Microstructural Evolution:

Current Understanding of Precipitate Formation (in V-4Cr-4Ti)

D.T. Hoelzer and J. Bentley
Metals and Ceramics Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831

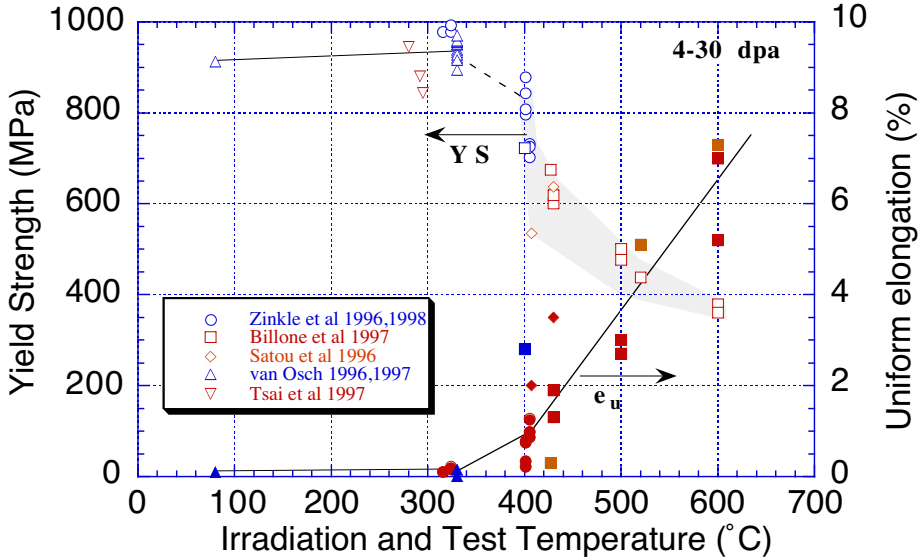
6th IEA and JUPITER Joint Workshop on Vanadium Alloys for Fusion Energy Applications

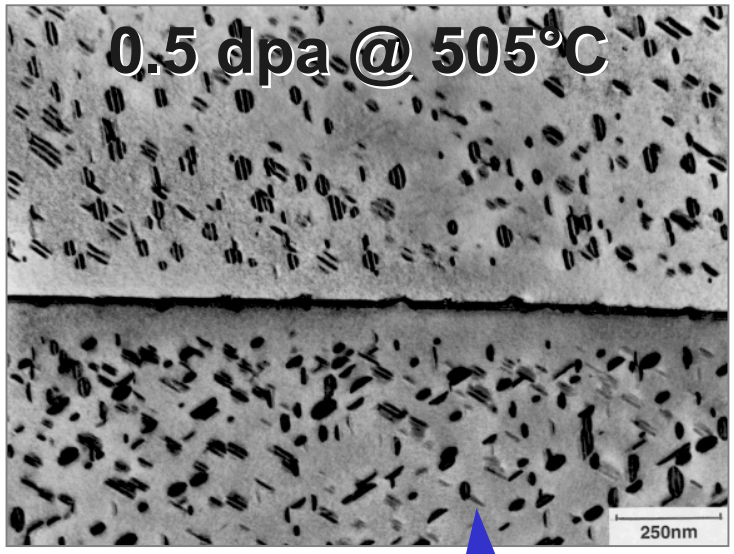
Tucson, Arizona (USA)
June 21 - 22, 2002

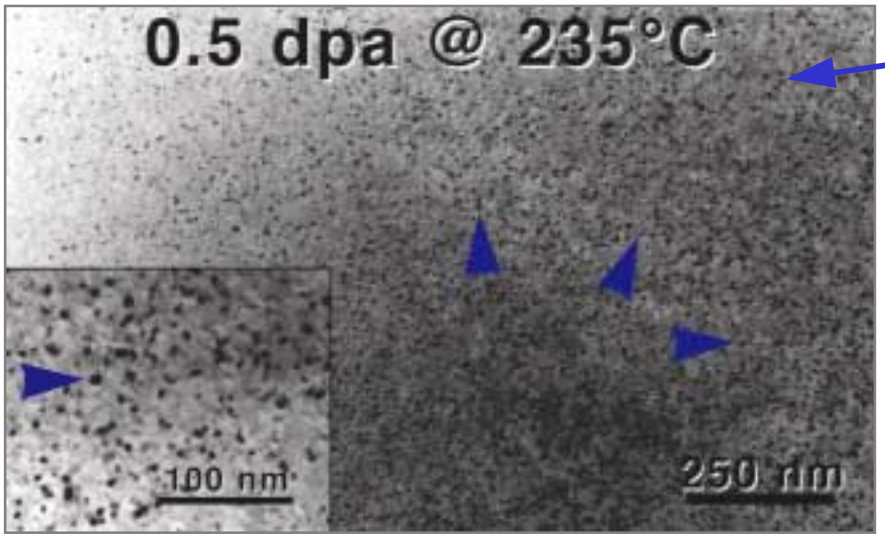
Introduction

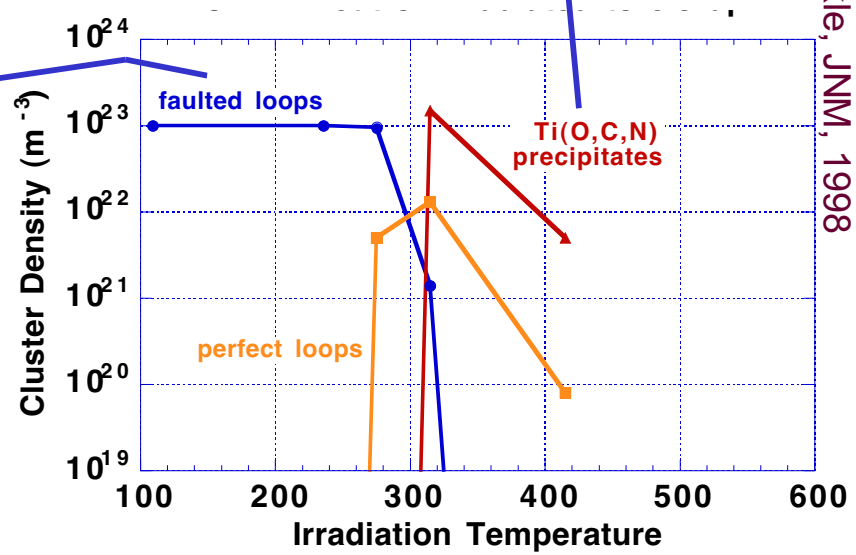
- **The mechanical behavior of V-4Cr-4Ti is strongly influenced by interstitial solutes (O, C, N)**
  - exhibits the classic BCC characteristics of load drop, Lüders extension, and dynamic strain aging (DSA) during straining
  - shows significant irradiation hardening below ~400°C
  - shows low temperature embrittlement
- **Ti(O,C,N) formation removes interstitials from solution**
  - improves low temperature embrittlement (oxidation, weld)
  - results in recovery of radiation hardening above ~400°C
  - could be used to improve the high temperature strength
- **Microstructural development depends on Ti(OCN) formation**
  - banded microstructure affects fabrication process

Enhanced Precipitation Improves the Mechanical Properties of Neutron-Irradiated V-4Cr-4Ti









Rice and Zinkle, JNM, 1998

Objective

- To develop a better understand of precipitates and precipitation behavior in V-4Cr-4Ti and to study how they affect the microstructural development

