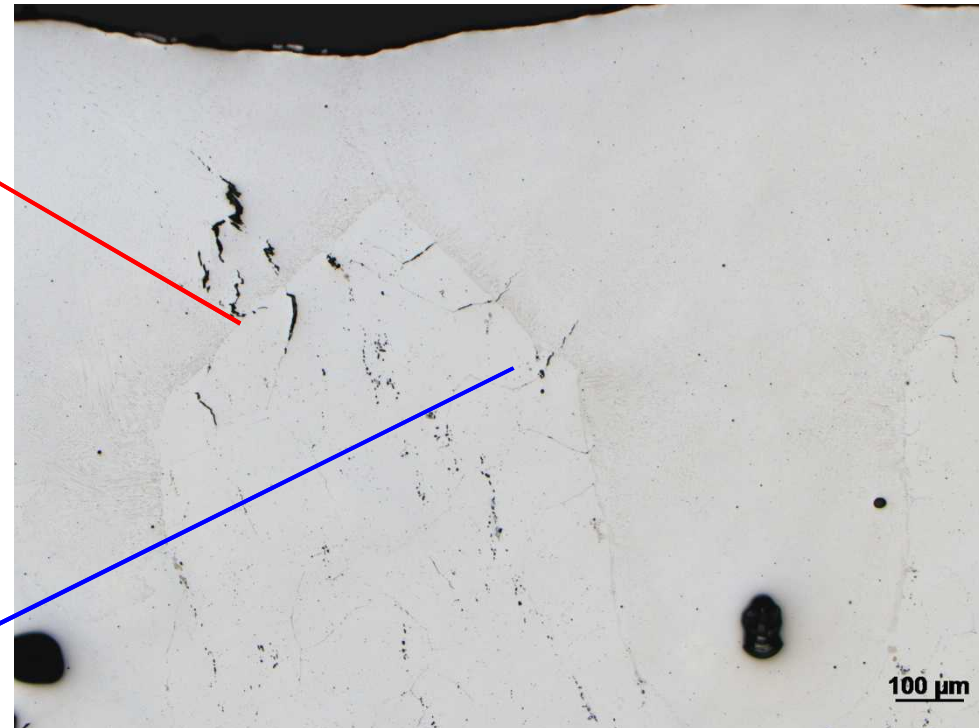
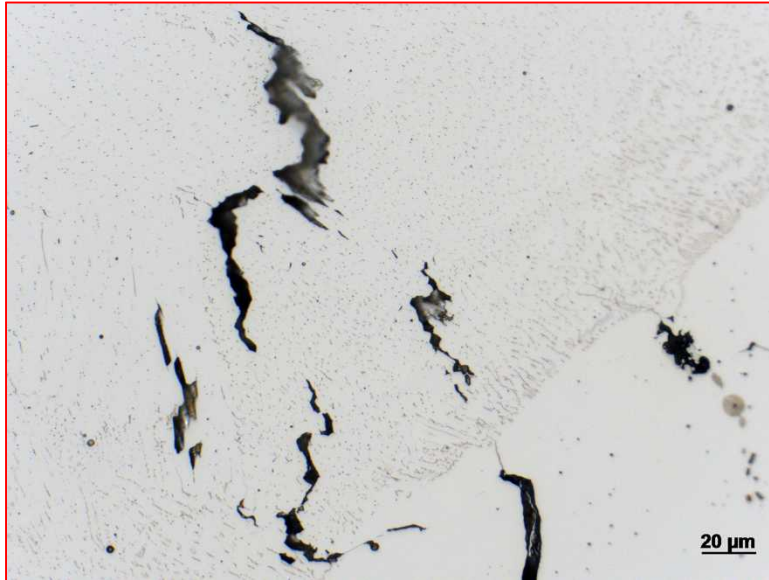


