LA-UR-12-23903
Approved for public release; distribution is unlimited.

Title:	Atom Probe Tomography Examination of Carbon Redistribution in Quenched and Tempered 4340 Steel
Author(s):	Clarke, Amy J. Miller, Michael K. Alexander, David J. Field, Robert D. Clarke, Kester D.
Intended for:	ShaRE Peer Review Meeting at Oak Ridge National Laboratory, 2012-08-08/2012-08-09 (Oak Ridge, Tennessee, United States)

Atom Probe Tomography Examination of Carbon Redistribution in Quenched and Tempered 4340 Steel

A.J. Clarke[1], M.K. Miller[2], D.J. Alexander[1], R.D. Field[1], K.D. Clarke[1]

[1]Materials Science and Technology Division; Materials Technology - Metallurgy (MST-6), Los Alamos National Laboratory, Los Alamos, NM 87545, USA

[2]Materials Science and Technology Division; Microscopy Group, Oak Ridge National Laboratory, Oak Ridge TN, 37831

LA-UR 12-XXXX

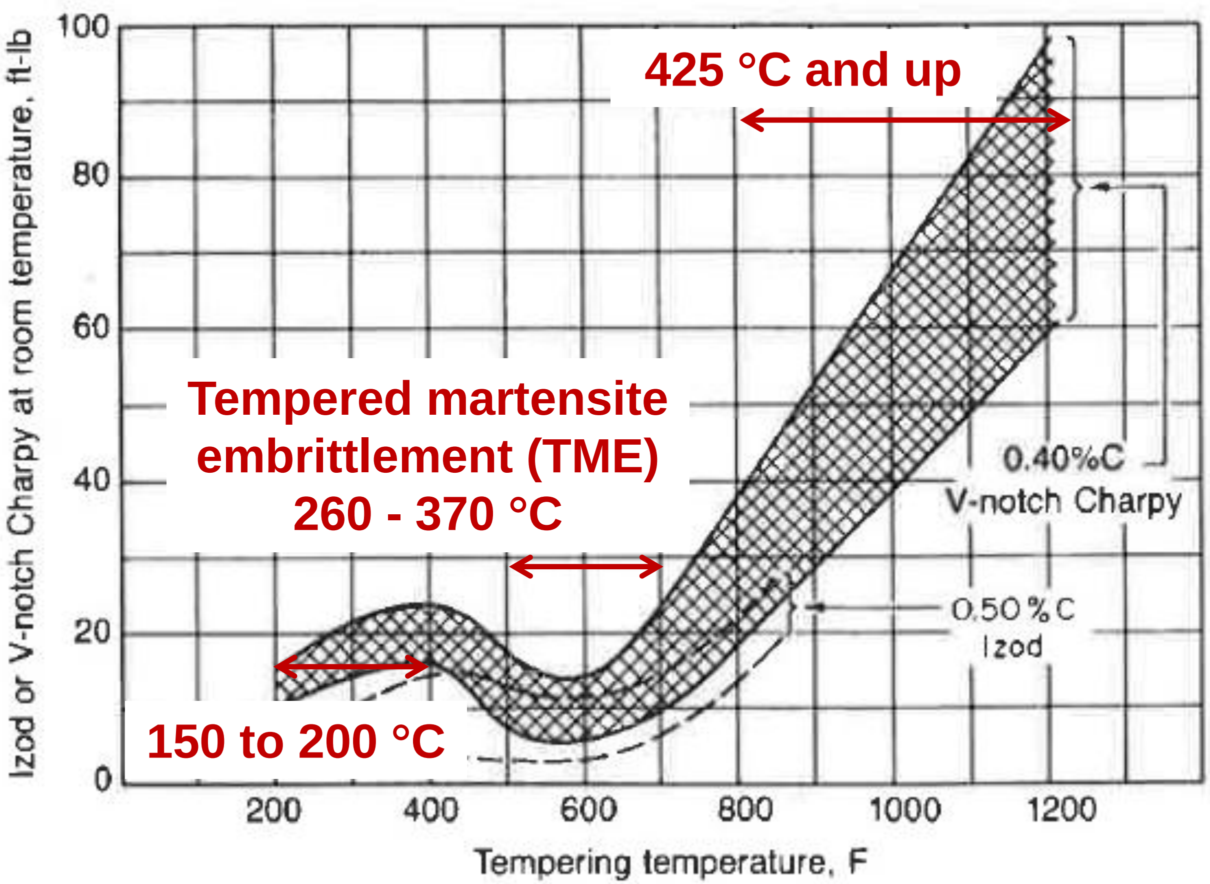
Shared Research Equipment User Facility
an Office of Science User Facility

Motivation

- Quenching and tempering produces a wide range of mechanical properties in medium carbon, low alloyed steels
  - Study fragmentation behavior as a function of heat-treatment
- Subtle microstructural changes accompany the mechanical property changes that result from quenching and tempering
  - Characterize the location and distribution of carbon and alloying elements in the microstructure using atom probe tomography (APT)
  - Perform complementary transmission electron microscopy (TEM)

The Influence of Tempering on Impact Toughness

High strength; fatigue resistance; compressive loading; high hardness; wear resistance



High toughness; potential for temper embrittlement (isothermal holding, slow cooling)

M.A. Grossmann and E.C. Bain, Principles of Heat Treatment, 5th ed., American Society for Metals, 1964
G. Krauss, Steels: Processing, Structure, and Performance, ASM International, 2005

4340 Steel Compositions

¼ inch plate

	C	Cr	Mn	Mo	Ni	Cu	P	Si	S
(wt.%)	0.42	0.83	0.78	0.24	1.78	0.03	0.010	0.26	0.003
(at.%)	1.92	0.88	0.78	0.14	1.67	0.03	0.018	0.51	0.005

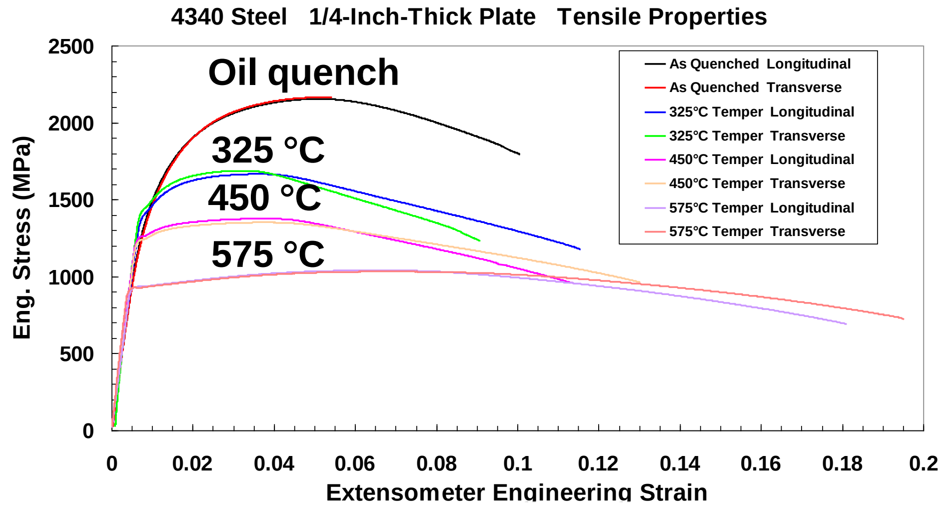
½ inch plate

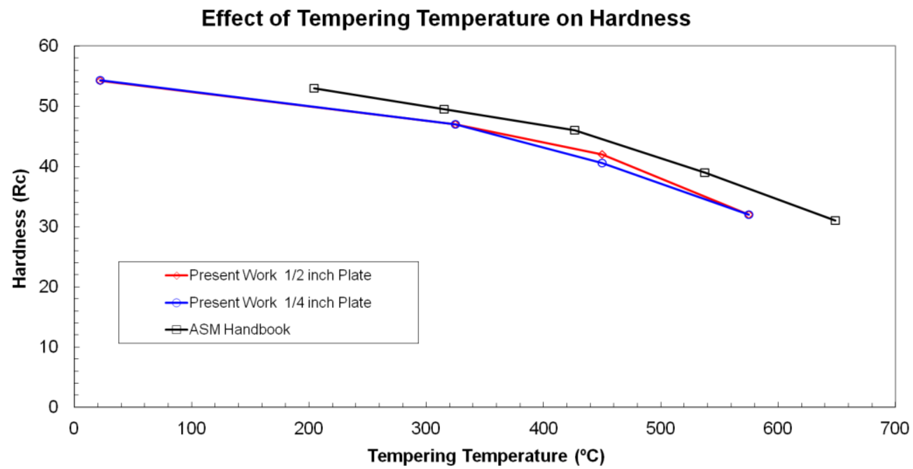
	C	Cr	Mn	Mo	Ni	Cu	P	Si	S
(wt.%)	0.40	0.84	0.79	0.24	1.79	0.03	0.010	0.29	0.003
(at.%)	1.83	0.89	0.79	0.14	1.68	0.03	0.018	0.57	0.005