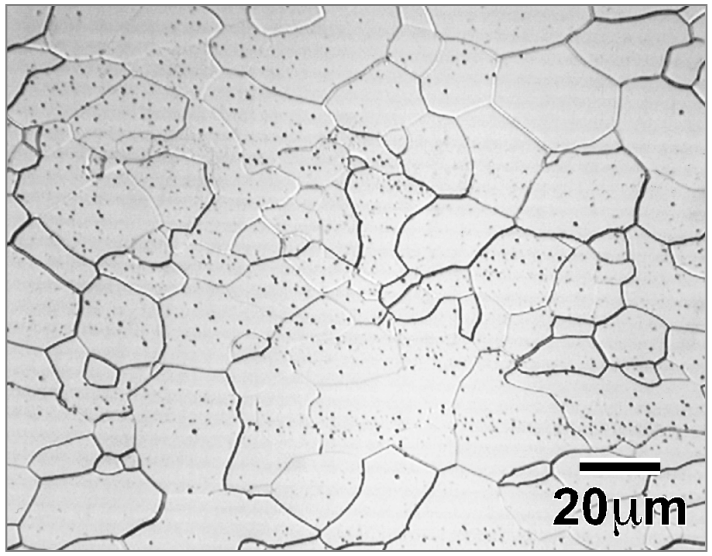
- Redistribute the interstitial solute population in a uniform dispersion of fine Ti(OCN) particles
  - improve the high temperature strength properties
  - develop a more uniform and isotropic grain structure
  - provide sites for trapping He bubbles
  - lower the interstitial solute concentration to reduce the radiation hardening

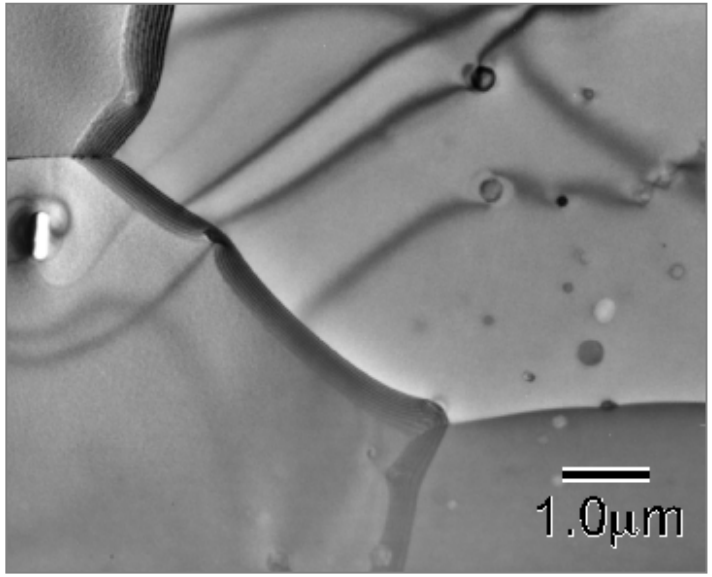
Outline

- Microstructural development during recrystallization
- Interaction between Ti and the interstitial solutes
  - resistivity/hardness property changes
  - dynamic strain aging (DSA)
- Precipitate formation during:
  - annealing
  - oxidation
  - neutron irradiation

Annealing at 1000°C Results in a Fully Recrystallized Microstructure in V-4Cr-4Ti

- equiaxed grains
- typical grain size of 10-30μm
- formation of coarse globular shaped precipitates, referred to as primary Ti(OCN)
- non-uniform distributions of inter- and intra-granular precipitates
- “Stringers” of precipitates running across several grains
- common to all heats of V-4Cr-4Ti alloys
- stable during neutron irradiation

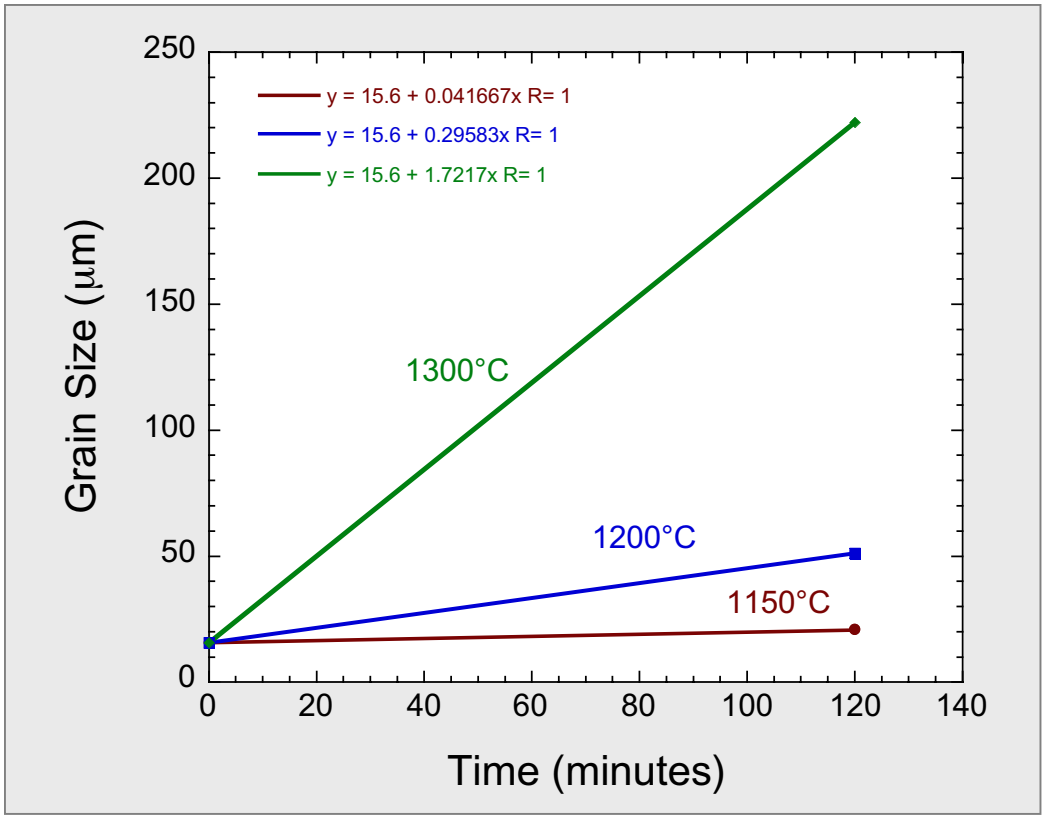




Grain Growth Behavior in V-4Cr-4Ti

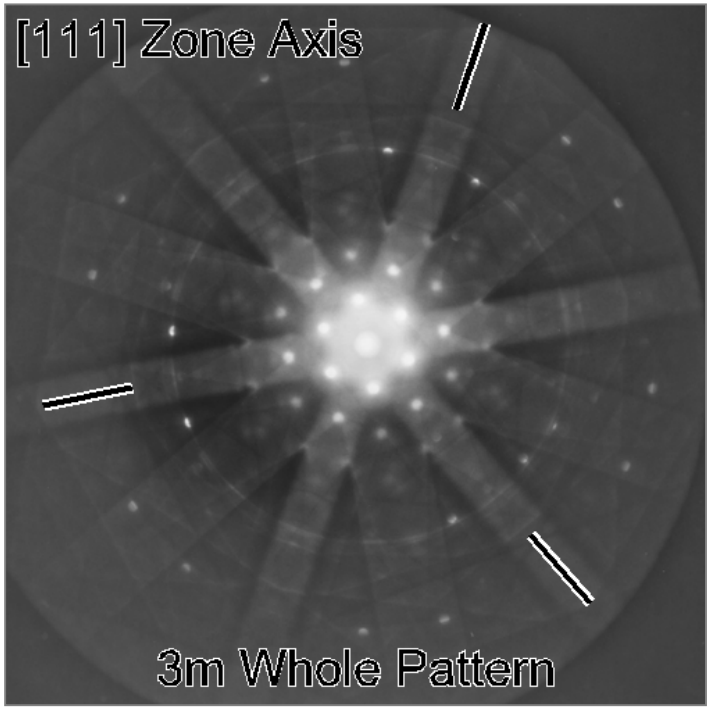
- Reference
  - samples annealed at 1000°C for 2h
  - initial grain size 15.6 μm (± -0.7 μm)
- Grain size measurements