96 wt. ppm B



# CW Laser Weld: 340 wt.ppm B

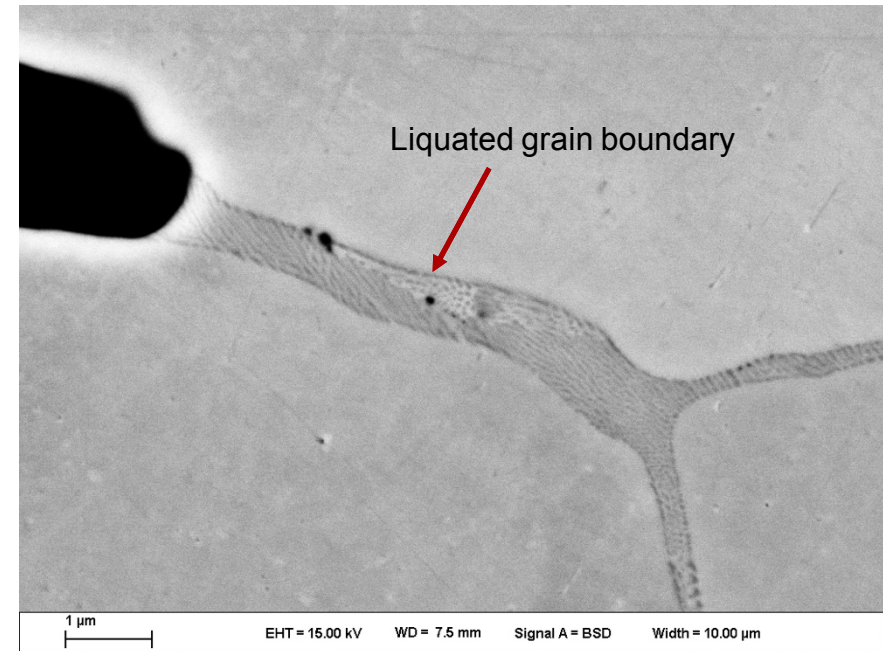
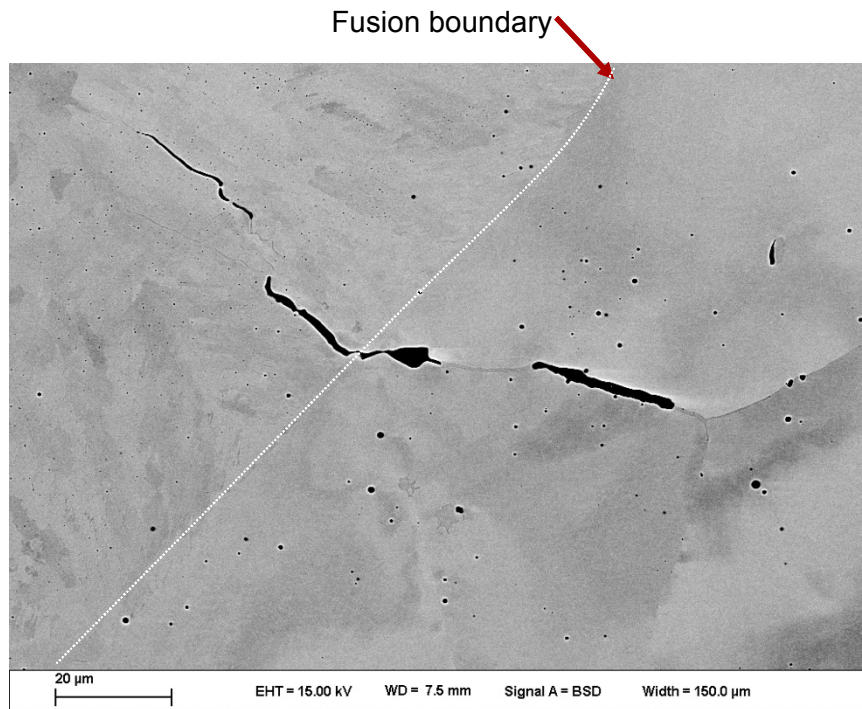
- Extensive HAZ liquation cracking in highest B condition
- Weld metal solidification cracks also observed





# CW Laser Weld: 340 wt.ppm B Electron Microscopy

- High-resolution backscatter electron imaging reveals fine-scale microconstituent decorating liquated HAZ austenite grain boundaries
  - Eutectic structure considerably finer in LBW vs. GTA welds exhibiting liquation



# Summary

- Boron-rich second phase observed in controlled-chemistry 304L heats with bulk B content  $\sim 20$  wt.ppm
- Gleeble hot ductility testing does not show apparent liquation cracking risk for B content  $\leq 100$  wt.ppm. Likely cracking risk at 340 wt. ppm B condition
  - HAZ cracking behavior in autogenous GTA welds agrees well with Gleeble data
- Applicability of Gleeble Hot Ductility data as a screening technique for laser weld HAZ crack susceptibility is limited due to different thermomechanical history.
- Laser weld HAZ cracking observed in 304L with  $\geq 36$  wt.ppm B reinforcing need for tight chemistry limits on 304L used for beam welding processes.
- While not circumventing boride formation, current B limit of 20 wt.ppm does not exhibit laser weld HAZ weldability issues

