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Alloy Depletion and Martensitic Transformation During Glass-to-Metal Sealing

Don Susan, Matt Perricone[a], Charlie Robino,
Joe Michael, Bonnie McKenzie, and Mark Rodriguez

Sandia National Laboratories
Albuquerque, NM

[a]RJ Lee Group, Inc., Monroeville, PA

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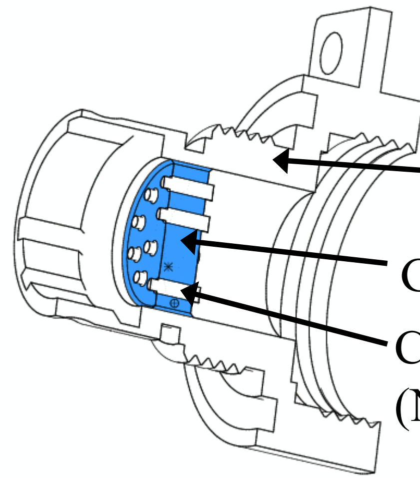
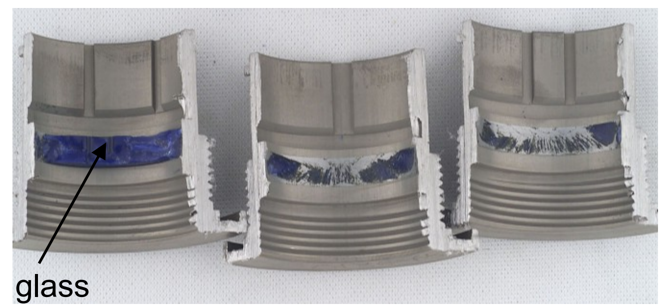
Background

- **Glass-to-metal (GtM) seals must provide a hermetic barrier in high-reliability connectors. "Compression" type seals – outer SS shell with a high CTE, glass with a low CTE, and low-expansion pin material (with CTE approximately matching the glass.)**

- **Good chemical adhesion is also required between the glass and metal, through the formation of a transitional oxide layer. This layer is provided by *"pre-oxidation" of the stainless steel prior to glass/metal joining.***





Examples of good vs. poor glass adherence

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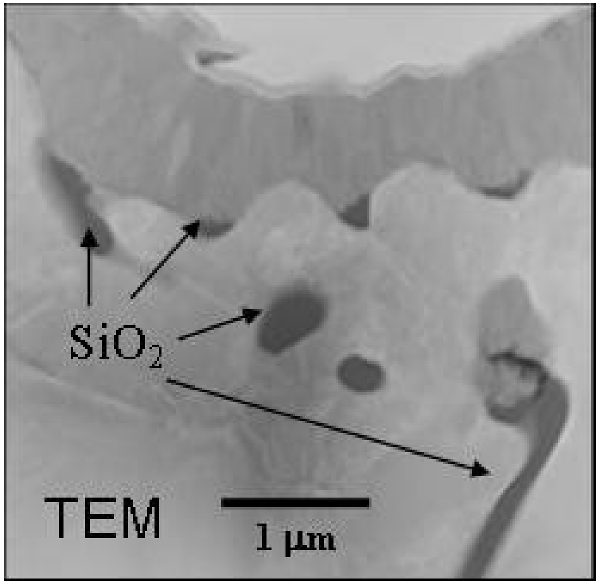
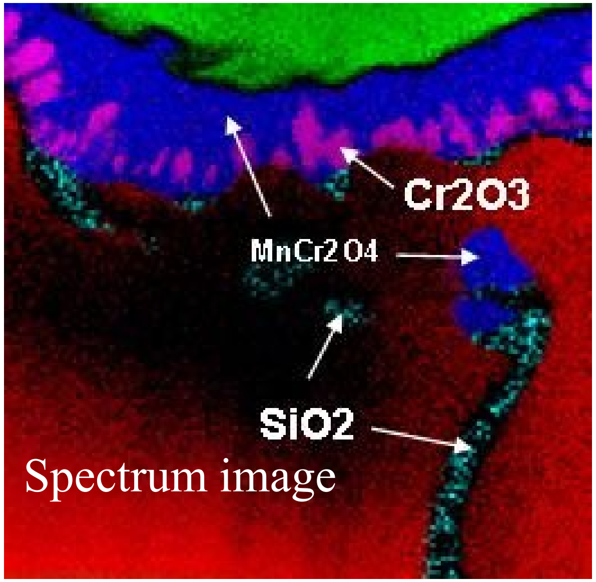
Previous work: Investigation of the oxide chemistry and morphology

- Analyzed several heats of 304L and 316L
- Pre-oxidation of stainless steel:
  - 1000, 1050, and 1095˚C
  - 30 and 90 minutes, cool to room temp.
  - Low pO_2 atmosphere, to avoid Fe oxidation
- GtM sealing:
  - 920 to 970˚C, ~15 minutes, N_2/H_2 atmosphere, cool to room temp.





- Pre-oxidation produces thin oxide with Cr_2O_3, $MnCr_2O_4$, and SiO_2 phases.
- Provides transitional layer with bonding to both the metal and the glass

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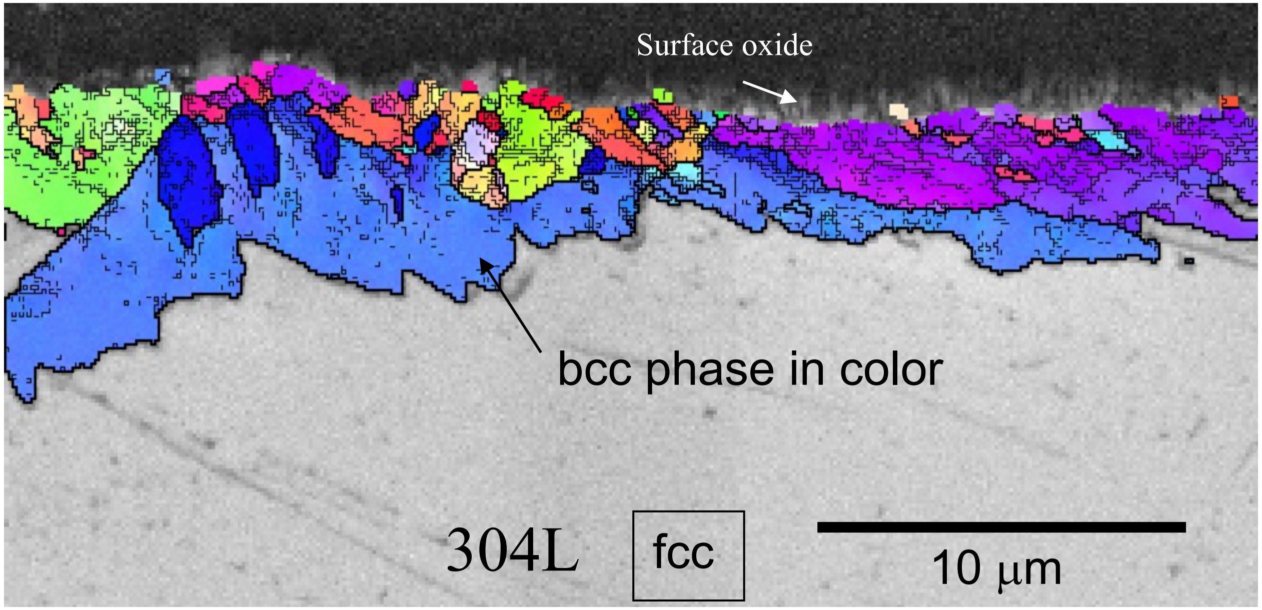
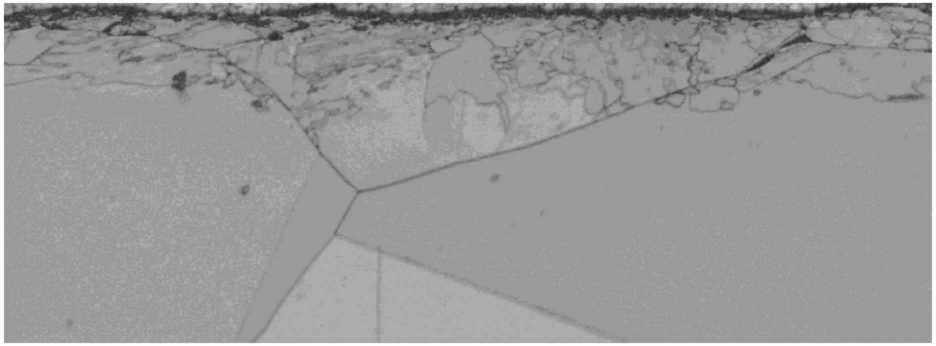
Motivation for Current Work: Observed a bcc transformed layer near the surface of 304L

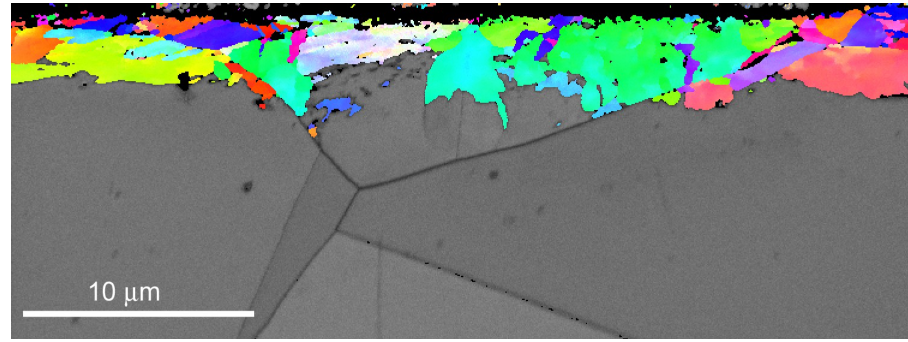
- Issues: Phase transformations in the alloy, near the metal/glass interface, could be detrimental to GtM sealing.
  - An fcc-to-bcc transformation produces material with a lower CTE than the bulk austenitic 304L (possible loss of compression seal).
  - The transformation also produces a volume change and possibly high stresses near the glass interface which could result in glass/oxide cracking and/or loss of adhesion.