Temperature (°C)	Grain Size (μm)
1150	20.6
1200	51.1
1300	222.2



- Grain size does not change significantly below 1150°C
- Rapid increase in grain size occurs above 1200°C
  - possible correlation with dissolution of globular Ti(OCN)

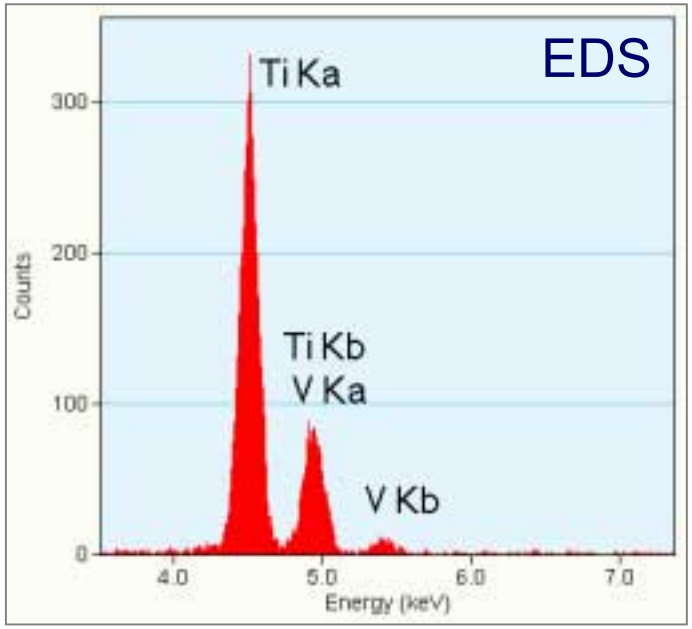
Crystal Structure of Globular Shaped Precipitates

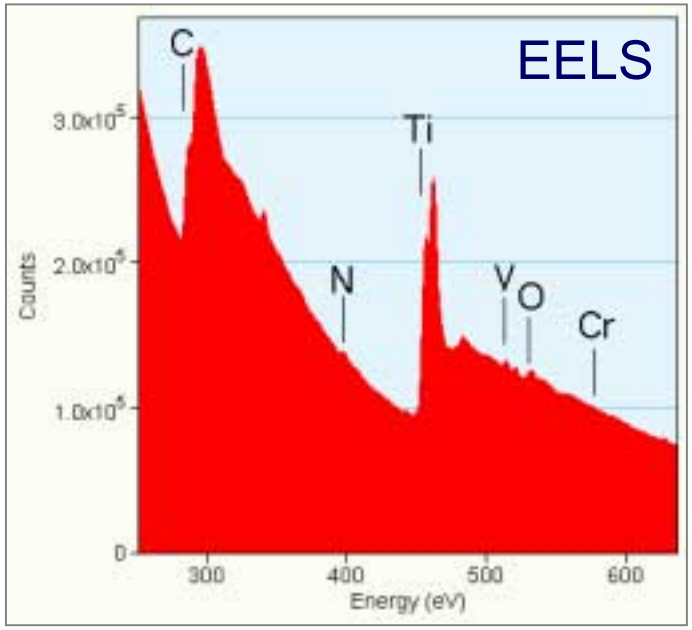


- Consistent with m3m point group and Fm3m space group of TiC, TiN, and γ-TiO; i.e. isomorphous composition of Ti(OCN)
  - 3m [111] and 4mm [100] whole pattern symmetries
  - interplanar angles, d-spacings, and structure factor contained in SAD patterns

Composition of Globular Shaped Precipitates

- EDS and EELS analyses show that the globular precipitates are TiC-rich *(Ti, V)(C, O, N)* with no detectable Cr

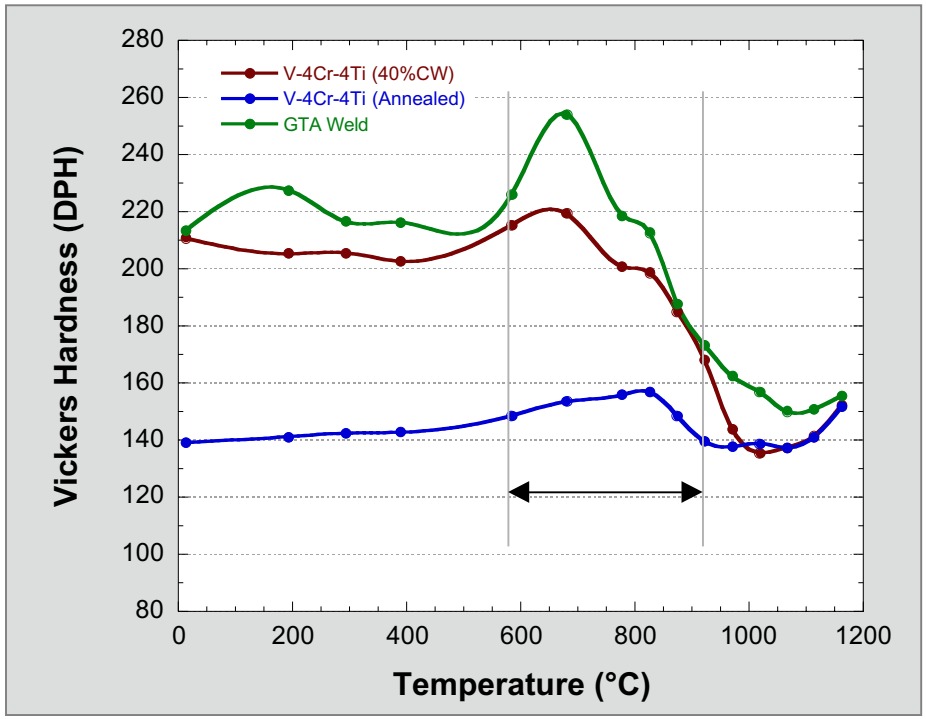


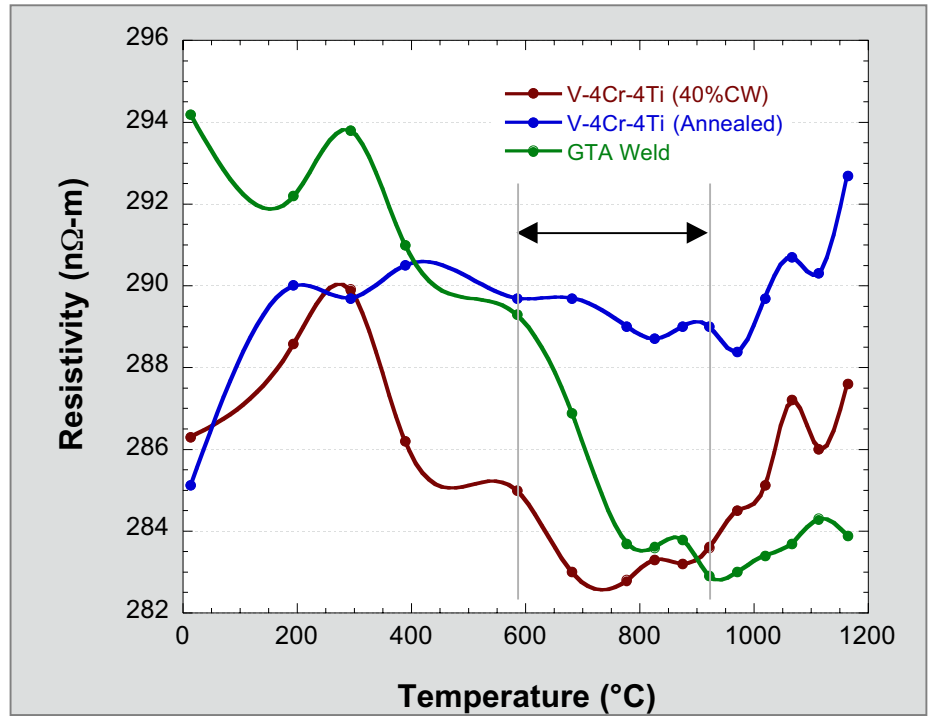


- *V-4Cr-4Ti was oxidized at 500°C (765wppm O) and homogenized for 100h at 600°C*