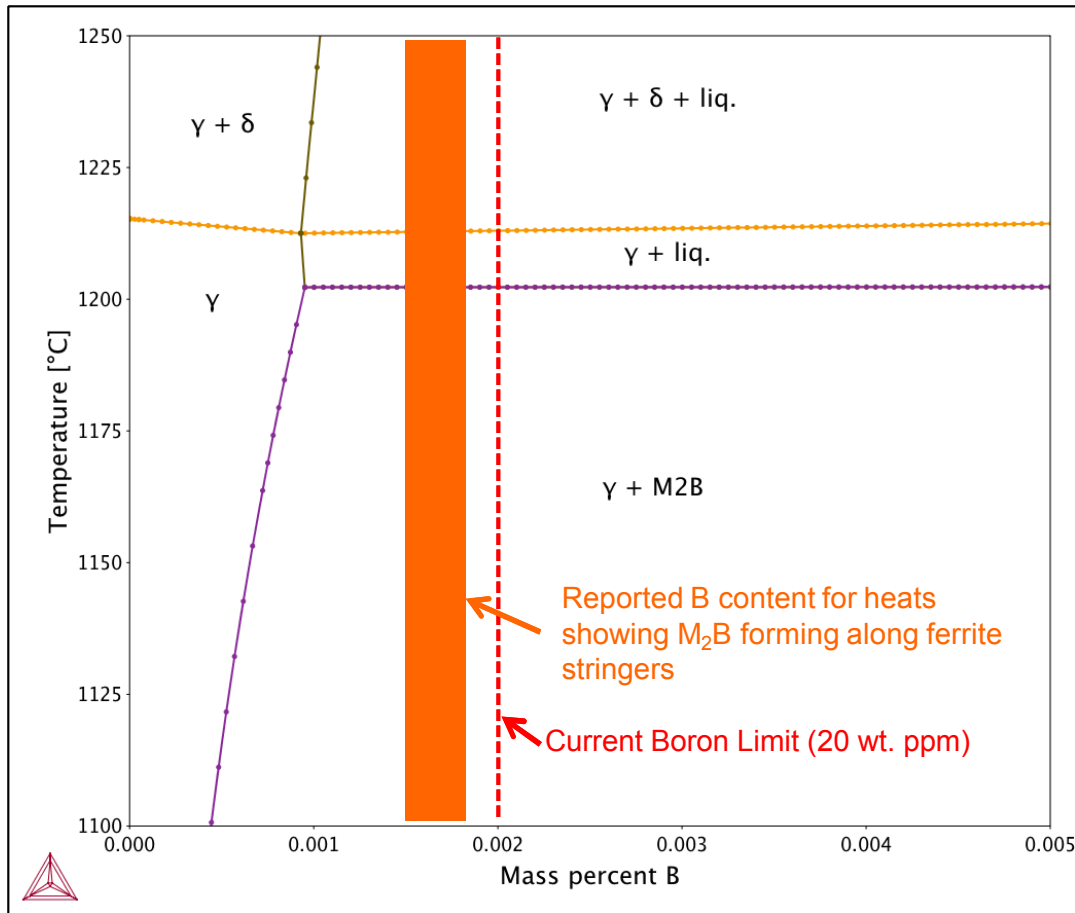
## On-going work

- Additional electron characterization to better understand liquation mechanisms in laser welds at B level below 340 wt.ppm
- Understand variability in on-cooling hot ductility behavior for 304L with 340 wt.ppm B

# Backup Slides

# CALPHAD Analysis of Boride Phase in 304L

- Pseudobinary for simplified 304L-like system shows very little high-temperature solubility for boron—max. ~10 wt.ppm B
- In equilibrium,  $M_2B$  (i.e.  $Cr_2B$ ) formation is expected for Electralloy-reported B values (16-18 wt.ppm)!
  - Simplified 304L composition used for analyses presented
    - [Fe-X] – 19.19 Cr – 10.25 Ni – 0.024 C – X B , wt. %
  - Calculations performed using Thermo-Calc 2016a with TCFE8 v.8.0 database