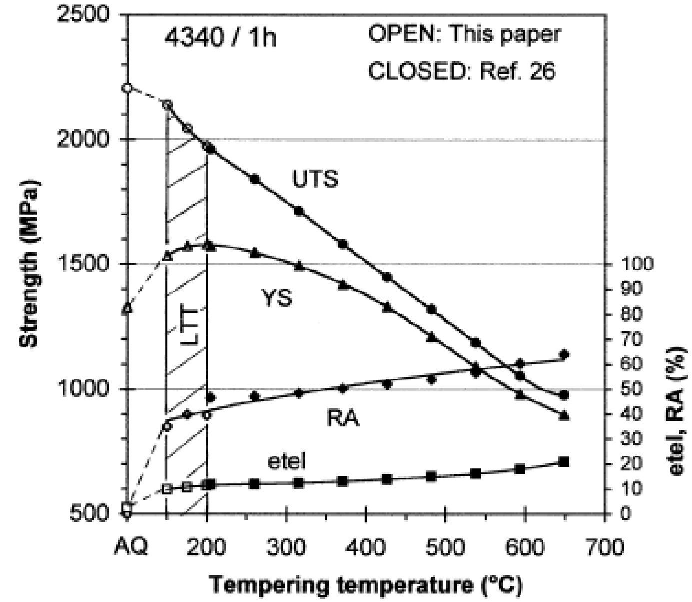
Heat-Treatments

- ¼ and ½ inch plate: austenitized in vacuum for 30 min at 845 °C, oil quenched
  - Tempered in air for 2 hr at 325 °C (TME?)
  - Tempered in air for 2 hr at 450 °C
  - Tempered in vacuum for 2 hr at 575 °C
- ¼ inch plate: encapsulated in quartz under UHP Ar, re-austenitized for 30 min at 845 °C, ice water quenched

Effect of Quenching and Tempering on Stress-Strain Response and Hardness





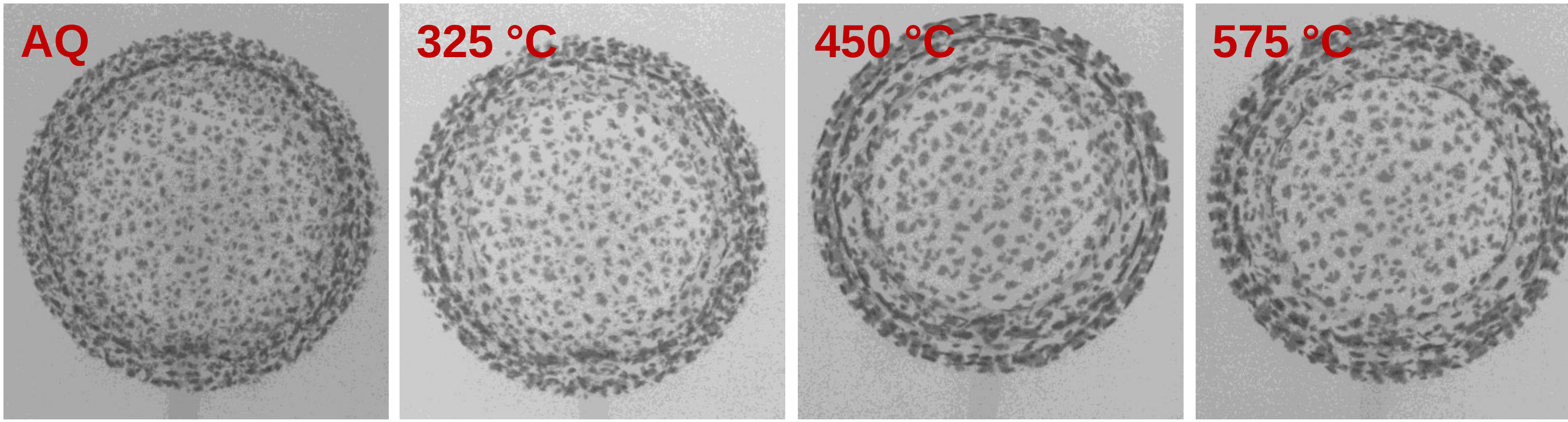


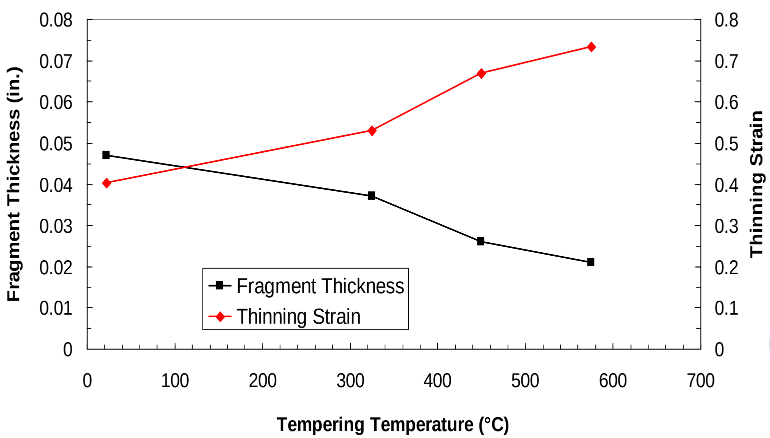
M. Saeglitz and G. Krauss, Metallurgical and Materials Transactions A, 1997, 28A:377-387

Filled-Hemispheres Used to Examine Fragmentation Behavior

- "Point" initiation and spherical expansion
- Small, simple for repeat tests
  - Circular blanks cut from aircraft-quality 4340 mill-annealed ¼ inch thick plate
  - Blanks were formed into 40 mm diameter hemi-shaped preforms
  - Preforms were austenitized and oil quenched
  - Tempering at 325, 450, or 575 °C
  - Machined after heat-treatment (as-quenched or quenched and tempered)

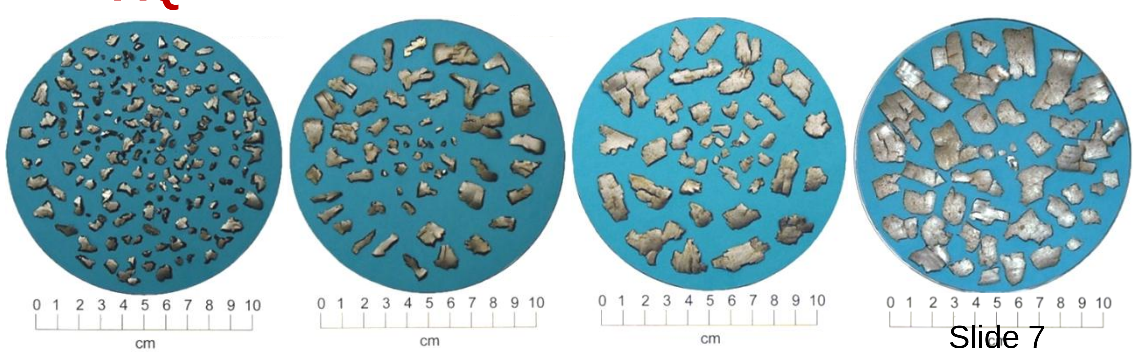
Effect of Increased Tempering on Fragmentation - Area, Thickness, Thinning Strain