  (Bently and Pint, MSA, 2001)

Properties Measurements Highlight Dislocation and Solute Atom Interactions

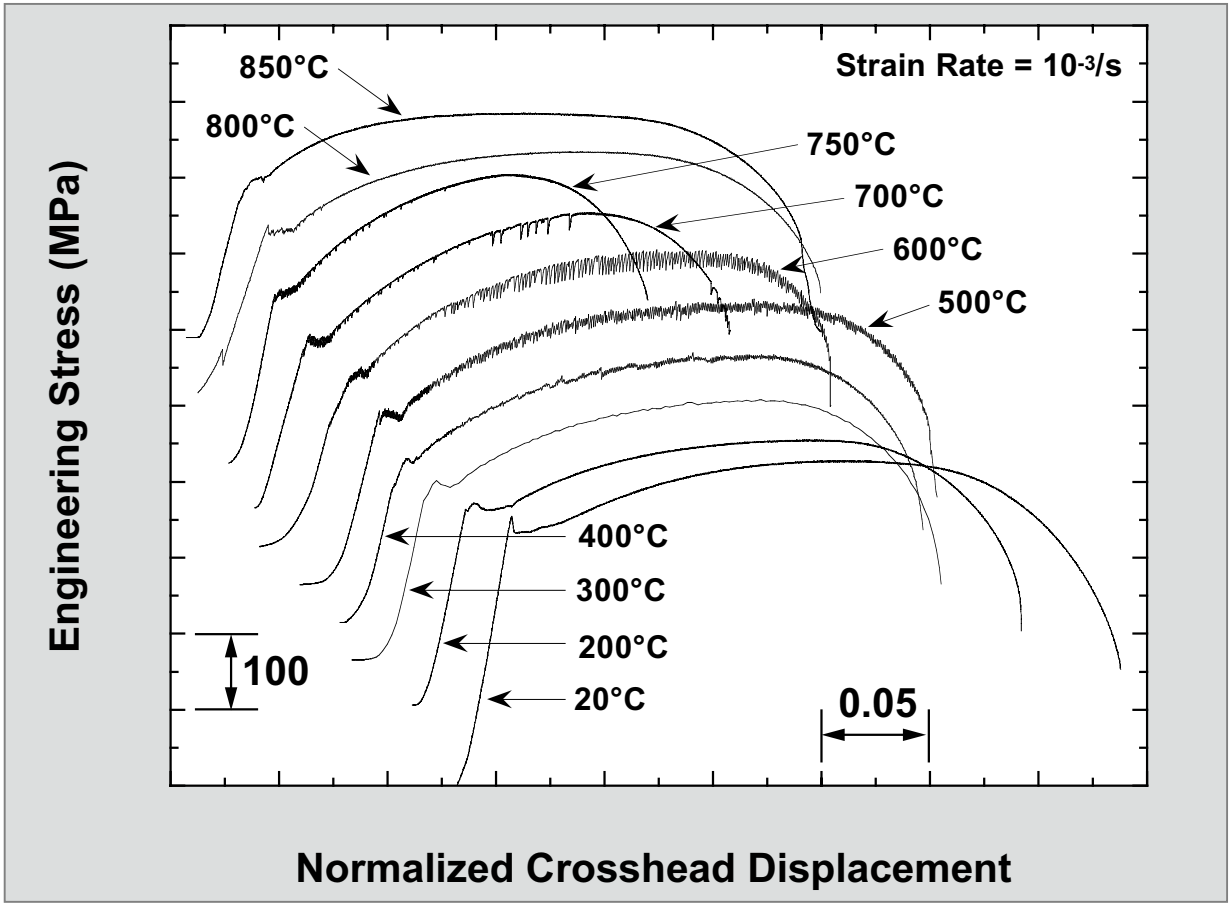




- Precipitation reaction occurs in V-4Cr-4Ti at T>600°C
  - hardness peak near 700°C
  - interstitial solute atoms removed from solution at T>300°C

Dynamic Strain Aging (DSA) Study Probes the Interaction Between Ti and Interstitial Solutes

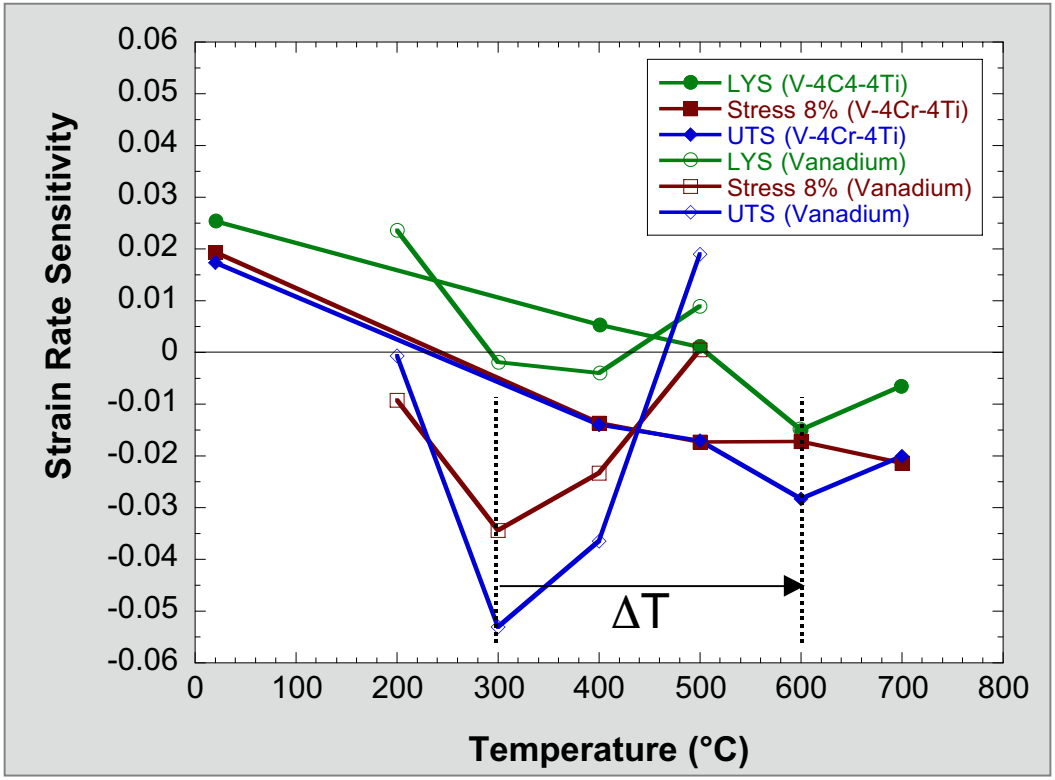
Annealed 1000°C/2h V-4Cr-4Ti



- Serrations indicate that a large fraction of interstitials (O, C, and N) are untrapped by Ti and are mobile above ~400°C

Strong Interaction Between Ti and Interstitials Solutes

- Segregation of interstitial solutes to dislocations begins at ~200°C in vanadium and ~300°C in V-4Cr-4Ti



- Alloying with Ti:
  - lowers the mobility of interstitial solutes
  - increases the amplitude of oscillations (barrier strength)
  - shifts the maximum negative SRS by 300°C