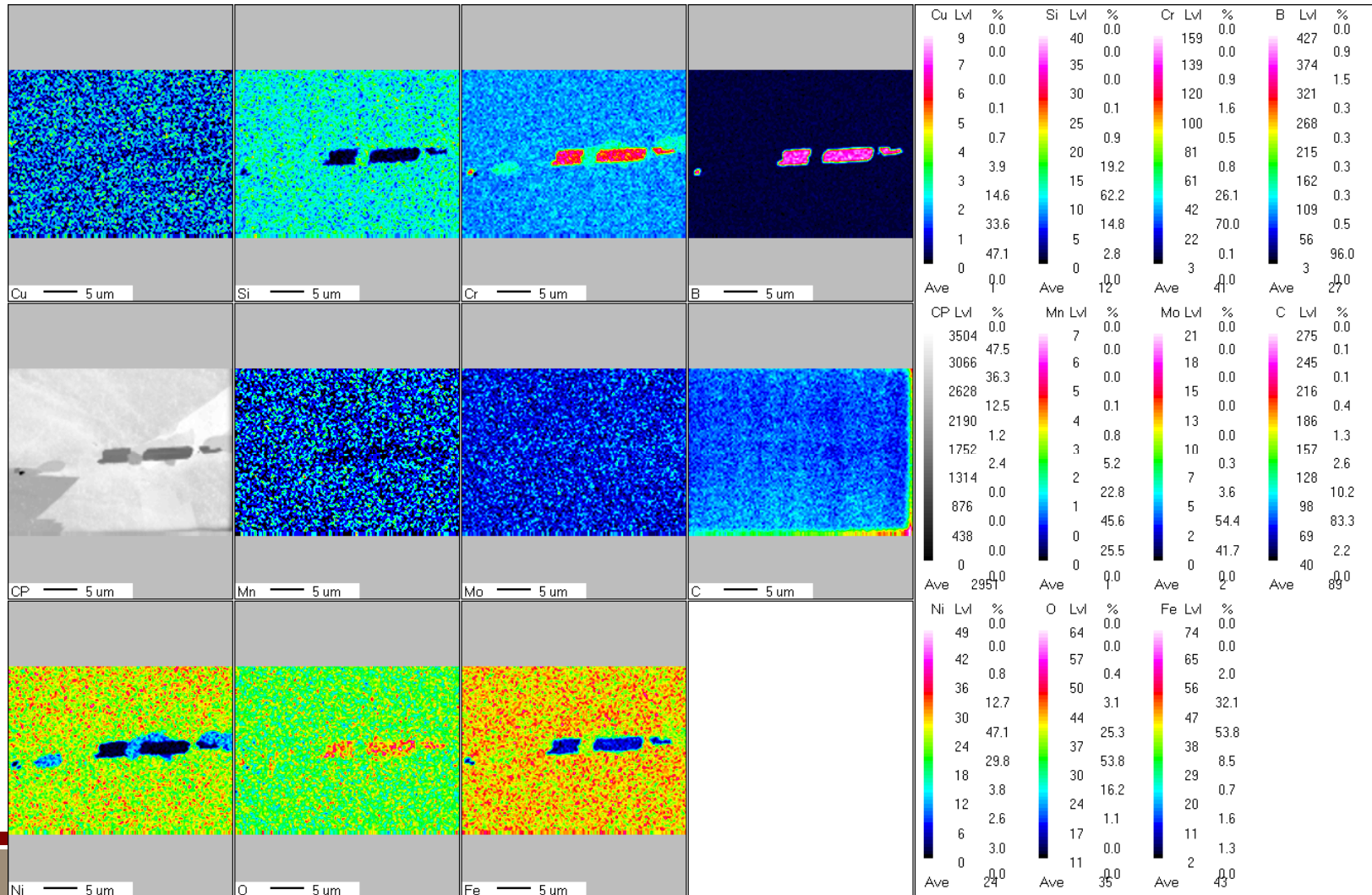
Solubility of B in 18Cr-15Ni stainless  
(original technical basis for 20 wt.  
ppm B limit)