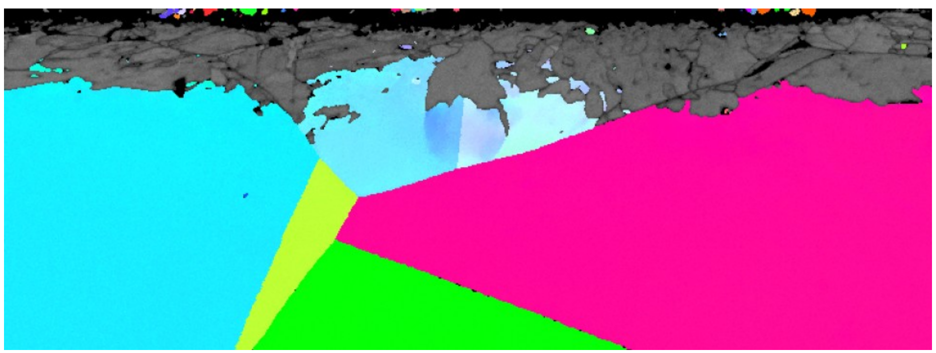
SEM, EBSD Results



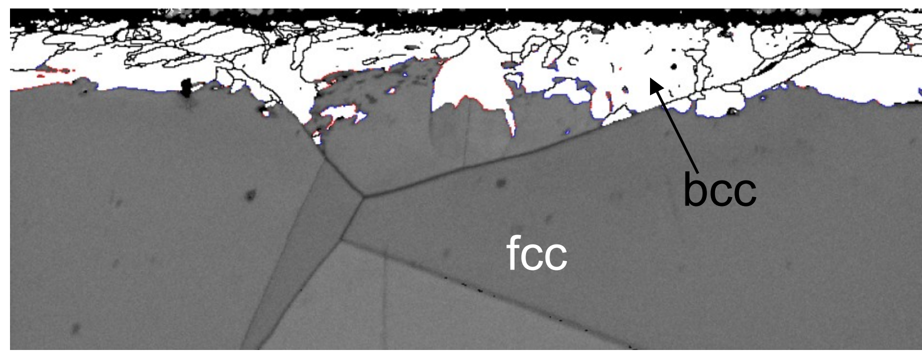
Band Contrast



Ferrite (body-centered)



Austenite (fcc)



Kurdjumov-Sachs relationship – blue
Nishiyama-Wasserman relationship - red

- What causes the fcc-to-bcc transformation near the alloy surface?
- What type of transformation (diffusional, martensitic, etc.)?

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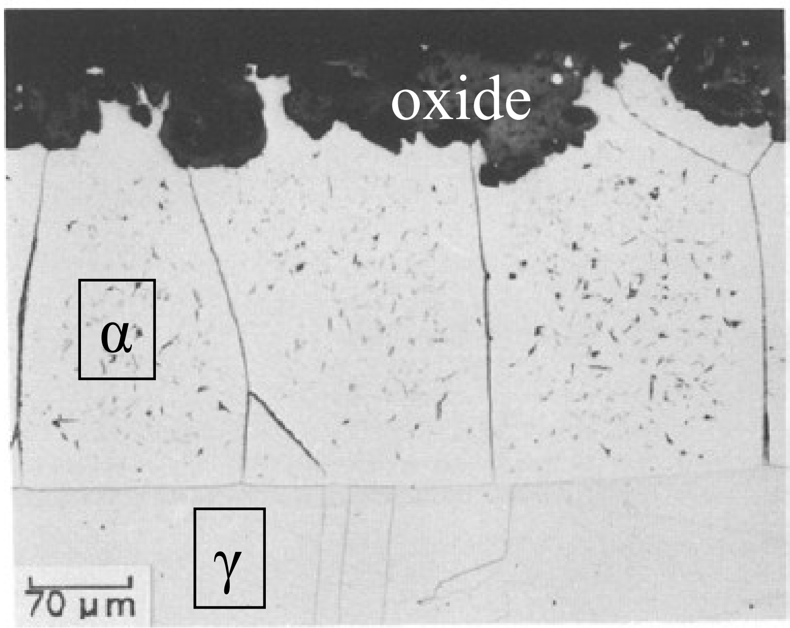
- **Possible sources of bcc layer:**
  1. **Diffusional transformation during high-temperature processing. This can occur due to alloy depletion by diffusion and oxidation. Many examples in literature.**
  2. **Martensitic transformation on cooling: This would be unusual for 304L, which has Martensite-start (M_S) temp. of approximately -250˚C. Our samples were never cooled below room temperature.**



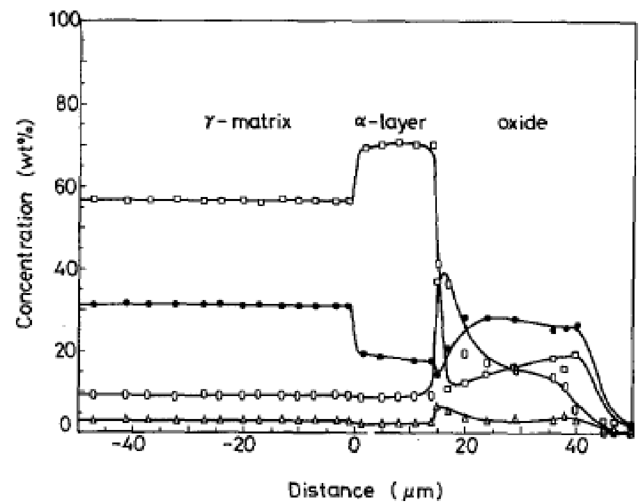


Figure 8 Concentration profiles of the sample oxidized at 800° C for 48 h. (□) Fe, (●) Mn, (△) Cr, (○) Al.

Example of diffusional bcc formation *during oxidation*: Duh et al., *J. Mat. Sci*., Vol. 23, 1988, p. 2649-60. (Fe-Al-Cr-Mn alloy)

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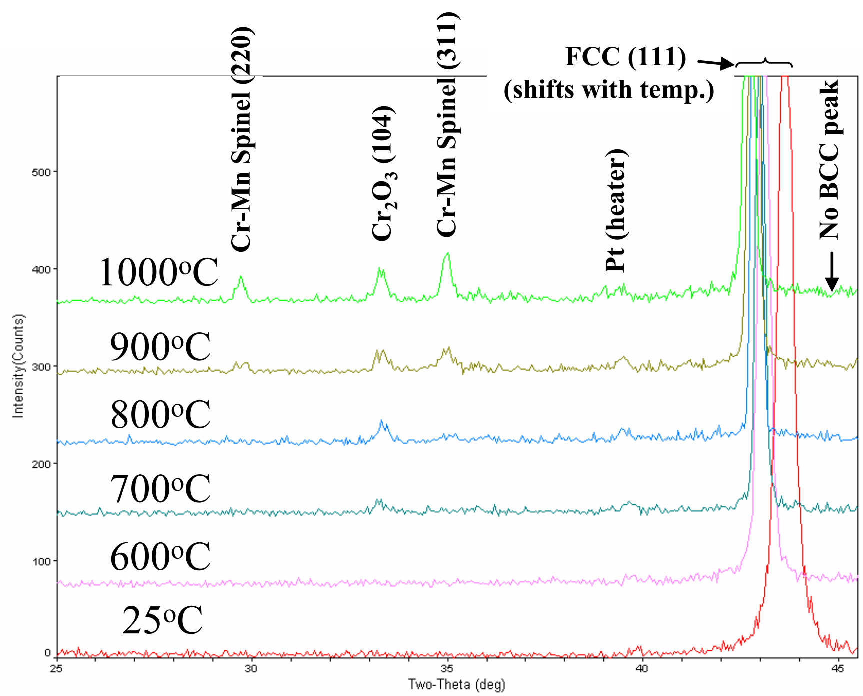
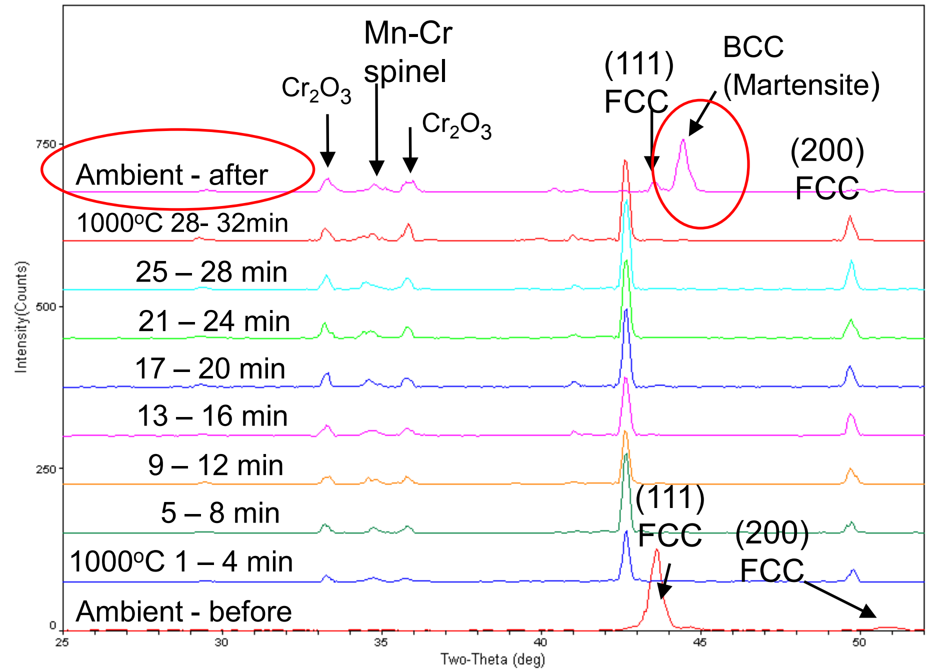
“Dynamic” XRD showed that bcc formation occurred *During Cooling*