Microstructural Evolution in V-4Cr-4Ti

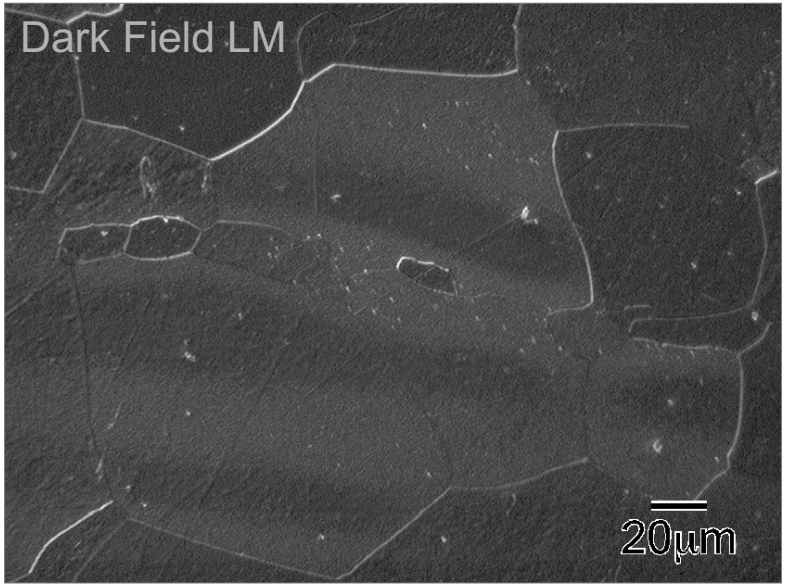
- Thermal
  - segregation of interstitials to dislocations beginning at ~300ºC (static and dynamic strain aging)
  - recrystallization above ~800°-900°C
  - precipitation above ~600°C

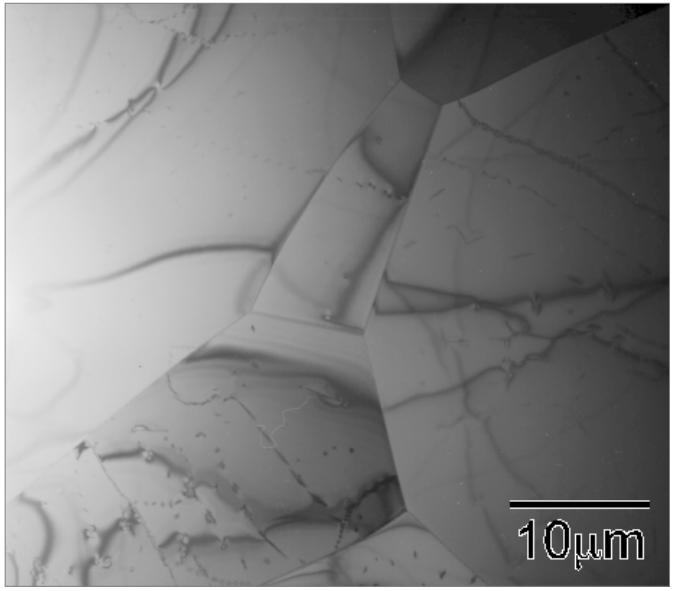
- Irradiation
  - significant radiation hardening from 60°-350°C
  - <110> faulted and <111> perfect interstitial loops primarily responsible for low temperature radiation hardening
  - Ti-enriched {001} defects develop at >300ºC

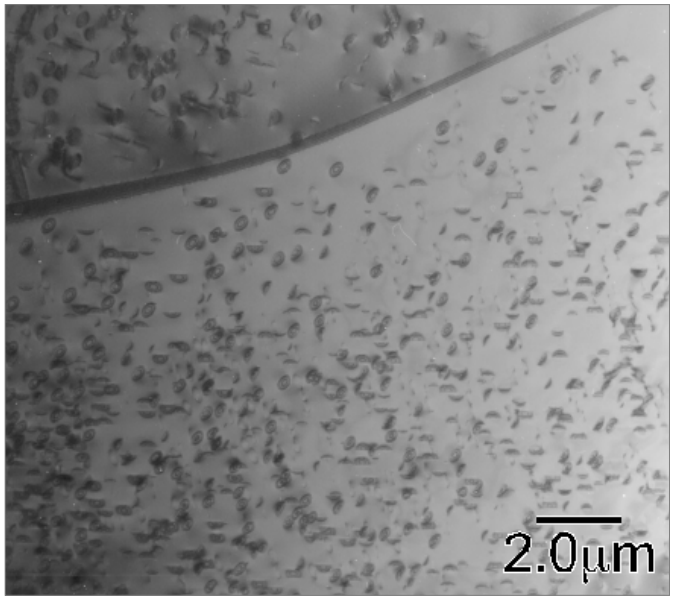
- Important to understand the structure and factors affecting the formation of precipitates