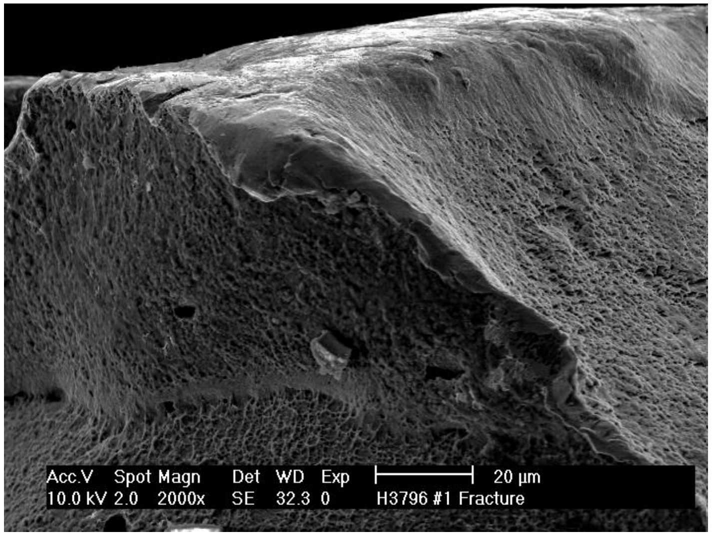
Radiographs of filled-hemi shots (above) and example recovered fragments (below)

AQ → 575 °C

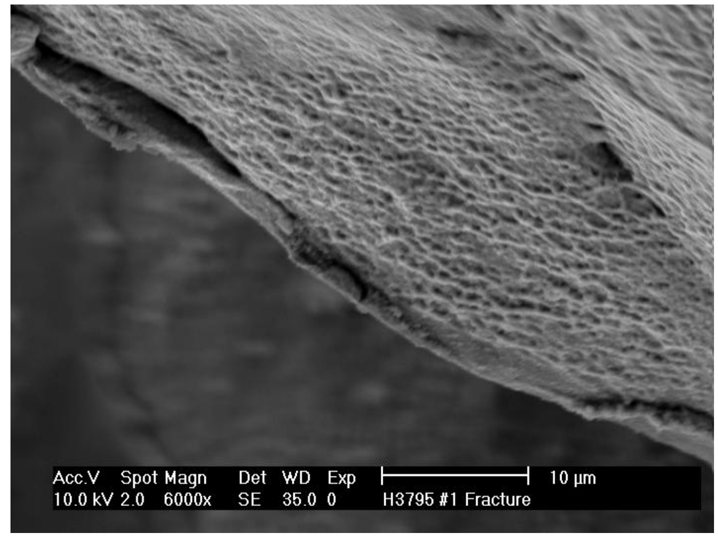


Fracture by Localized Shear and Ductile Rupture (No Evidence of TME)

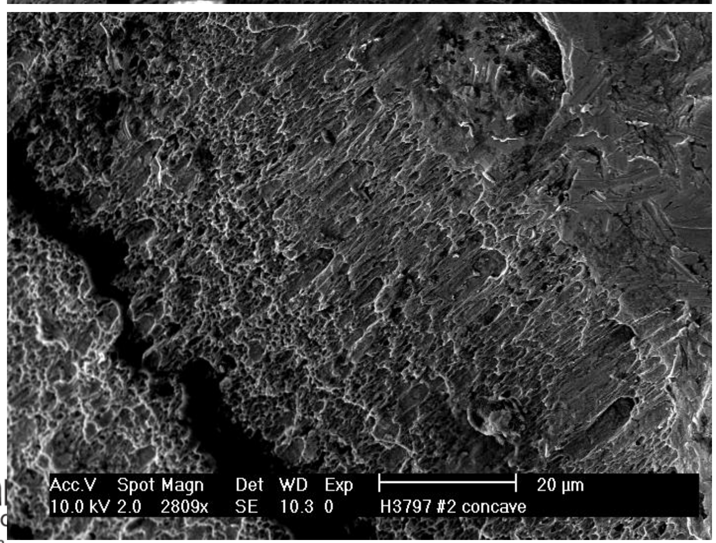
AQ



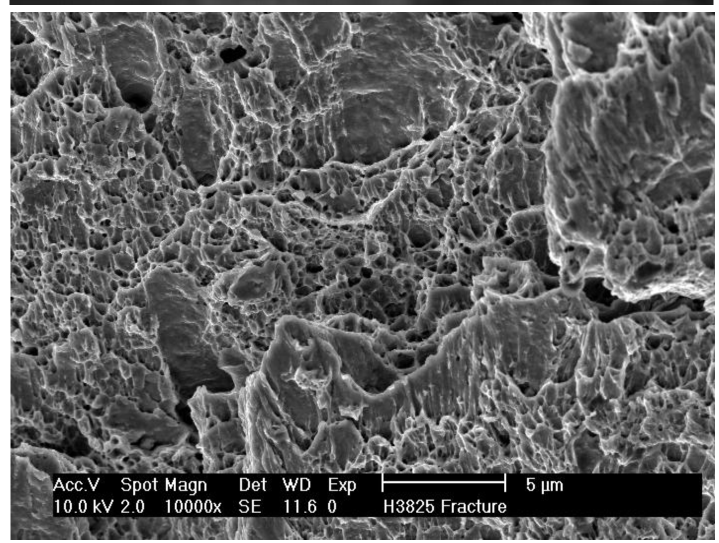
325°C



450°C

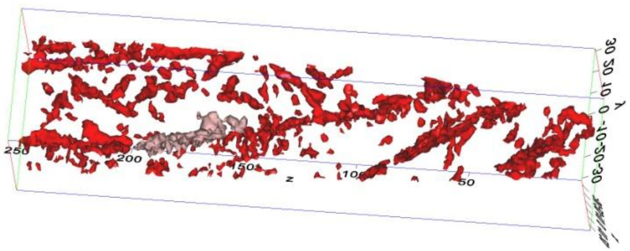


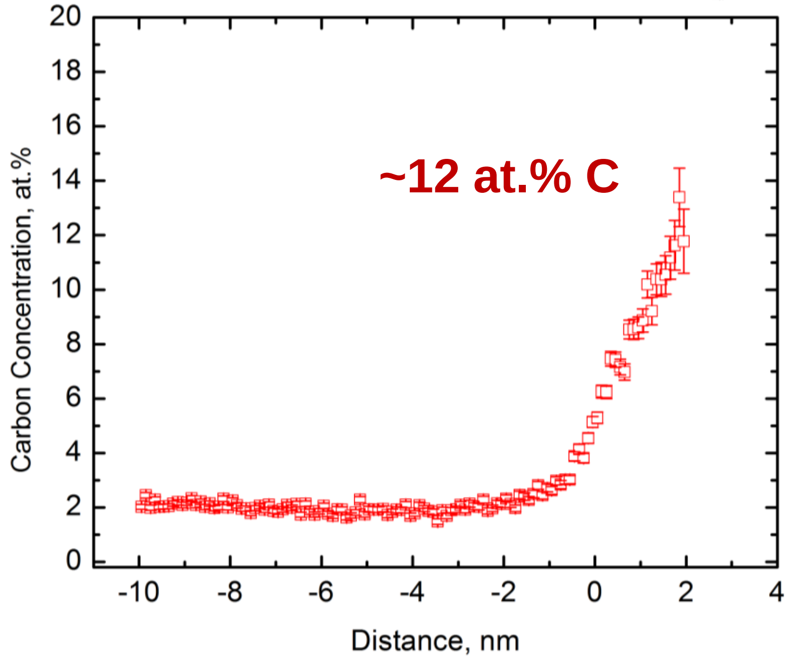
575°C



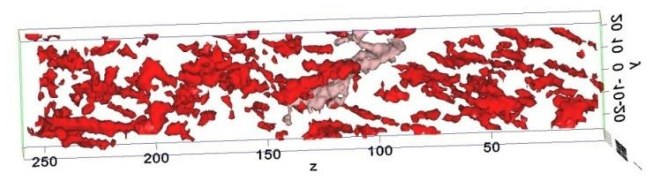
APT of Ultrafine Scale Carbon Clustering After Quenching