Heating experiment



Hold 30 min. at 1000˚C

- No bcc peak during heating or at the oxidation temperature, for up to 30 minutes.
- BCC peak present *after cooling* to room temperature.

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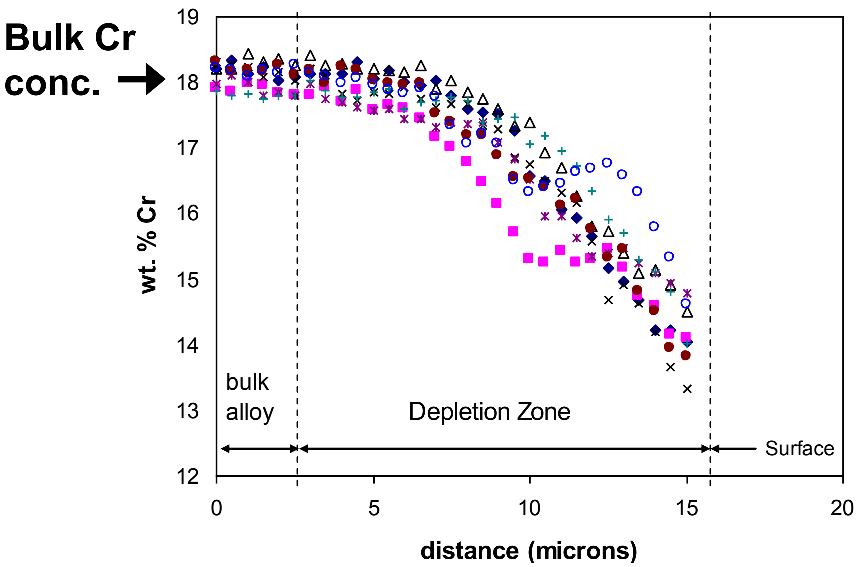
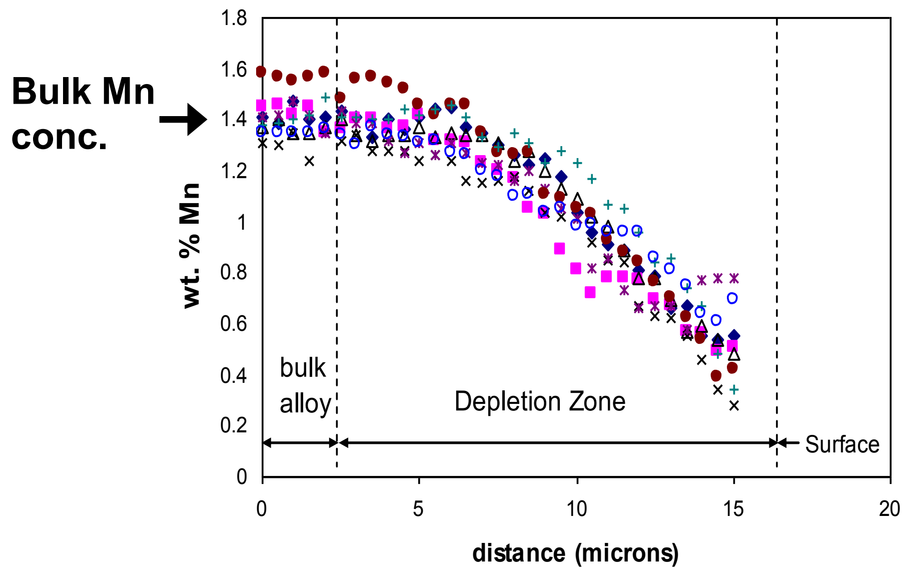
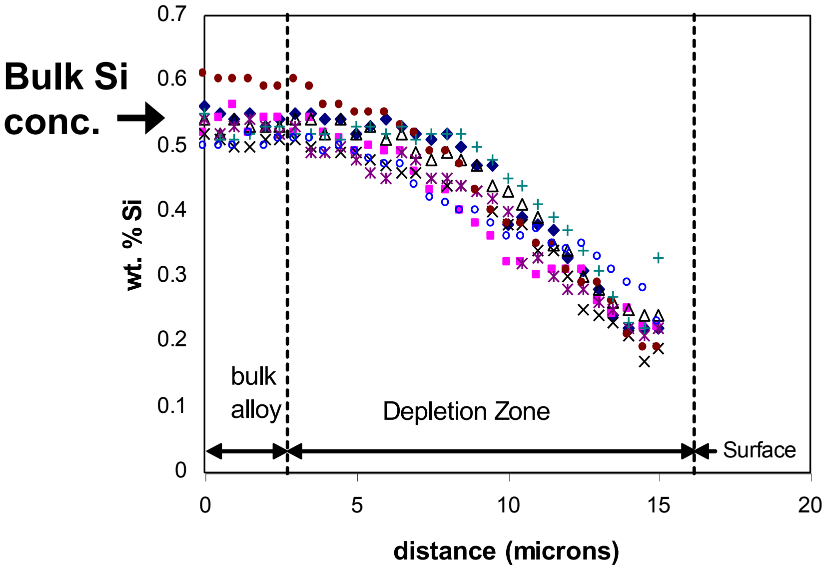
EPMA shows alloy depletion near the surface







- 1095˚C, 30 min. oxidation
- Multiple EPMA traces performed on each sample.
- Significant depletion of the elements Cr, Mn, and Si, *all involved in surface oxidation*. (oxide phases formed on 304L are Cr_2O_3, $MnCr_2O_4$, and SiO_2)