Goldschmidt, *Journal of the Iron and Steel Institute* 209 (11): 900-911. 1971



# Wavelength Dispersive Spectroscopy Used to Map Chemical Composition near Ferrite Stringer

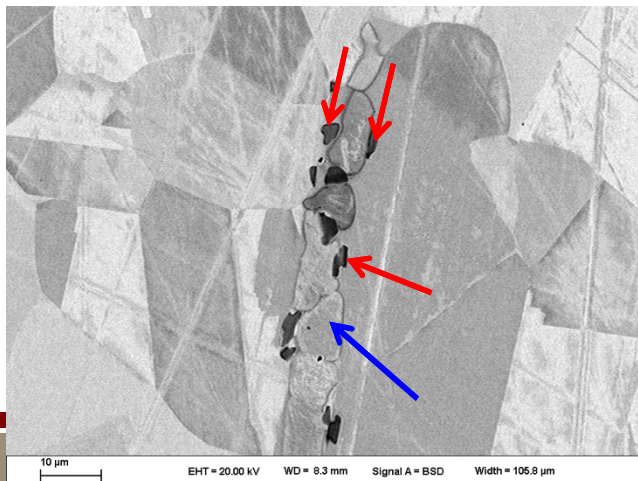
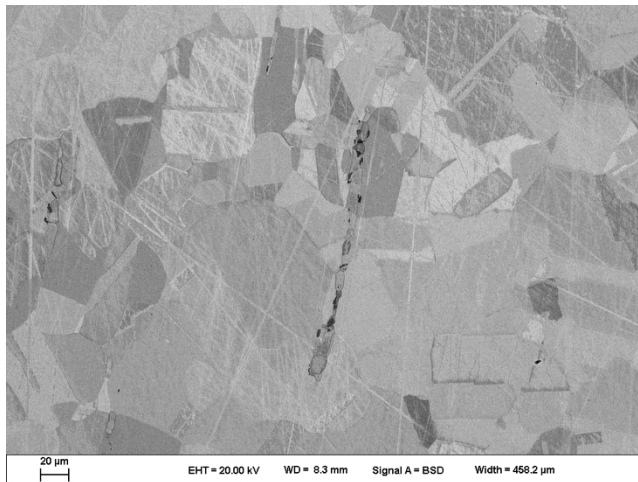
- Suspect boride phase is indeed rich in B and Cr relative to ferrite and austenite matrix. Boride phase appears to have some solubility for O.
- Boride phase is Cr-rich, but also contains some Fe. Negligible C and Ni signal detected.
- Low-Z of B presents challenges in the quantification of phase composition



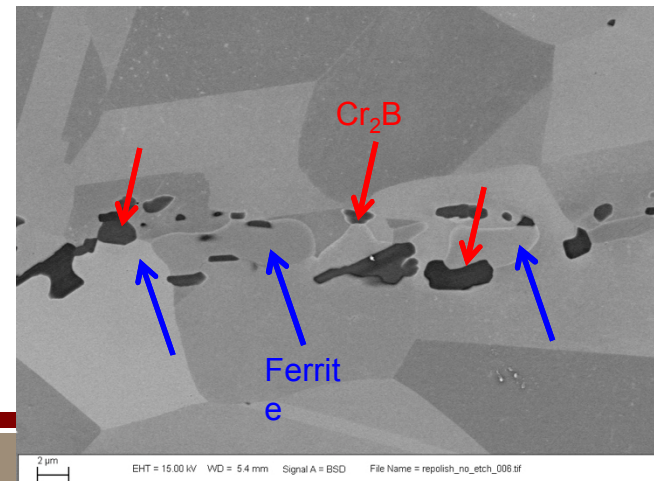
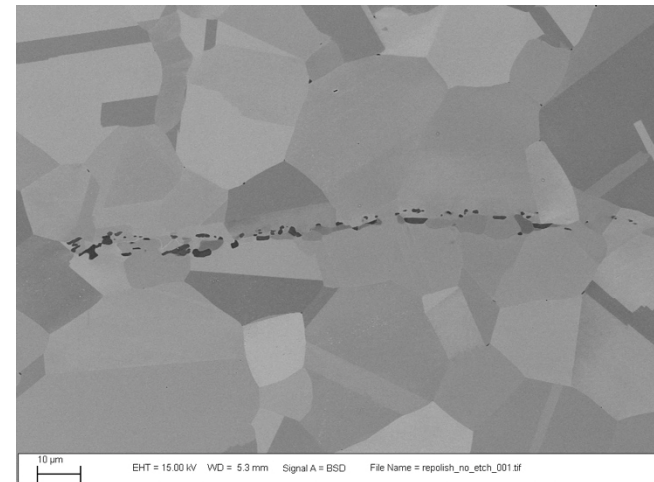
# Comparison of 2016 304L VAR to Cr<sub>2</sub>B-containing 2011 304L: Electron Imaging

- Backscatter electron micrographs of 2016 304L VAR show suspect phase is consistent with relatively low atomic number (Z) Cr<sub>2</sub>B phase found in 2011 304L VAR material. Phase appears dark relative to matrix.