Secondary Precipitation During 900°C Anneal

- Annealing condition:
  - 1175°C/2h, then 900°C/1h

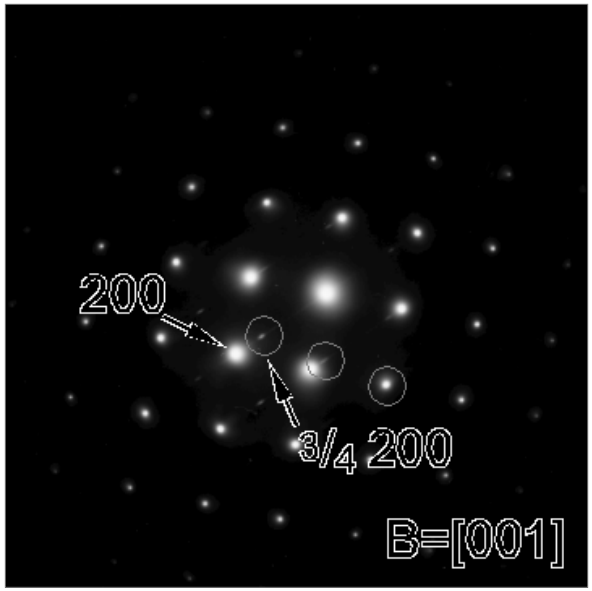


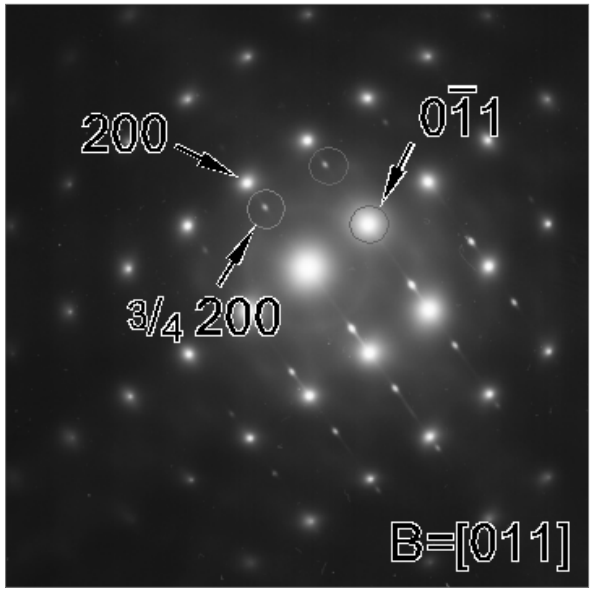


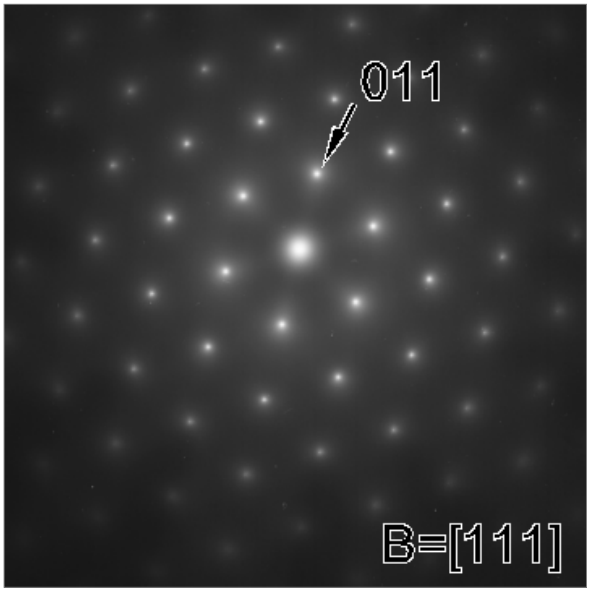


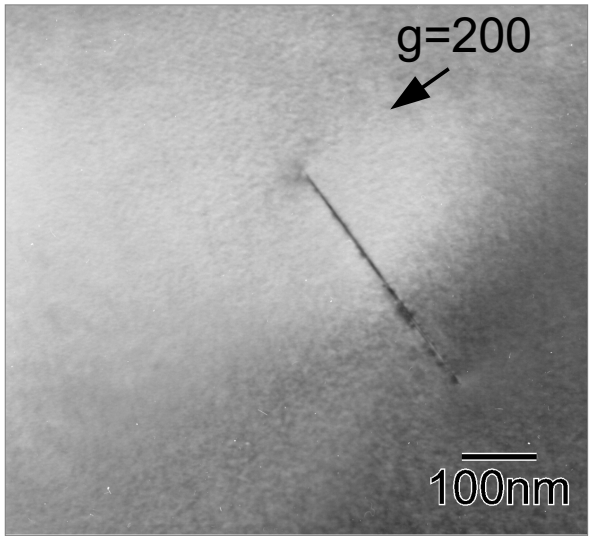
- Inhomogeneous distribution of precipitates
  - different TEM thin foils
- Non-uniform composition in Ti and/or interstitial solutes

Plate Shaped Secondary Precipitates





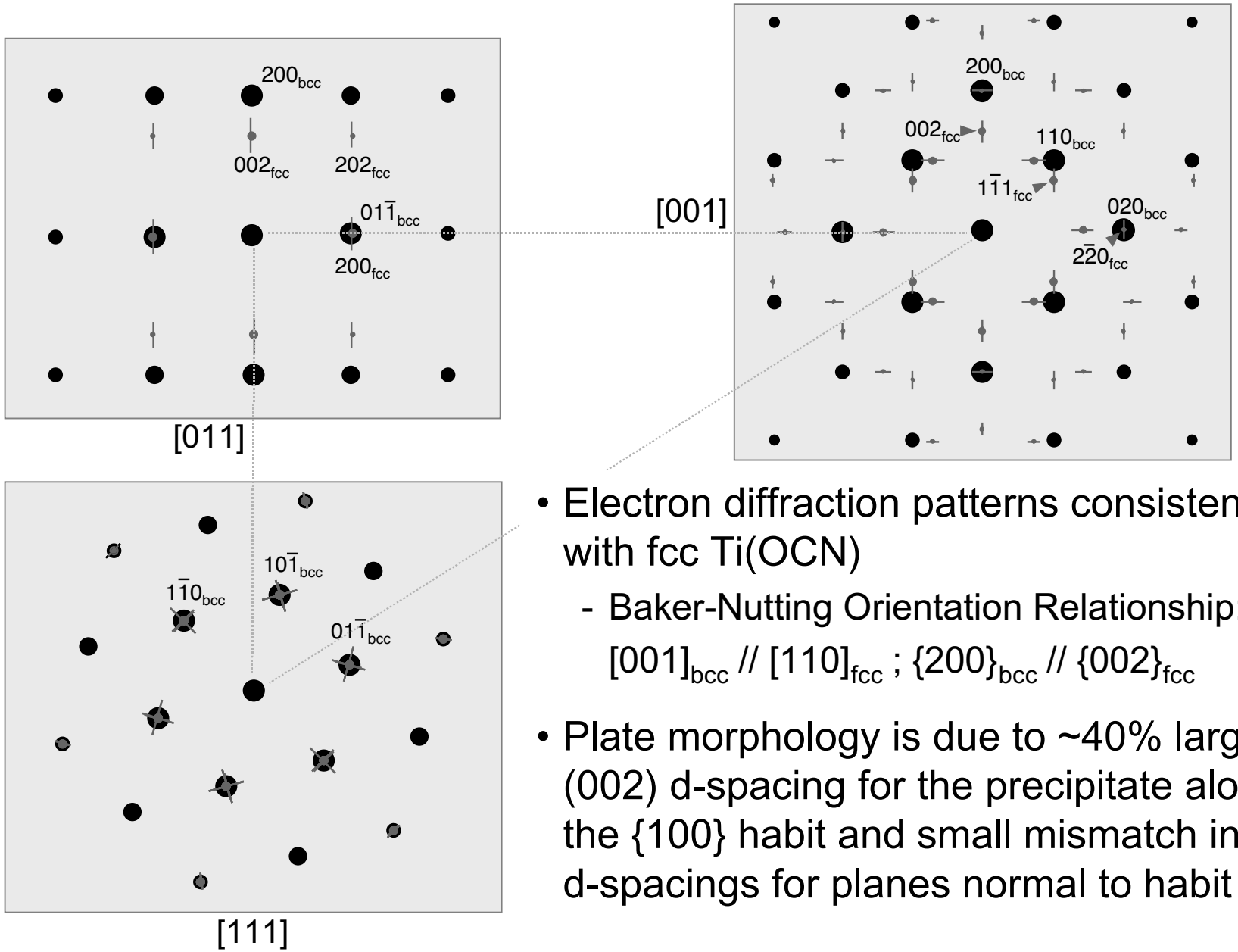




Close to [001]

- {001} habit
  - thickness <10nm
  - consistent with previous studies
- shows diffuse streaks aligned parallel to <100>bcc
  - intensity maxima at 3/4<200>
  - orientation relationship with bcc matrix
- only bcc fundamental reflections at [111] ZA

Simulated Electron Diffraction Patterns



- Electron diffraction patterns consistent with fcc Ti(OCN)
  - Baker-Nutting Orientation Relationship: $[001]_{bcc}$ // $[110]_{fcc}$; $\{200\}_{bcc}$ // $\{002\}_{fcc}$
- Plate morphology is due to ~40% larger (002) d-spacing for the precipitate along the {100} habit and small mismatch in d-spacings for planes normal to habit

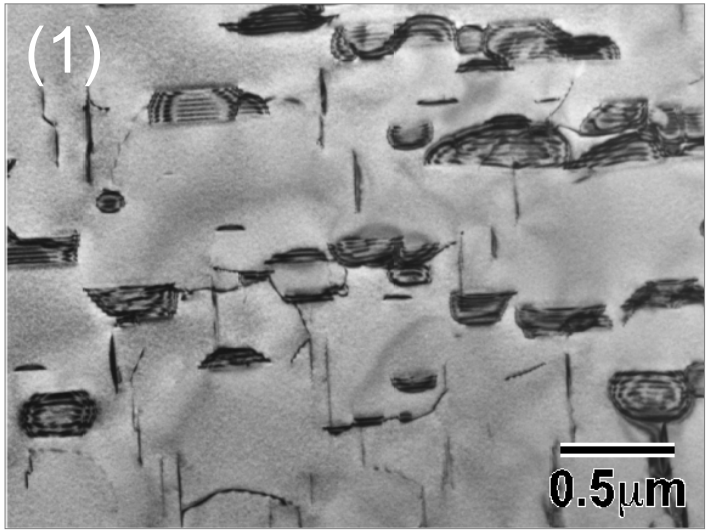
Plate Formation on {001} Habit Occurs in V-4Cr-4Ti at Temperatures <1000°C

Composition (EELS)