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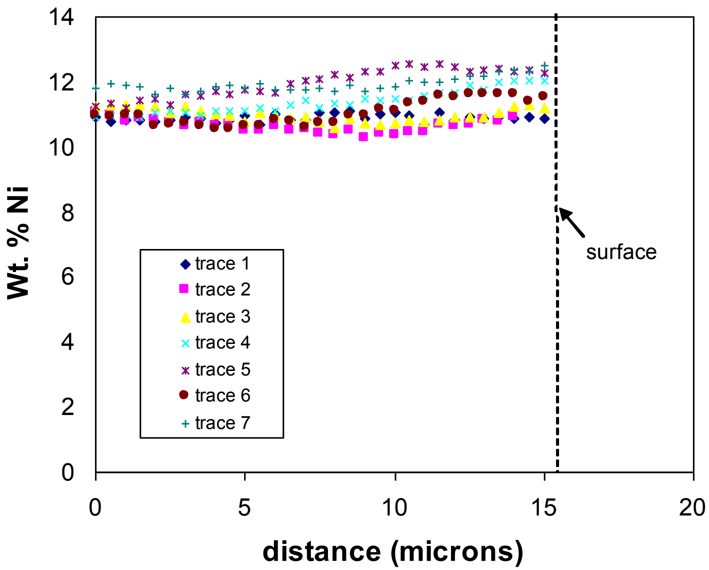
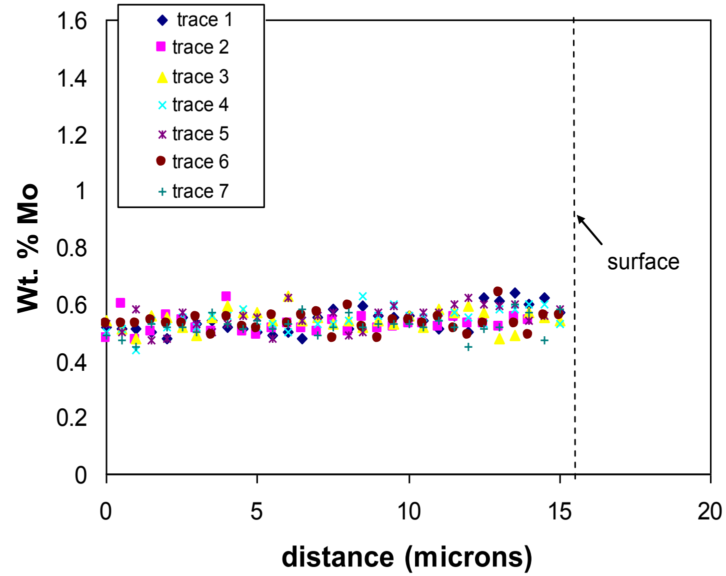
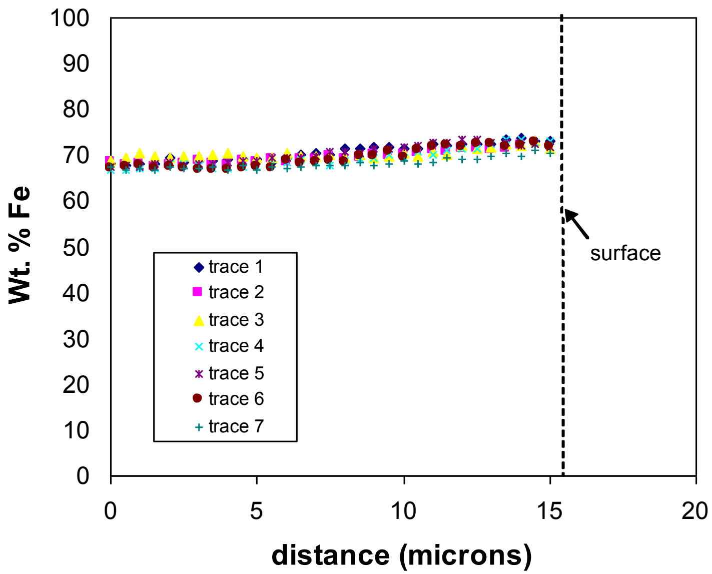
Fe, Ni, and Mo (not involved in oxidation) remain constant or slightly increase near the surface







- Low pO_2 oxidation atmosphere *avoids Fe oxidation*. This also results in an effective slight increase in Fe concentration near the surface

* Within the resolution of EPMA, no "step" in composition associated with the fcc/bcc interface

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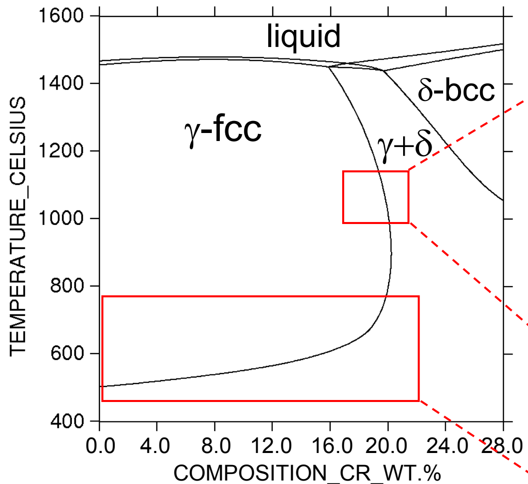
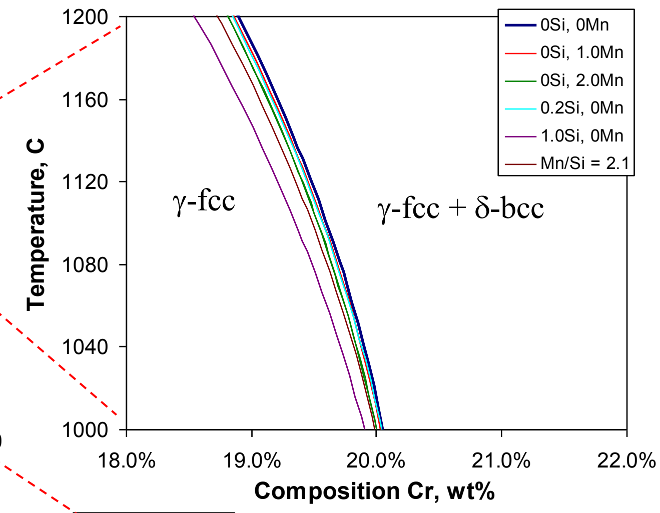
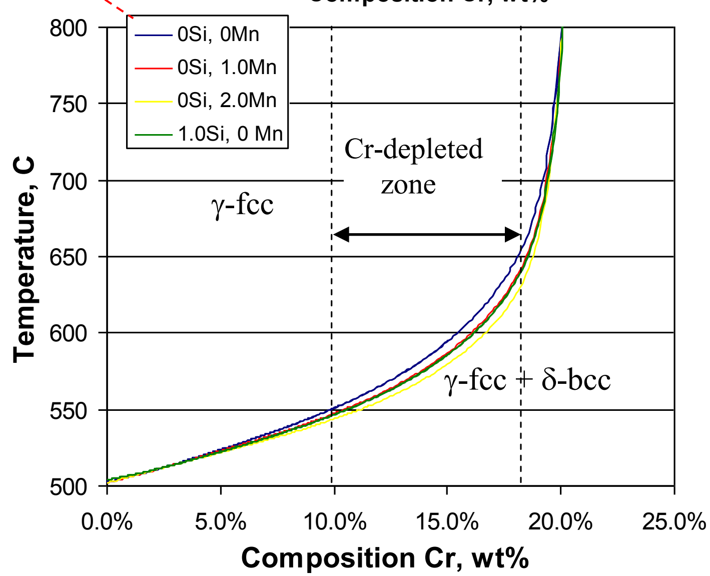
Two possible mechanisms remain for bcc layer: 1) Diffusional ferrite formation *during cooling*, or 2) Martensitic transformation





ThermoCalc:
With Cr depletion, fcc-to-bcc transformation occurs at *lower* temperatures. (Less favorable “kinetically” for diffusional mechanism)



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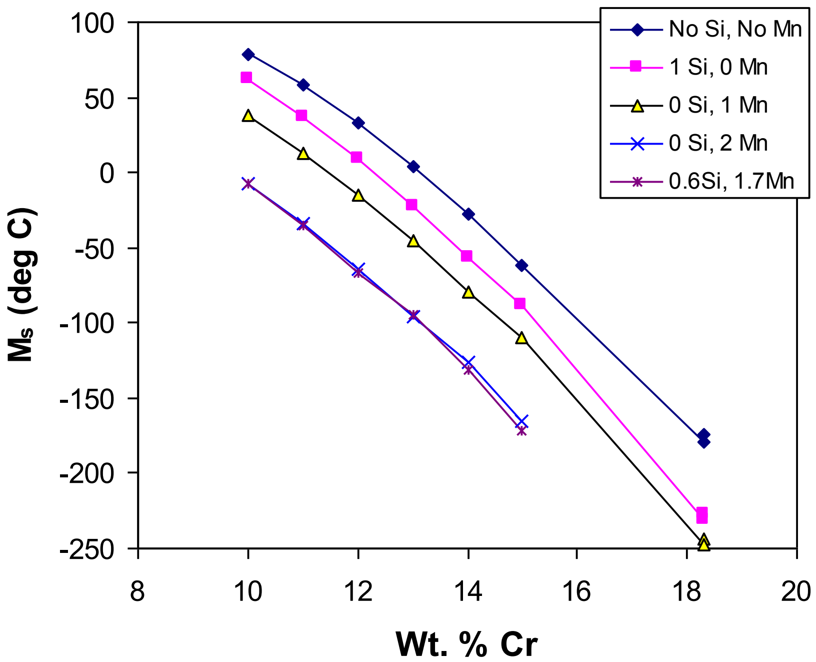
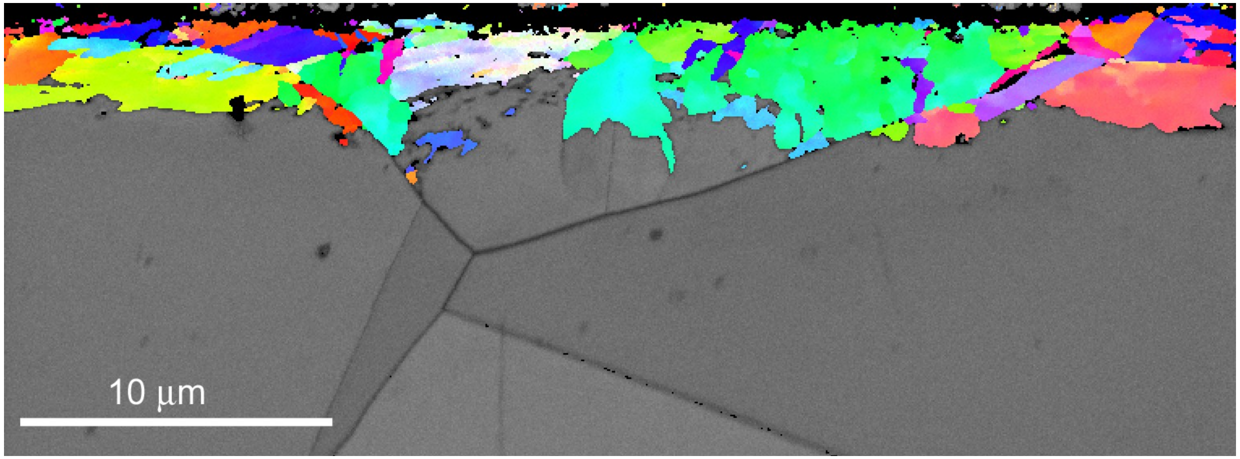
JMatPro: Calculated Martensite-start temperature *increases* with Cr Depletion