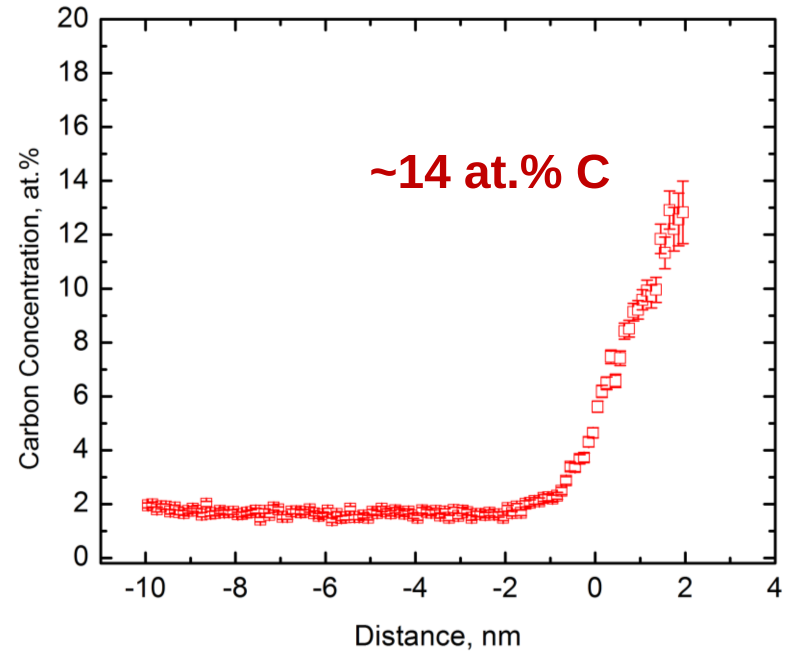
Ice water quench





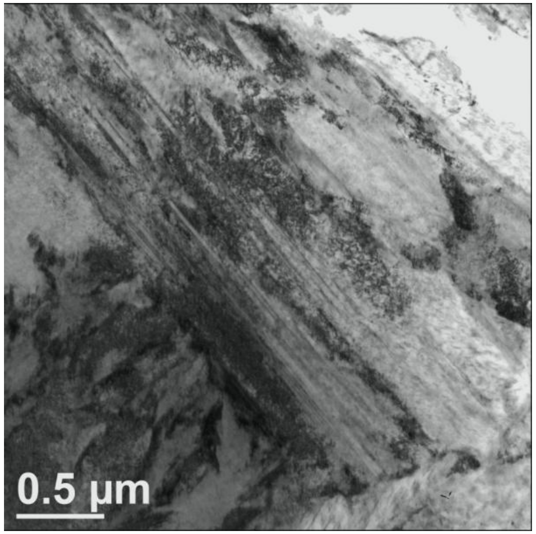
Oil quench

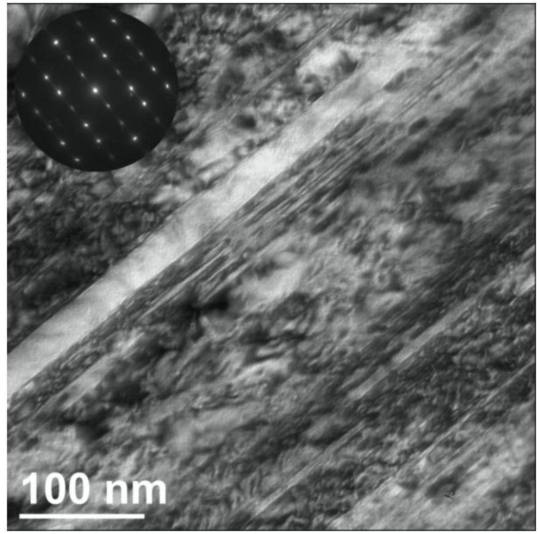




5 at.% isoconcentration surfaces
Proximity histograms of the highlighted regions

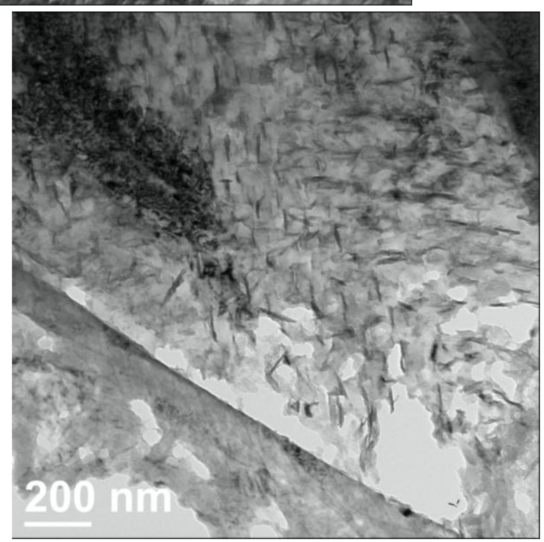
TEM of Twinned Martensite and Plate-like Precipitates After Oil Quenching

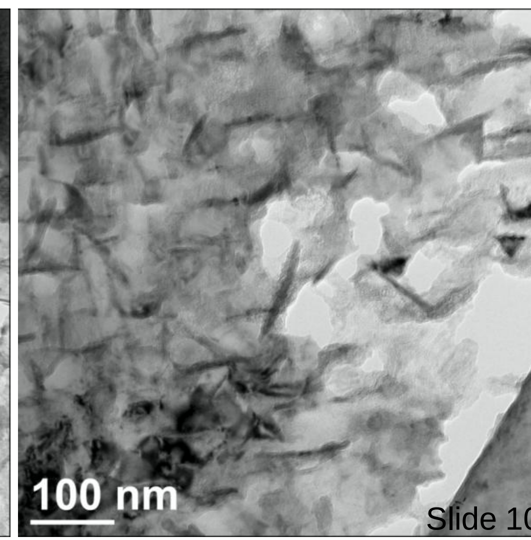




The inset SAD pattern is indexed as a <110> orientation of a {112} twinned microstructure

Precipitate length: ~100 nm
Precipitate thickness: 10-20 nm



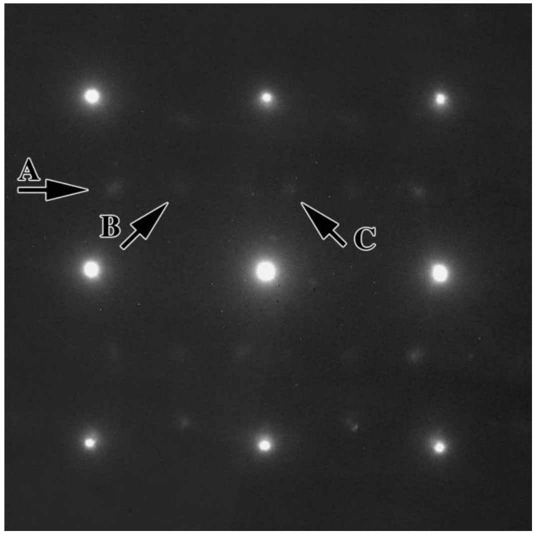


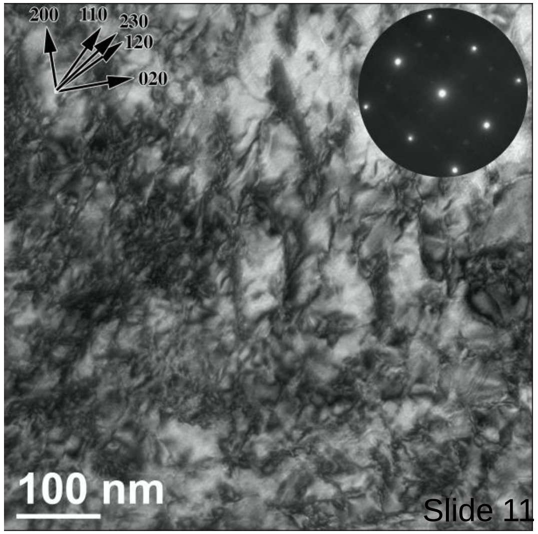
TEM is Consistent with Transition Carbide - Tilted to the [001]α' Zone Axis