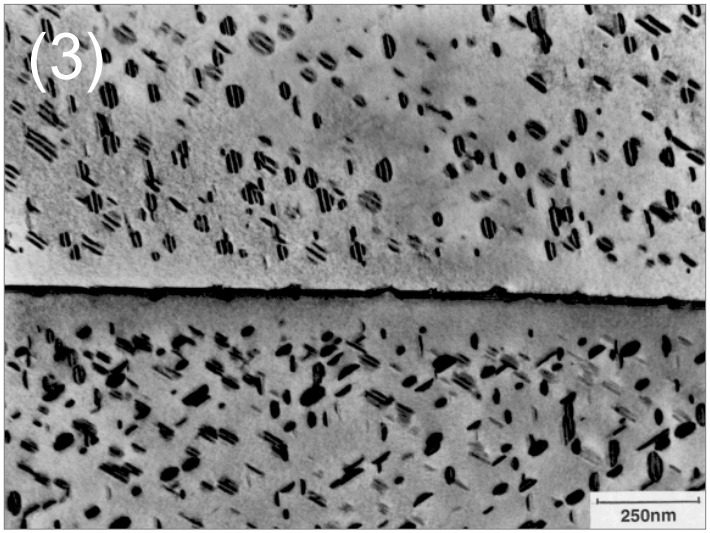
(1) GTA weld..... $Ti_{16}(O_3C_2N_3)$
- PWHT 950°C/2h [$Ti_2(O,C,N)_1$ ratio]

(2) Oxidized
- anneal 950°C/1h

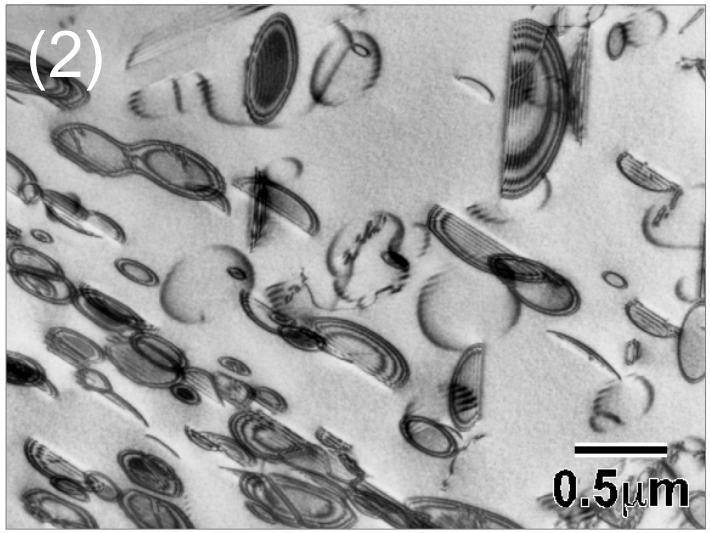
(3) Irradiated..... Ti-rich
- dose of 0.1dpa at 505°C



Grossbeck,Rice, et al.JNM, 1998



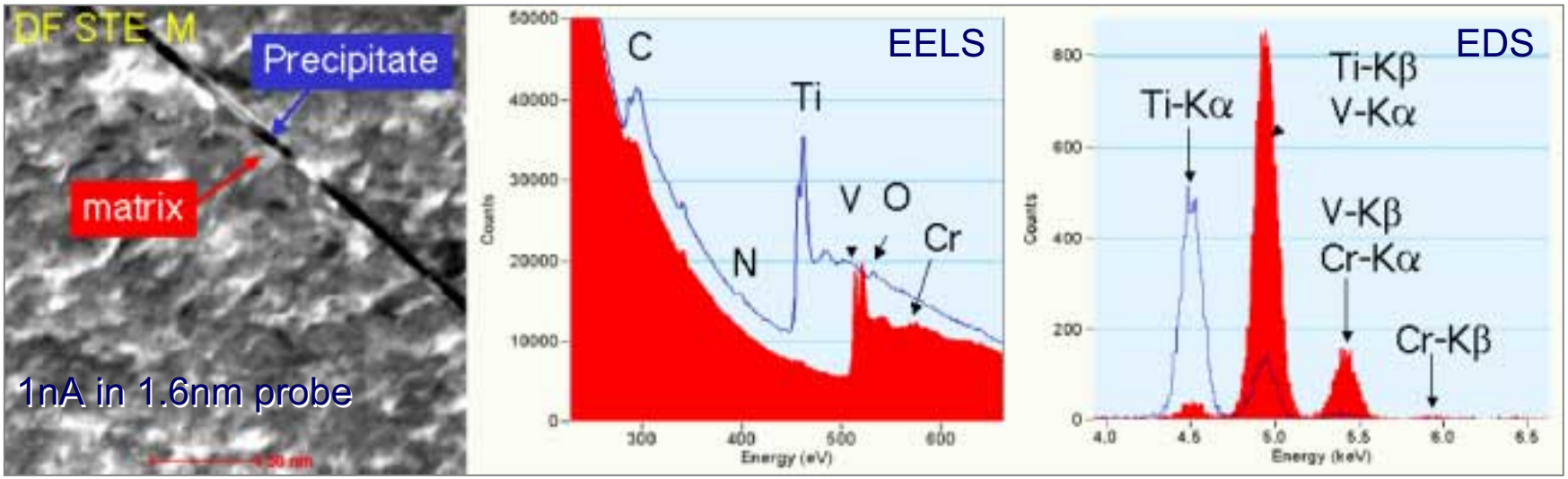
Rice and Zinkle, JNM, 1998



Bentley and Pint, MSA, 2001

EDS and EELS Spectrum Profiles Across Edge-On Plate Precipitate in Oxidized V-4Cr-4Ti

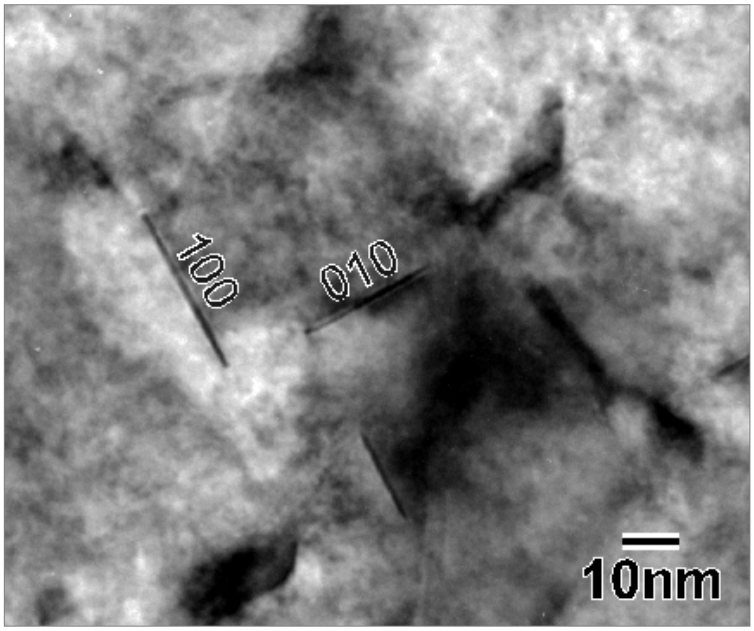
- Oxidized 500°C; homogenized 600°C/100h; annealed 950°C/4h
  - oxygen doping did not discernibly affect microstructure ~100μm from surface