• JMatPro results support a possible martensitic phase transformation in the depletion layer



• Layer morphology and crystallographic orientation relationships also support martensitic reaction

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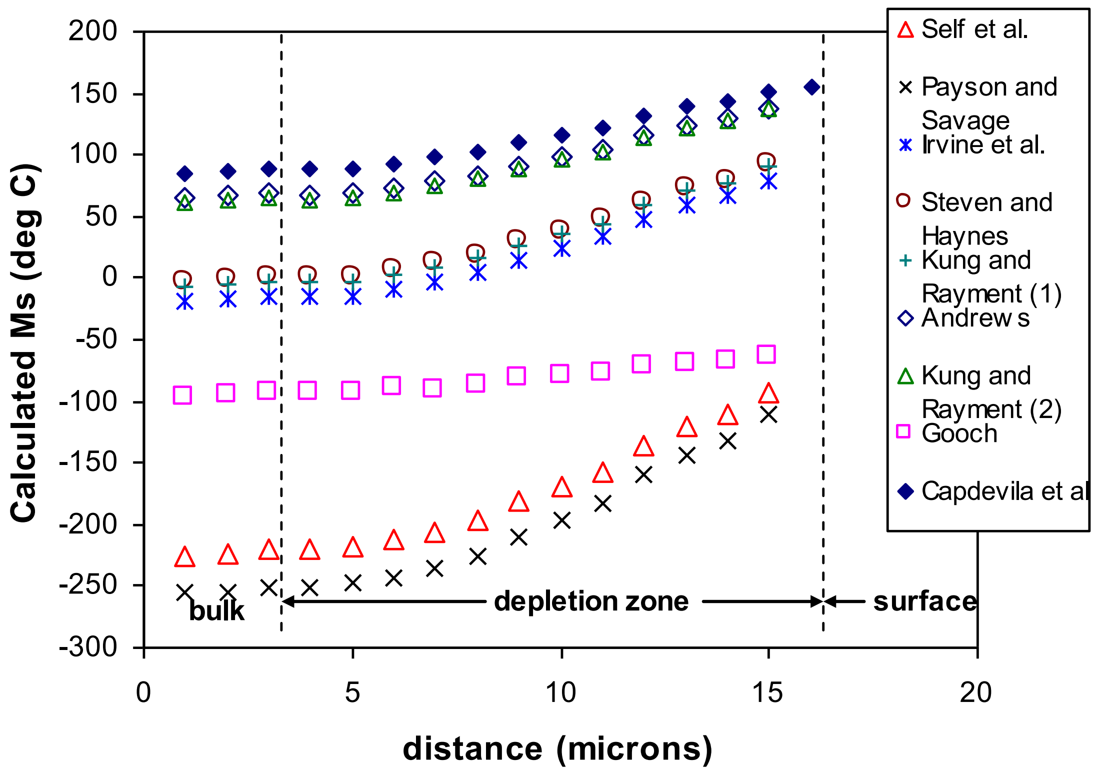
Correlate the near-surface depletion zone chemistry with M_s temperature

- Several empirical relations available in the literature -- Most were developed for low-alloy steels and may not be useful for M_S prediction in high-alloy stainless steels such as 304L.
- Input EPMA data from the alloy depletion zone into M_s equations



- Either: 1) The bulk alloy M_S temperature prediction is off, or 2) The effect of alloy depletion on M_S temp. does not predict M_S near room temp.

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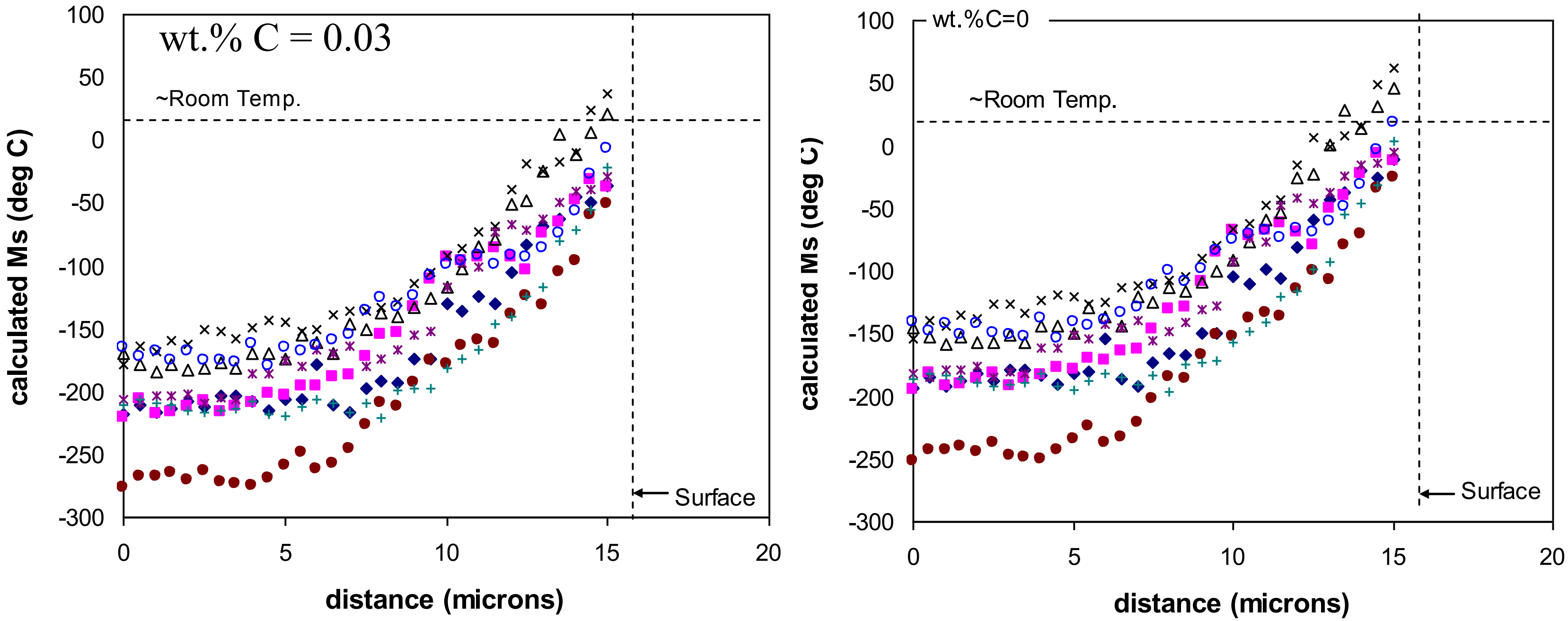
Eichelman and Hull equation - developed for high Cr steels (up to ~18 wt.%). Good correlations for both the bulk alloy M_S and the effects of alloy depletion.

$$(^\circ F)\quad M_S = 75(14.6 - Cr) + 110(8.9 - Ni) + 60(1.33 - Mn) + 50(0.47 - Si) + 3000(0.068 - [C + N])$$

Trans.ASM, V.45, (1953), p.77-104



- M_S temperatures at or near room temp. are possible in alloy depletion zone. (within experimental error of the empirical equation)
- Effect of carbon depletion also considered – calculations with 0% carbon result in slight further increase in M_S.