- Plate-like precipitates, generally consistent with ε' (or η) transition carbide (Taylor et al.)
  - Position A: ~0.20 nm d-spacing, consistent with {021} planes of ε' carbide, with the two following variants:

    (001)ε' II (110)α'
    [100] ε' II [001] α'

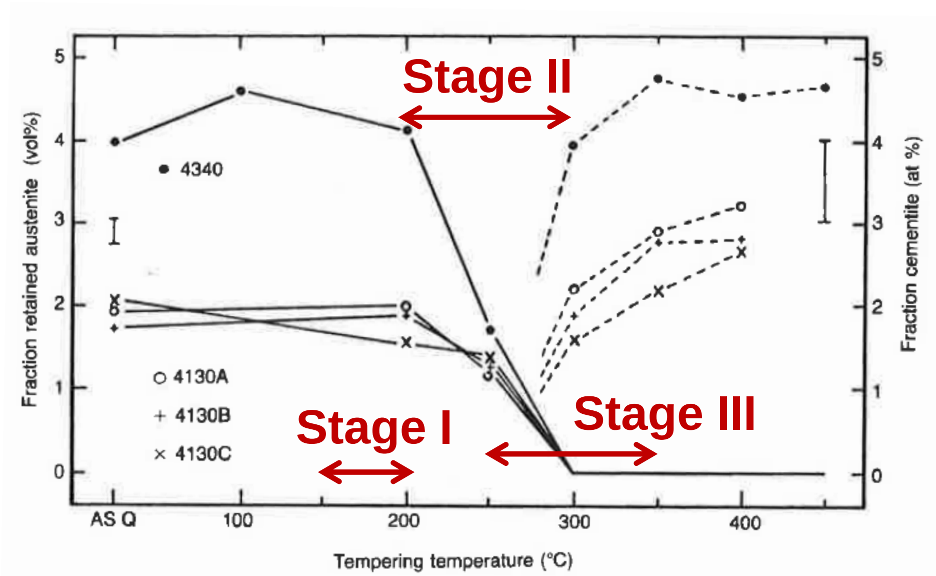
  - Position B: superlattice reflections for the ordered ε' carbide
  - Position C: double diffraction (between A and α' {110} reflections)
  - Habit planes near α' (020) (Taylor et al. reported that {023} 'spinodal' habit planes migrate toward {021} for larger precipitates)





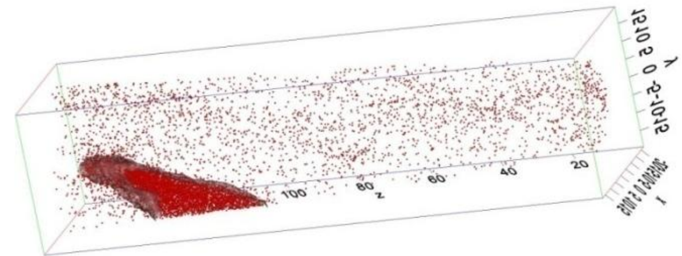
Taylor et. al, Metall. Trans. A, 1989, 20A:2749-2765

Para-equilibrium during Late Stage Tempering; 325 °C, 2 h

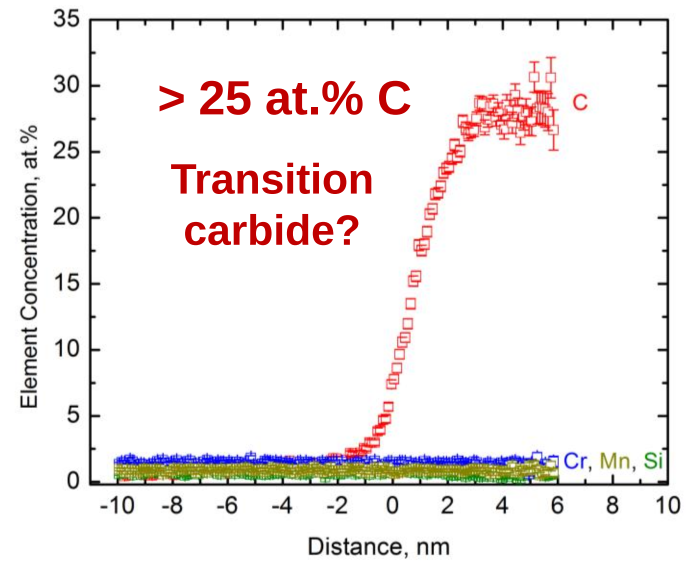


- Stage I: Transition carbide formation (ε or η)
- Stage II: Transformation of retained austenite to ferrite and cementite
- Stage III: Replacement of transition carbides and low-carbon martensite by cementite and ferrite

D.L. Williamson et al., Metall. Trans. A, 1979, 10A:379-382

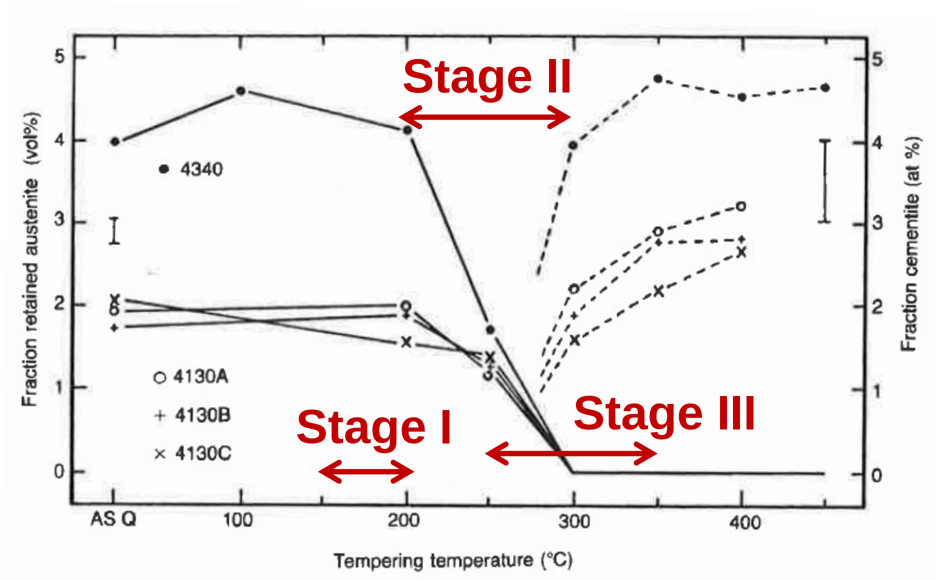


10 at.% isoconcentration surface

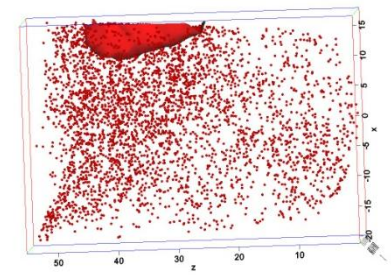


Proximity histogram of the highlighted region

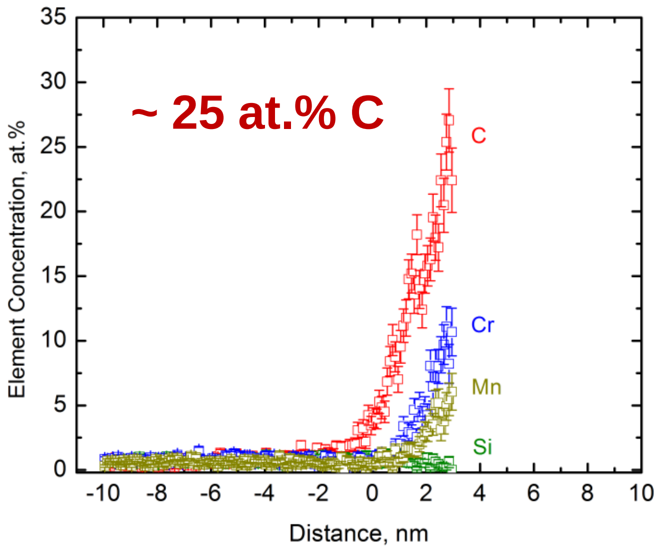
Complex Element Partitioning to Cementite during Late Stage Tempering; 425 °C, 2 h



Partitioning of Cr, Mn to cementite and Si to ferrite, in agreement with Zhu et al. and Babu et al.