201394-2 B = 17 wt. ppm



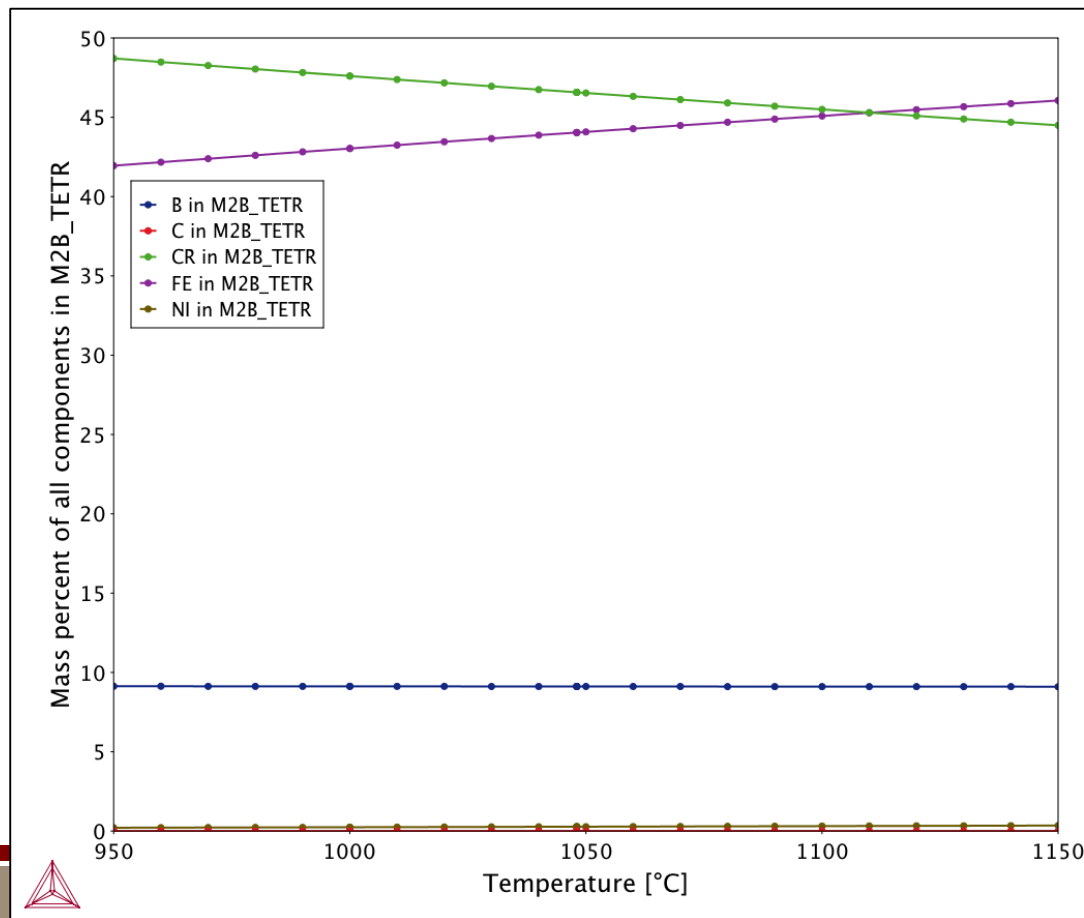
2011 304L VAR 200 wt.ppm B



\*Images from  
JR Michael,  
Boride Phase  
Analysis

# Calculated Boride Composition

- Boride composition at relevant solutionizing temperature range calculated using the following alloy composition:
  - Fe – 19.19 Cr – 10.25 Ni – 0.024 C – **0.0018 B** , wt.%
- Calculations are in agreement with measurements reported in literature and are qualitatively in agreement with WDS results presented earlier
  - Wt.%: 46Cr - 40Fe – 3.5Mn – 1.0Ni – 9.5B<sup>1</sup>



<sup>1</sup>Martin, J.W. "Effects of processing and microstructure on the mechanical properties of boron-containing austenitic stainless steels," Proc. Waste Management '89; Tucson, AZ (USA); 26 Feb - 2 Mar 1989. pp 293-302