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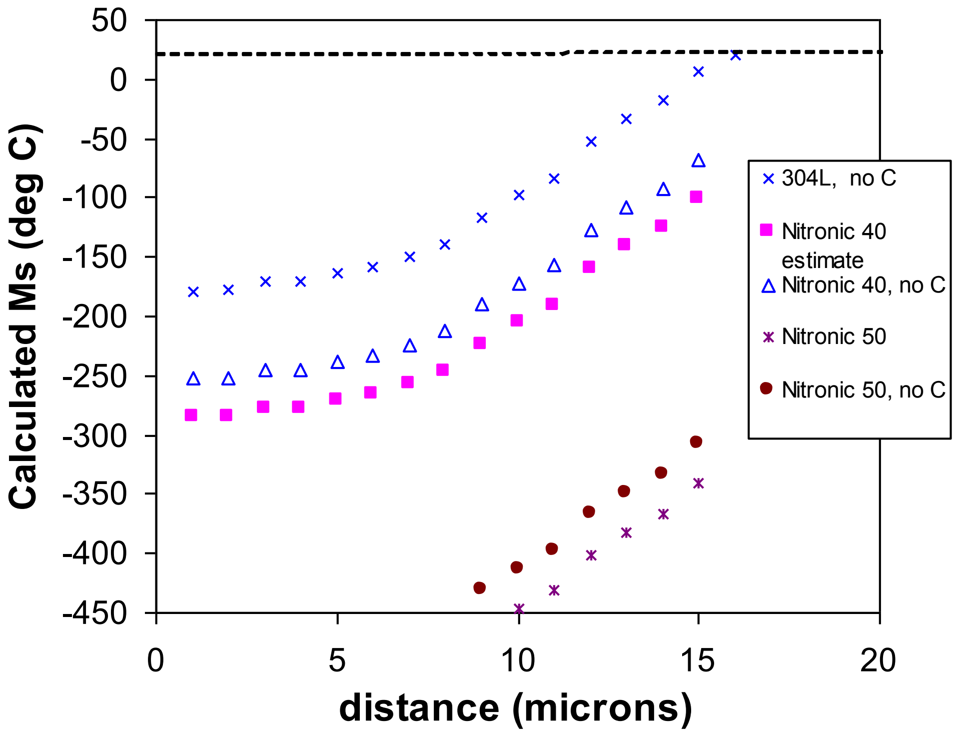
How can we reduce or avoid martensitic layer formation near the surface ?

- Selection of alternative alloys with even lower M_S temperatures. Keep M_S below room temperature, even with depletion of Cr and other elements.
- Candidate alloys: 21-6-9 (Nitronic 40) and 22-13-5 (Nitronic 50)



- "Simulated" alloy depletion profiles for Nitronic 40 and Nitronic 50.
- Calculated M_S temperatures are significantly lower than 304L.

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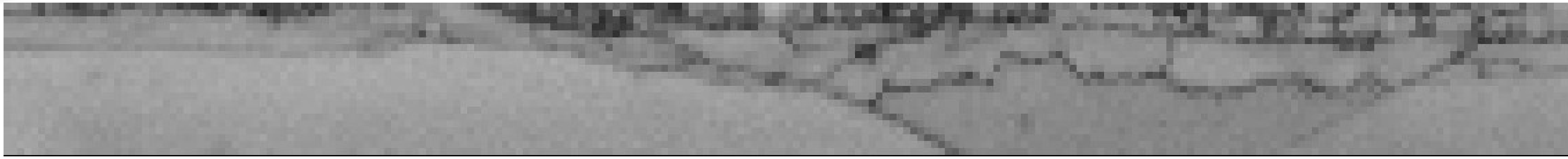
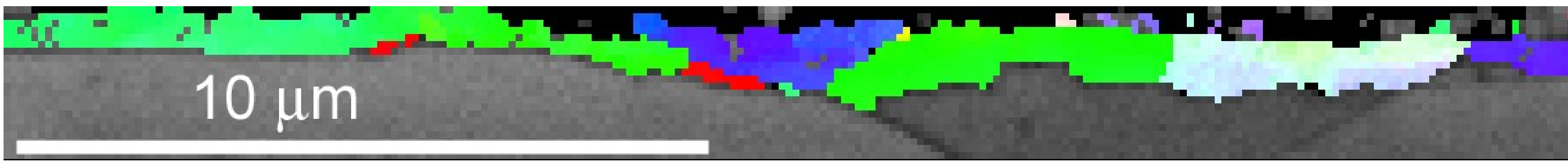
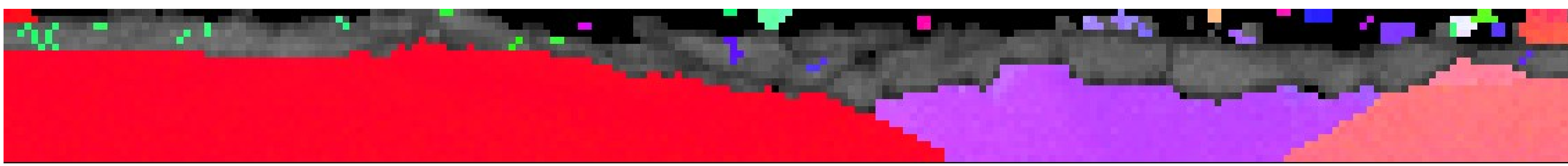
Nitronic 40 Results: Very small amount of bcc formation found after pre-oxidation and GTM sealing



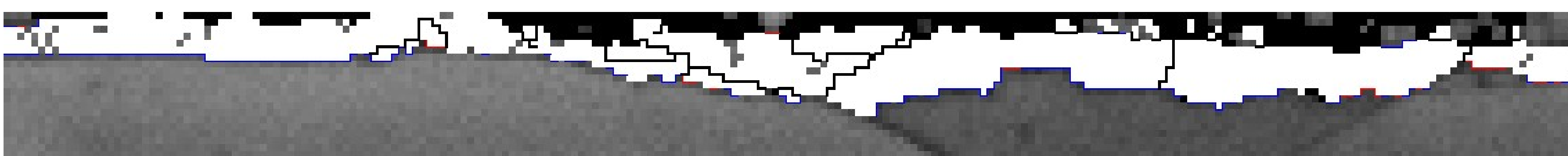
Band Contrast image



Ferrite

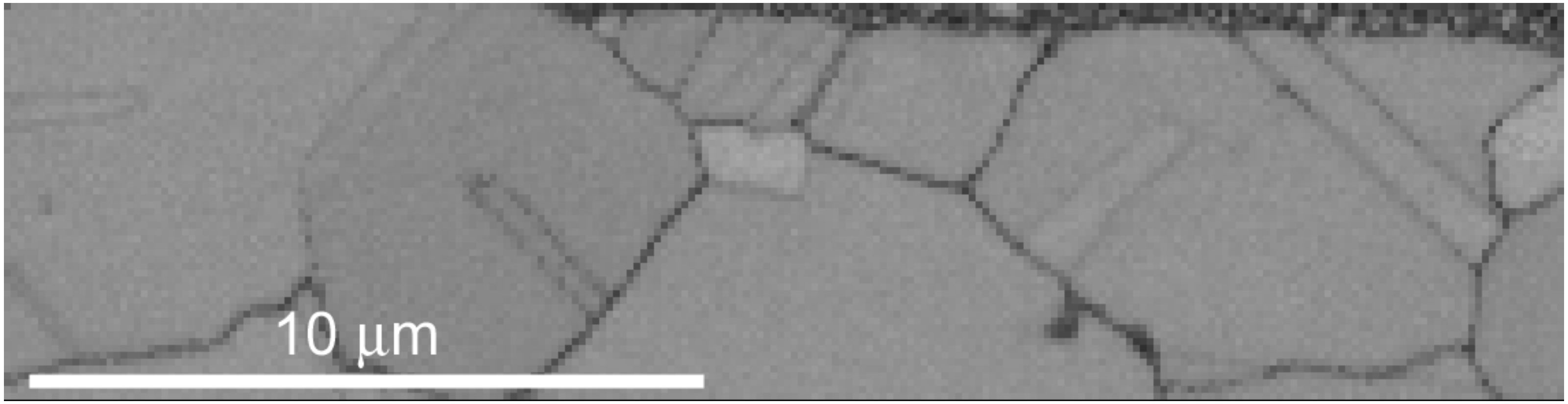


Austenite

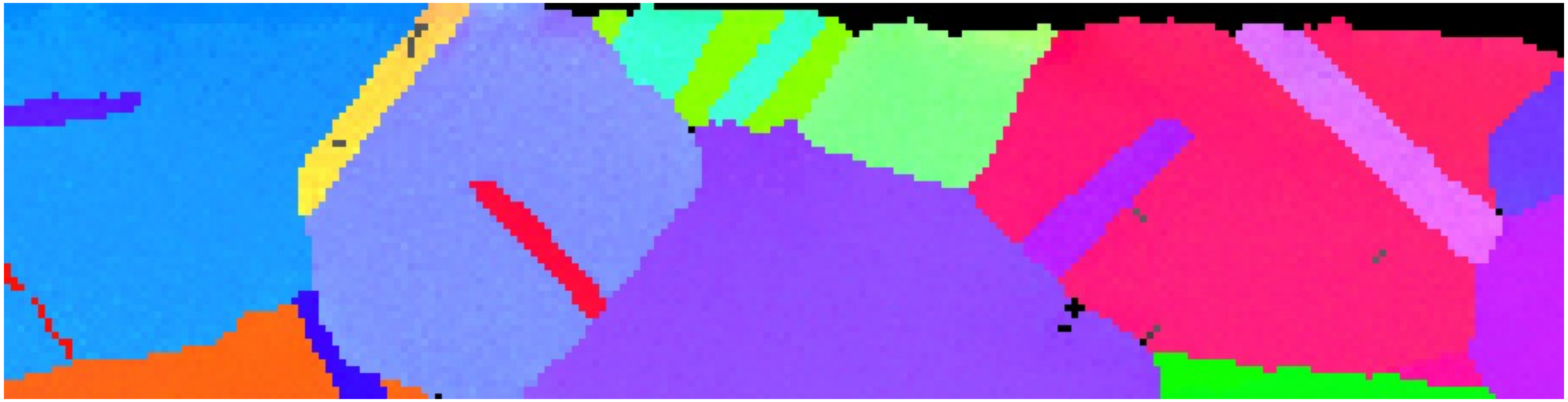


KS blue NW red

Nitronic 50 Results: *No bcc formation* at the surface after pre-oxidation and GTM sealing