5 at.% isoconcentration surface



Proximity histogram of the highlighted region

D.L. Williamson et al., Metall. Trans. A, 1979, 10A:379-382

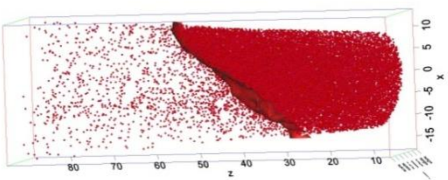
H.-C. Lee and G. Krauss, 1992 Speich Symposium Proceedings, ISS, Warrendale, PA, 1992, 39-43

S.S. Babu et al., Metallurgical and Materials Transactions A, 1994, 25A:499-508

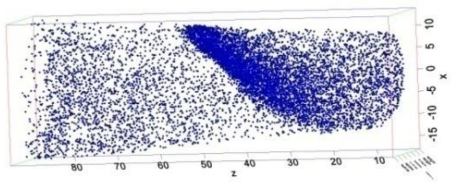
C. Zhu et al. , Ultramicroscopy, 2007, 107:808-812

Complex Element Partitioning to Cementite during Late Stage Tempering; 575 °C, 2 h

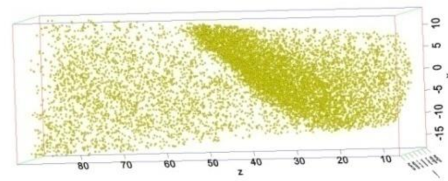
C



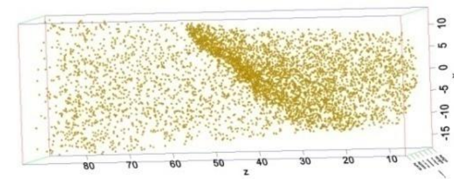
Cr



Mn

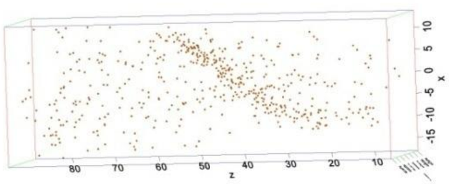


Mo

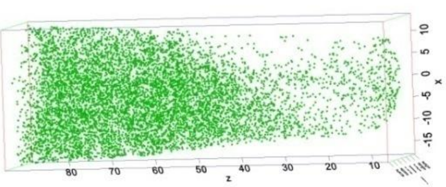


10 at.% isoconcentration surface

P



Si

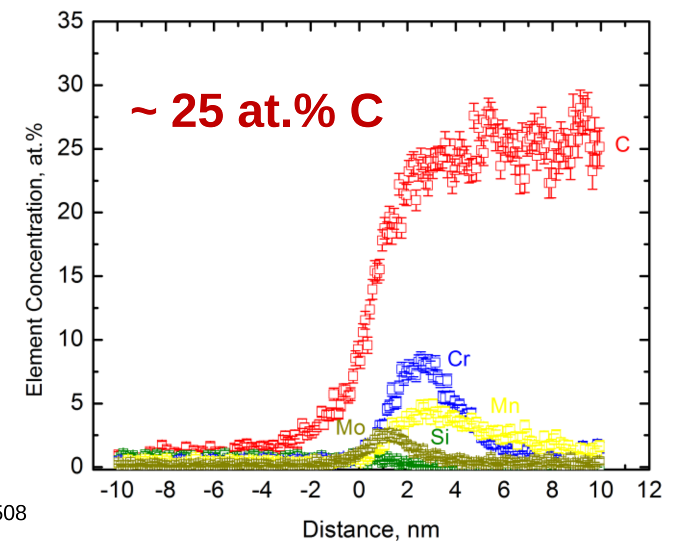


Partitioning of Cr, Mn to cementite and Si to ferrite, in agreement with Zhu et al. and Babu et al.

And, partitioning of Mo to cementite and P at the interface…

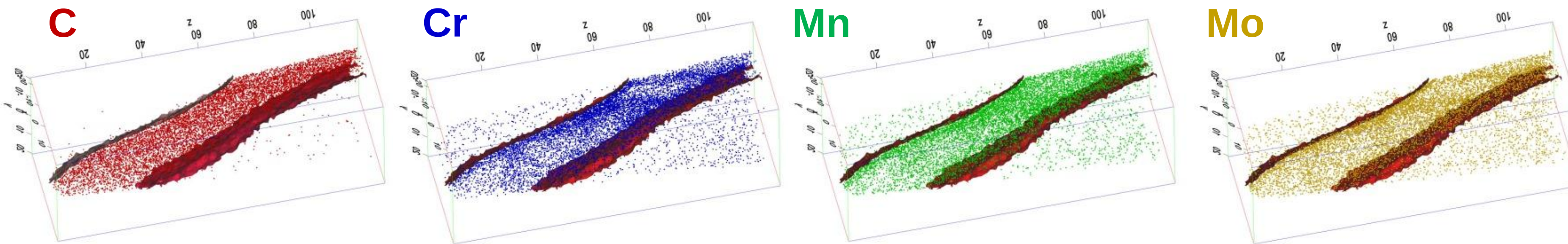
C. Zhu et al. , Ultramicroscopy, 2007, 107:808-812

S.S. Babu et al., Metallurgical and Materials Transactions A, 1994, 25A:499-508

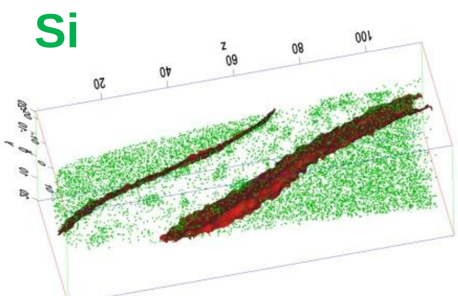


Proximity histogram of the ferrite/cementite interface

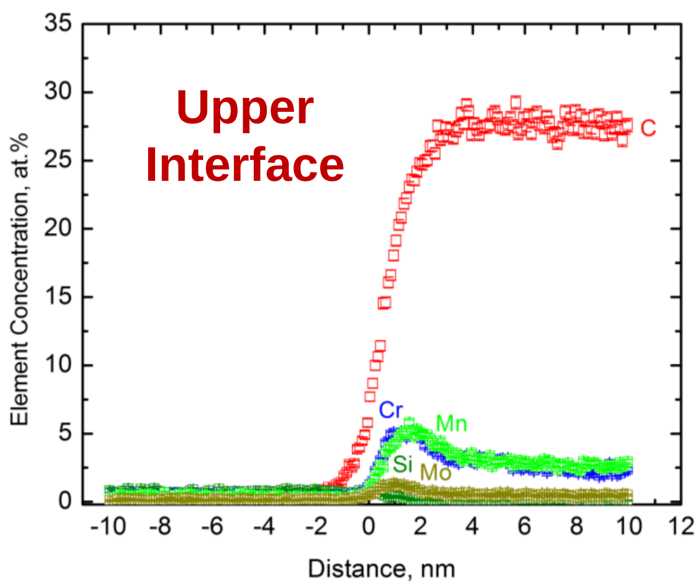
Complex Element Partitioning to Cementite during Late Stage Tempering; 575 °C, 2 h