Band Contrast image



Austenite

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Future Experiments

- **Further confirmation of martensite reaction: after GtM seal processing, quench alloy in liquid N_2 to "grow" the martensite layer deeper into the alloy. Layer should progress deeper due to progressively lower M_s temperatures.**
- **Dynamic XRD experiments *on cooling* to determine the transformation temperature. Expect transformation temps near room temp. (high transformation temps. would not support martensite)**

Summary

- A layer of body-centered crystal structure material is found at the surface of 304L after pre-oxidation and GtM sealing.
- The layer morphology and the continuous composition profile (no step) suggested it was formed by martensitic mechanism. Thermochemical modeling supported a martensitic reaction and discounted a diffusional transformation.
- Good correlations, in terms of bulk M_S and the effect of alloy depletion on M_S, were found using the Eichelman and Hull equation. M_S temperatures at or near room temperature are possible in the alloy-depletion zone at the surface of 304L.
- Alternative austenitic alloys, in particular Nitronic 50, are promising candidates to eliminate bcc layer formation at the glass/metal interface.

Acknowledgements

- **Mark Reece - sample preparation for pre-oxidation and GtM sealing**
- **Chuck Walker – Pre-oxidation and GtM sealing**
- **Alice Kilgo – metallography**
- **Paul Hlava – EPMA**

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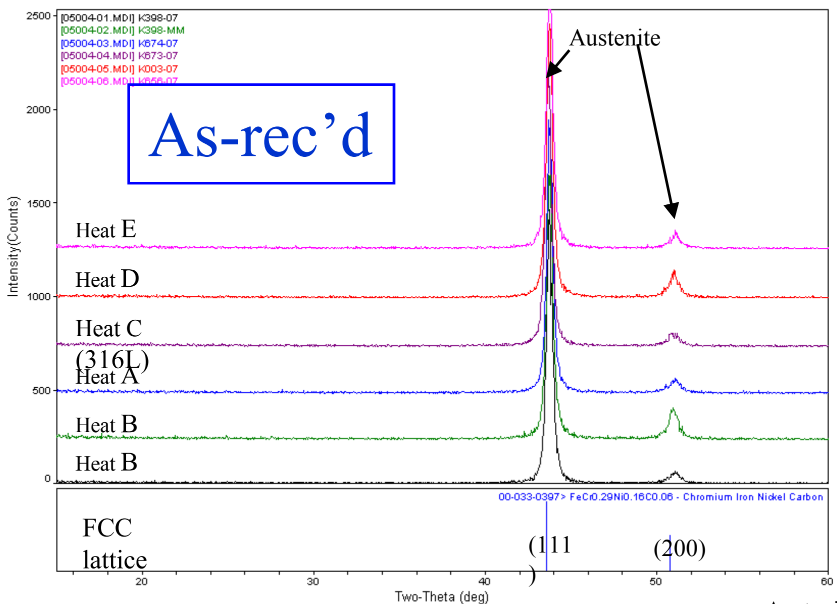
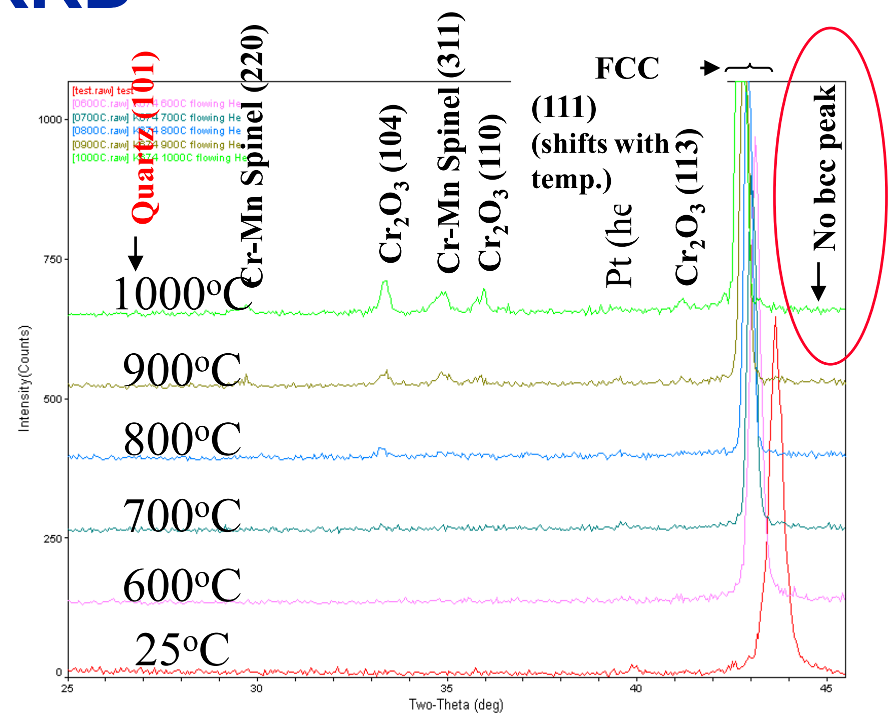
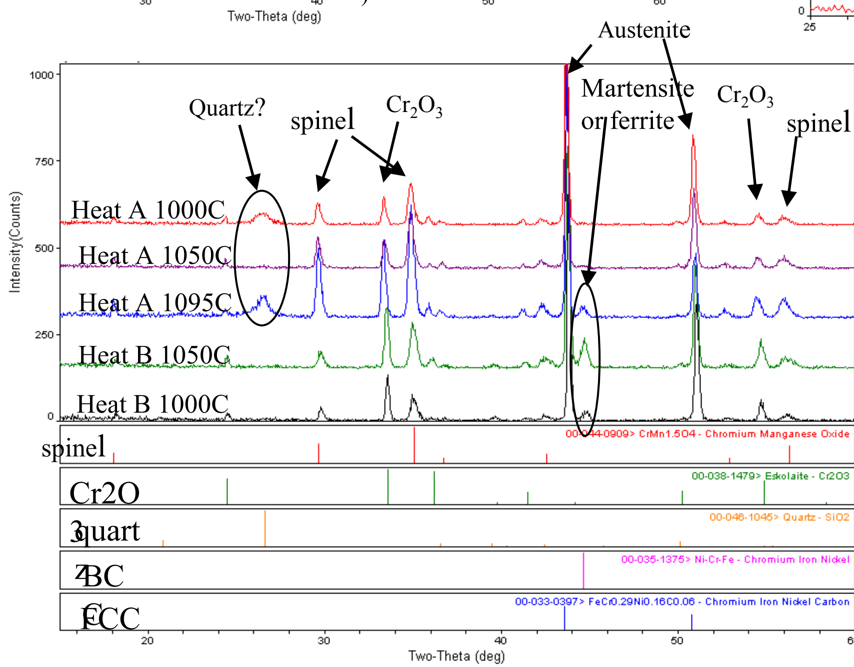
Extra Slides -- XRD