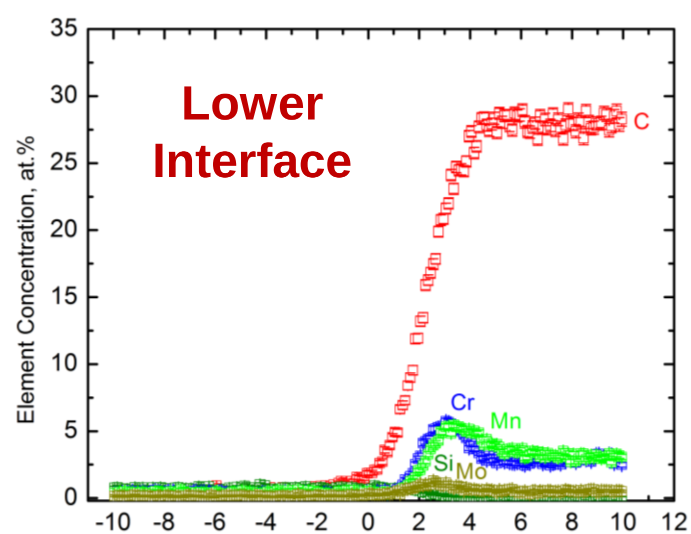


10 at.% isoconcentration surfaces

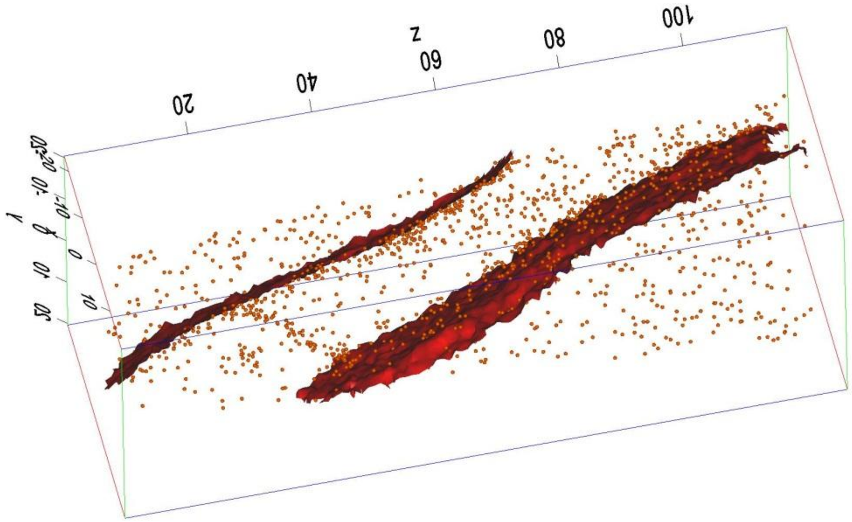


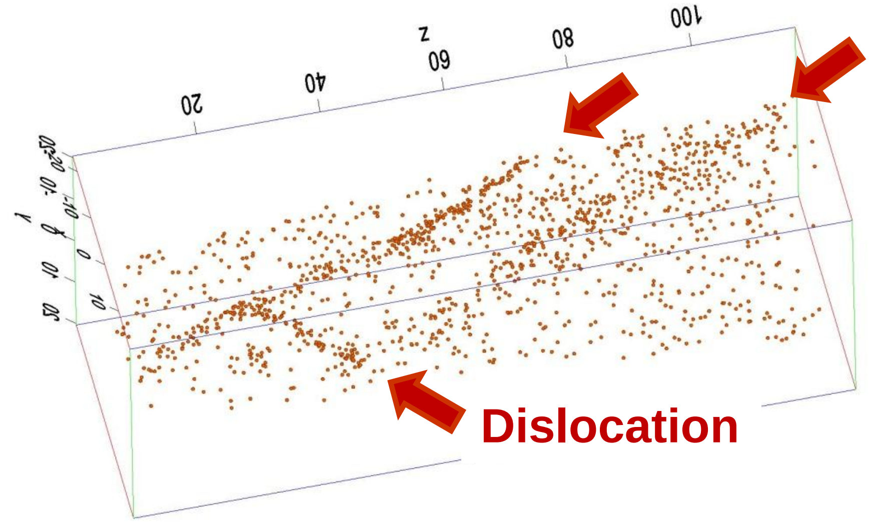
Partitioning of Cr, Mn, Mo to cementite and Si to ferrite…

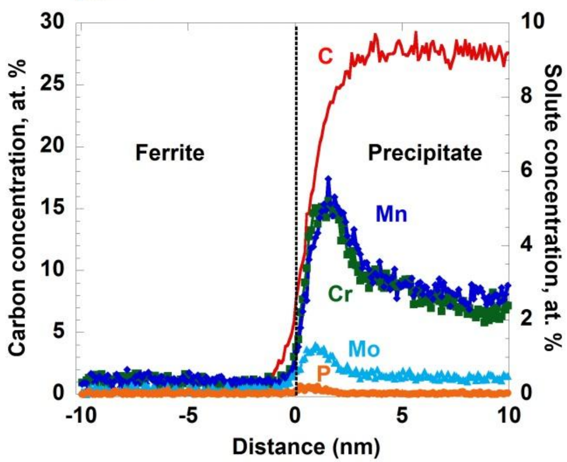




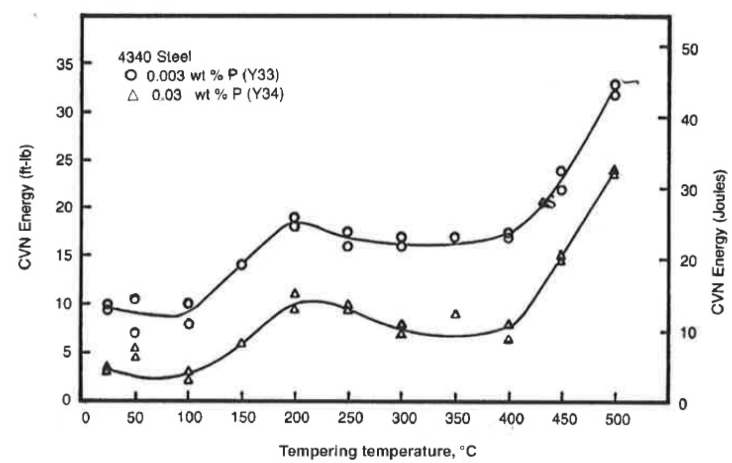
P Enrichment at the Interface and the Formation of Cottrell Atmospheres; 575 °C, 2 h







P influences impact toughness and may play a role in temper embrittlement



J.P. Materkowski and G. Krauss, Metallurgical and Materials Transactions A, 1979, 10A:1643-1651