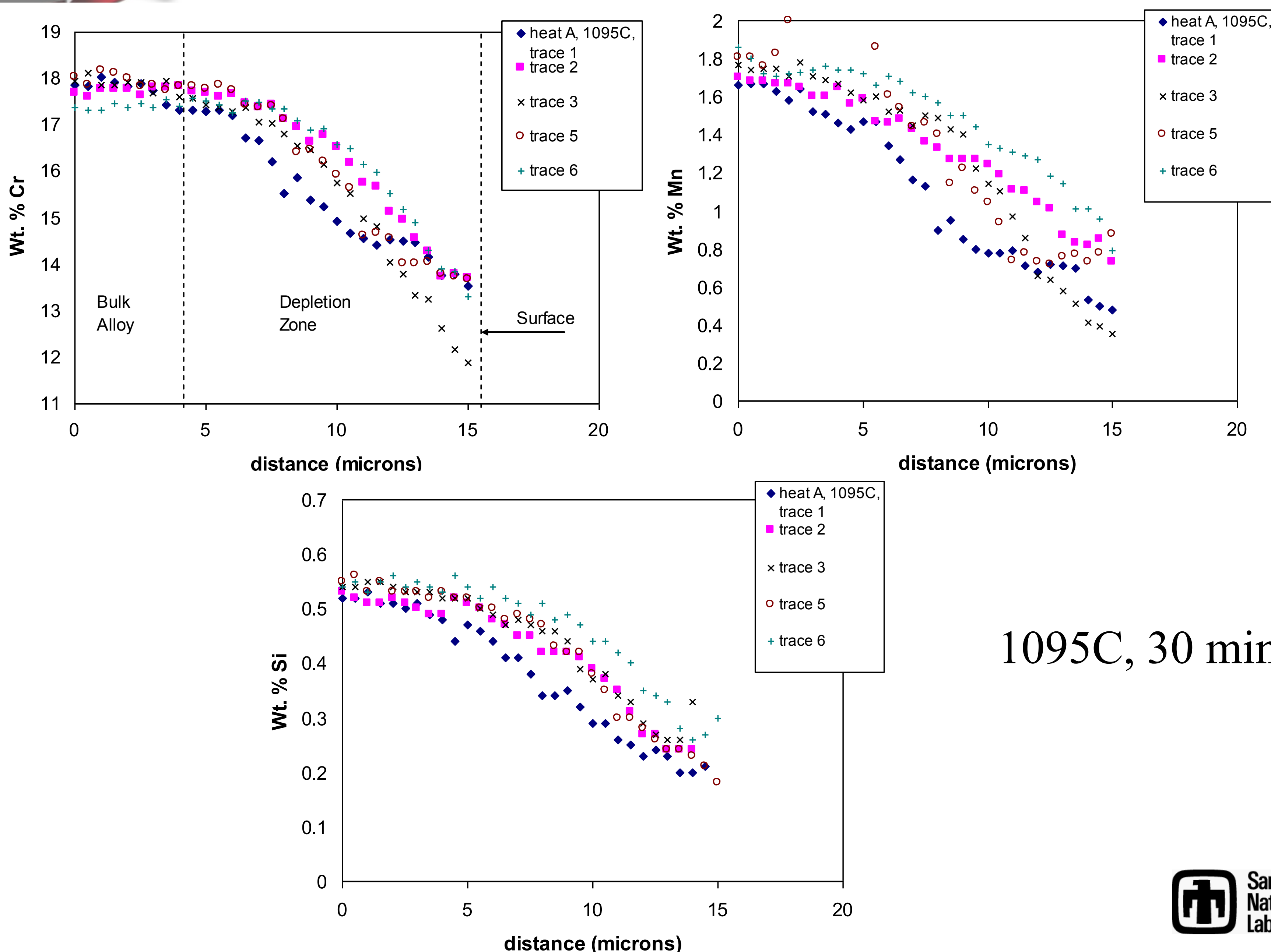


2[nd] Lot,
On-heating



2 heats of 304L,
3 oxidation temps.
- Some bcc peaks after cooling

Extra slides – EPMA on 2nd heat of 304L



1095C, 30 min

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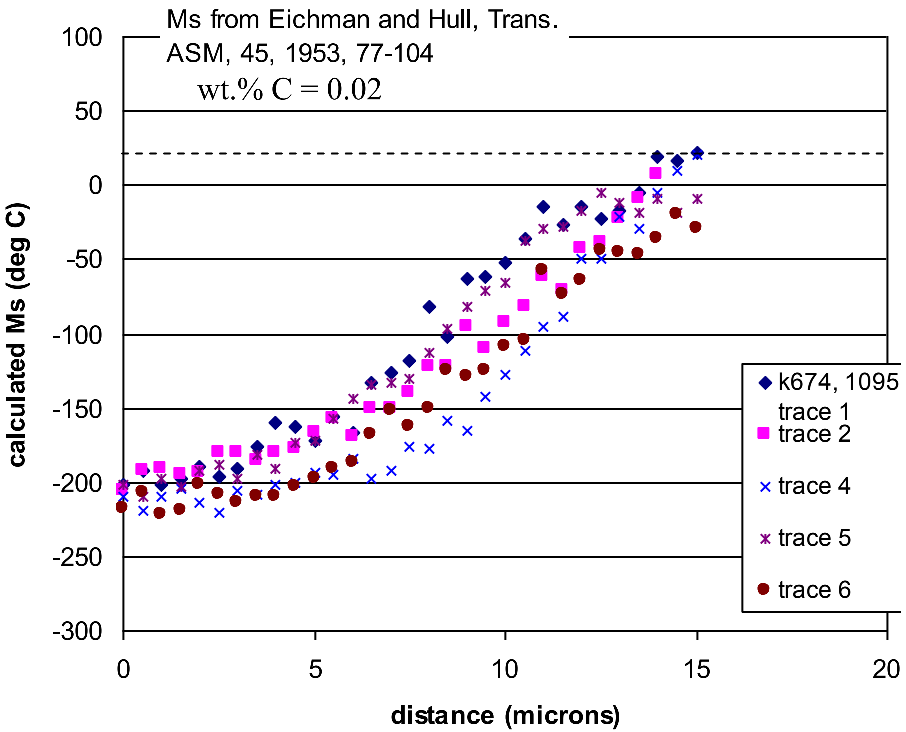
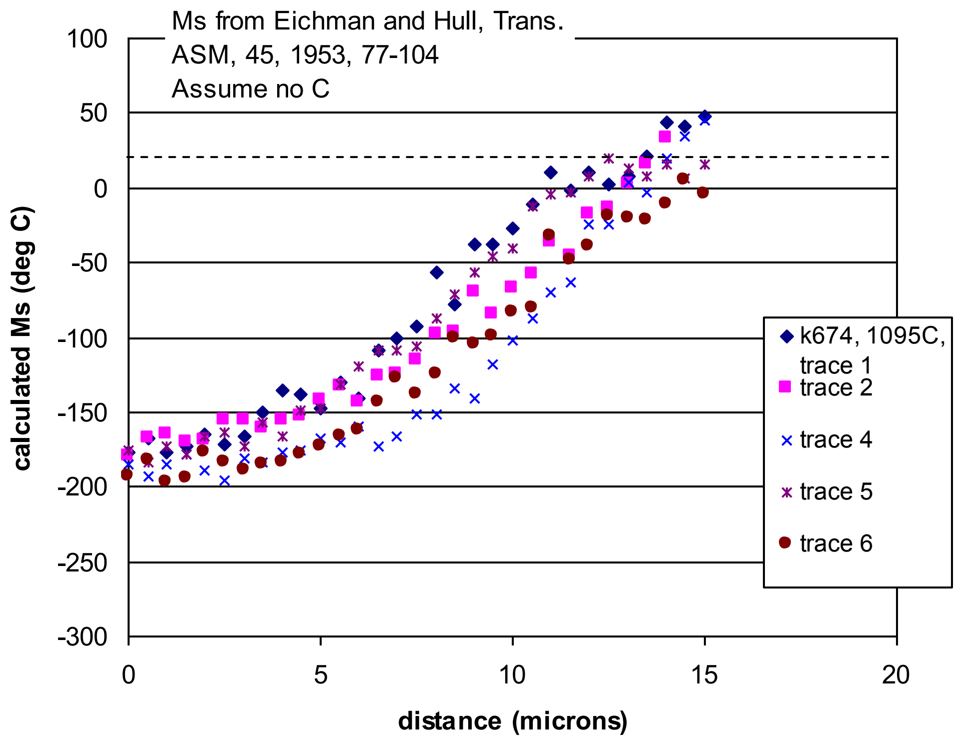
Ms Correlation – 2nd heat of 304L





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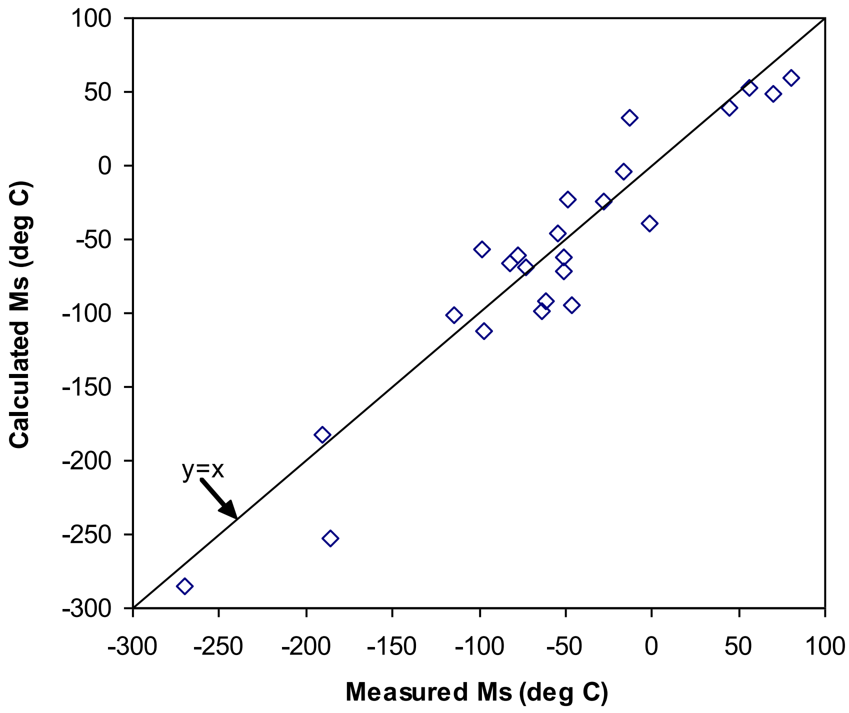

Original data from Eichelman and Hull paper

- Avg. difference between calculated and measured Ms = 39˚F (or 22˚C)
- So, any correlation of Ms temperature is only valid to within about +/- 40F