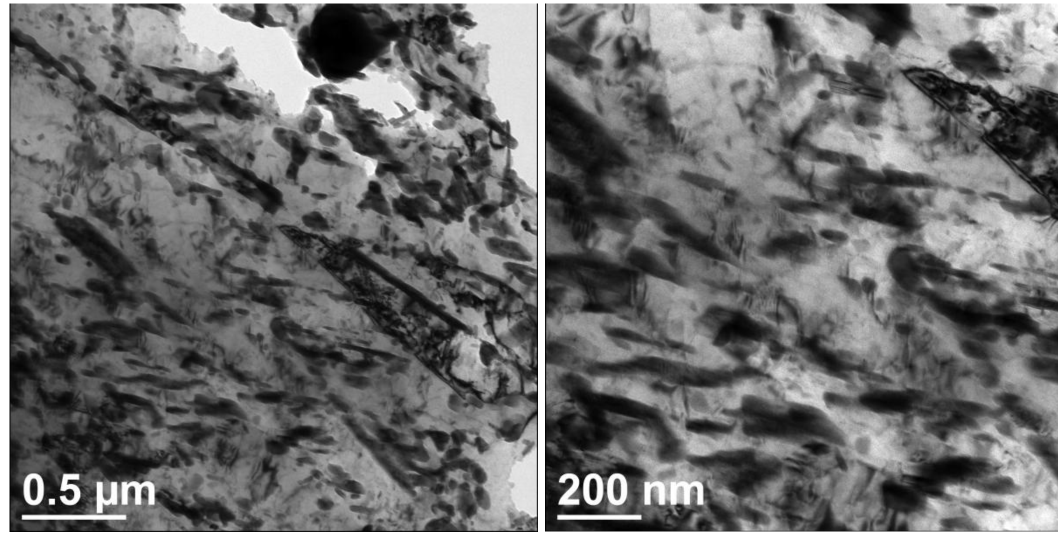
TEM of Cementite Tempered at 575 °C, 2 h

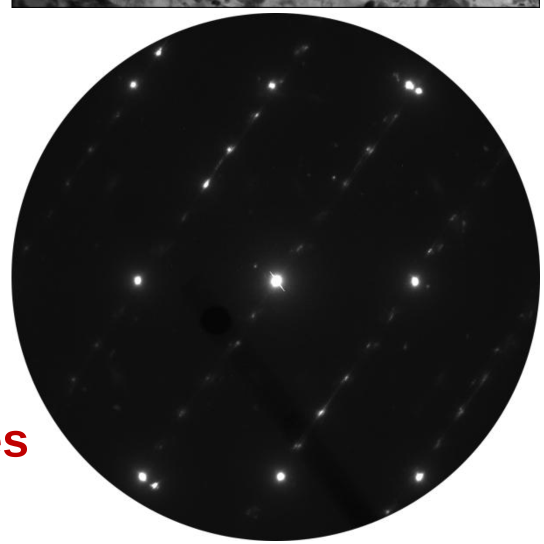
- Diffraction from four precipitates in three different alpha grains:

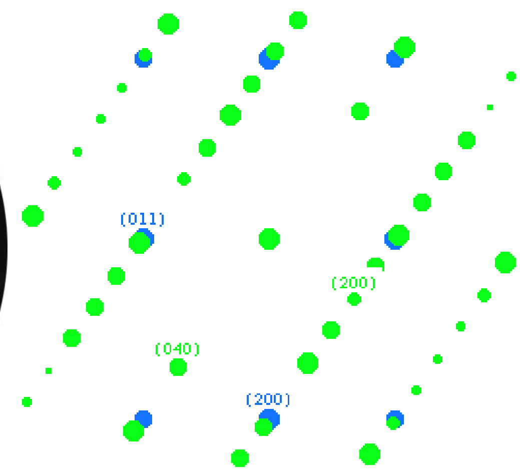
  Three matched cementite
  a = 5.090 A
  b = 6.748 A
  c = 4.523 A

- Bagaryatski orientation relationship

  [1-10]alpha || [001]Fe_3C
  (211) alpha || (010)Fe_3C







Example precipitates and diffraction

Summary

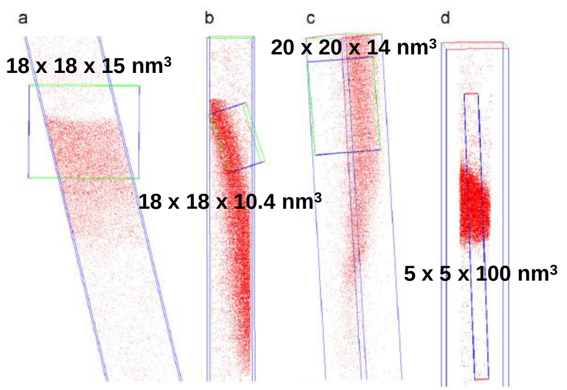
- Tempering influences the mechanical properties and fragmentation of quenched 4340 (hemi-shaped samples)
- APT revealed carbon-enriched features that contain a maximum of ~12-14 at.% carbon after quenching to RT (the level of carbon is perhaps associated with the extent of autotempering)
- TEM confirmed the presence of twinned martensite and indicates ε' (η) transition carbides after oil quenching to RT
- Tempering at 325 °C resulted in carbon-enriched plates (> 25 at.% C) with no significant element partitioning (transition carbides?)
- Tempering at 450 °C and 575 °C resulted in cementite (~ 25 at.% C) during late stage tempering; Cr, Mn, Mo partitioned to cementite and Si partitioned to ferrite
- Tempering at 575 °C resulted in P segregation at cementite interfaces and the formation of Cottrell atmospheres

Acknowledgements

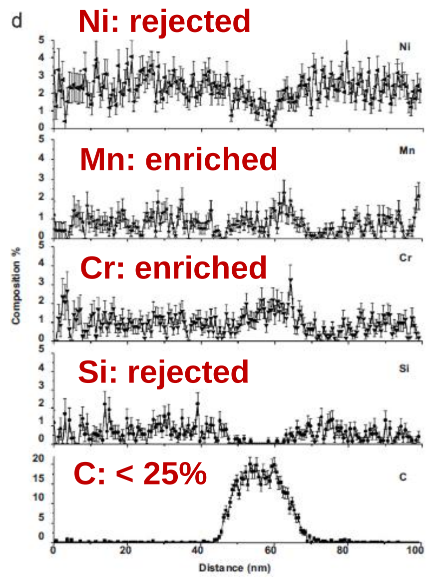
- Research at the Oak Ridge National Laboratory ShaRE User Facility was sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy
- Los Alamos National Laboratory; U.S. Department of Energy (contract AC52-06NA25396)
- APT specimen preparation was performed by Kathy Powers

Recent Atom Probe Tomography Examinations of 4340 (Smith and Co-workers)

Carbide/matrix interfaces in 4340 (2007)

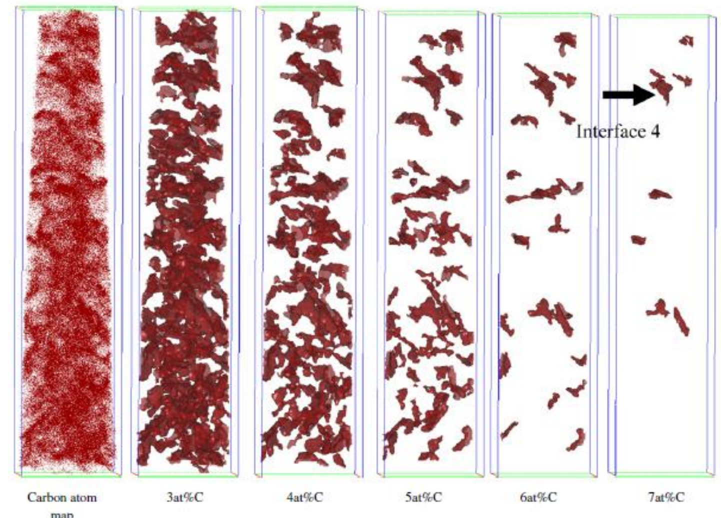


300 °C	350 °C	400 °C	400 °C
1 hr	1 hr	1 hr	10 hr



C. Zhu , X.Y Xiong, A. Cerezo, R. Hardwicke, G. Krauss, and G.D.W. Smith, Ultramicroscopy, 2007, 107:808-812

Tempering 4340 at RT for 1000 hr (2009)



(30 x 30 x 300 nm^3)

Carbon-rich regions in Fe-Ni-C and 4340 after 20-150 °C aging/tempering, with maximum carbon concentrations near 10at.%, confirm a stage of tempering prior to ε carbide precipitation (during which carbon atoms cluster within the (possibly faulted) martensite matrix)

C. Zhu , A. Cerezo, and G.D.W. Smith, Ultramicroscopy, 2009, 109:545-552