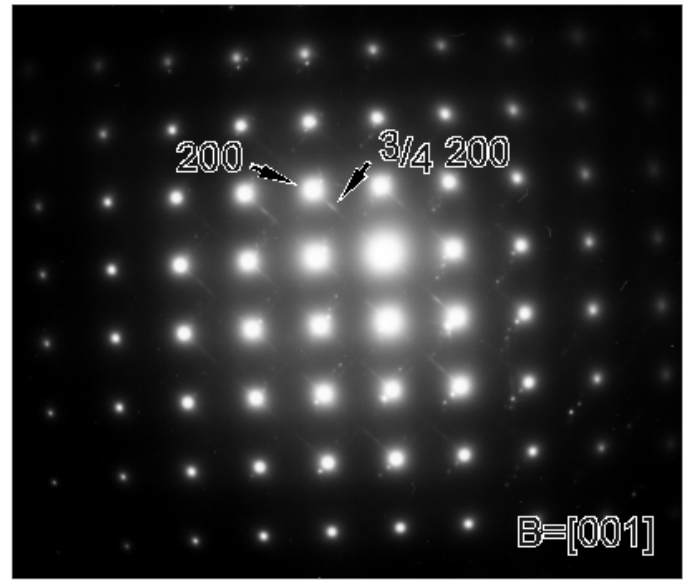


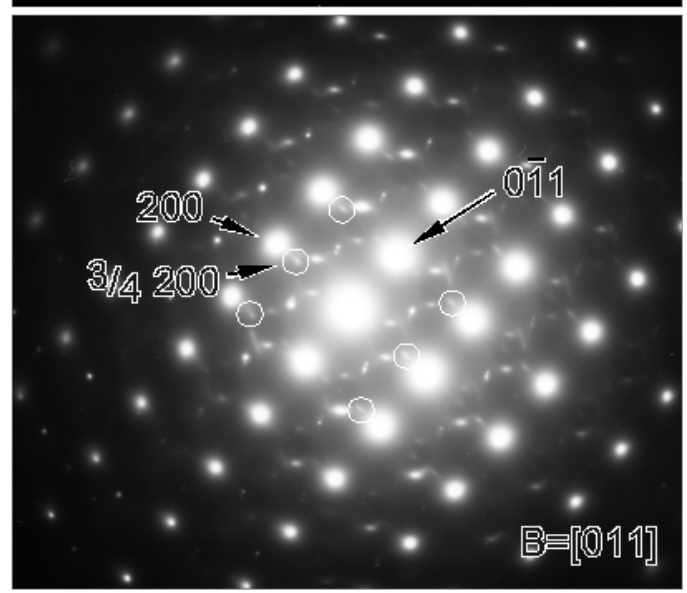
Bently and Pint, MSA, 2001

- **Precipitates are "TiC-rich" Ti(O,C,N)**
  - EELS: 58.2 Ti, 12.8 O, 24.1 C, 4.9 N (at.%)
- Reliable matrix composition by EDS (peak deconvolution)
  - beam spreading over-emphasizes V and Cr in precipitate
- Reliable precipitate compositions from EELS (except O)

Plate Formation in Periodic Temperature Variations of Neutron Irradiated V-4Cr-4Ti (HFIR 13J)

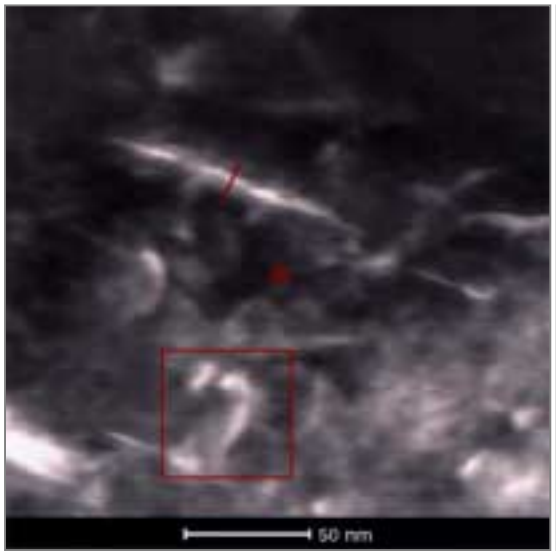


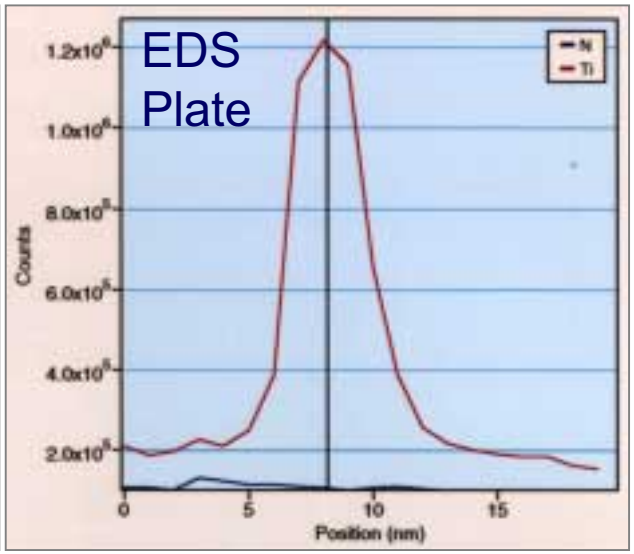


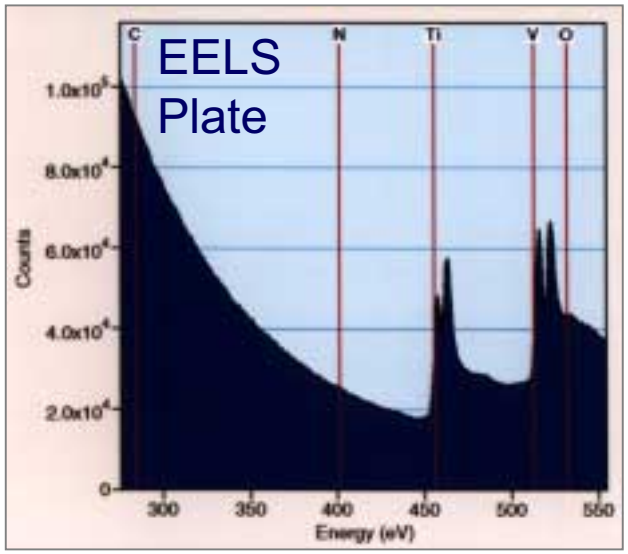


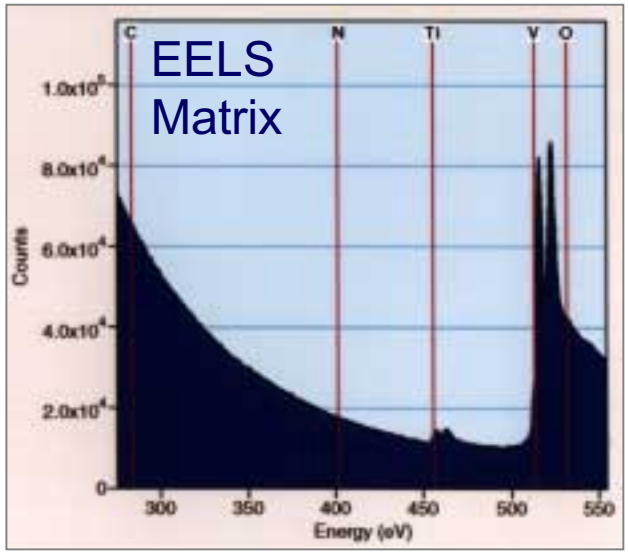
- ~4dpa @ 520°C and 340°C/520°C
- high number density of radiation enhanced {001} plate precipitates
- electron diffraction consistent with fcc Ti(OCN)
  - a=0.419 ± 0.010 nm
  - Baker-Nutting OR

EDS and EELS Spectrum Profiles Across Edge-On Plate Precipitate in Neutron Irradiated V-4Cr-4Ti









- **EELS Composition analysis**
  - Ti-rich containing <10 (O, N at.%) and no C
- Defect statistical models of TiO predict that vacancies can stabilize the structure by occupying sites on the Ti and O sublattices *(Giaconia and Tetot, J. Phys. Chem. Solids, 1997)*
  - between 16 and 25 at.%
  - cannot account for current results

Structural Analysis of Ti(OCN) Phase

- Lattice parameters from JCPDS and composition ranges

Phase	Composition (at.% x)	Space Group	Lattice Parameter	PDF Number
γ-TiO_x	34.9 to 55.5	Fm3m	4.177Å	8-0177
TiN_x	28 to > 50	Fm3m	4.256Å	6-642
TiC_x	32 to 48.8	Fm3m	4.3285Å	6-614

- Globular shaped - Primary (unirradiated)
  - lattice parameter: 0.436 +/- 0.009 nm
  - best agreement with TiC
- Plate shaped - Neutron irradiated (HFIR 13J)
  - lattice parameter: 4.19 +/-0.01 nm
  - best agreement with TiO
- Temperature may be an additional factor

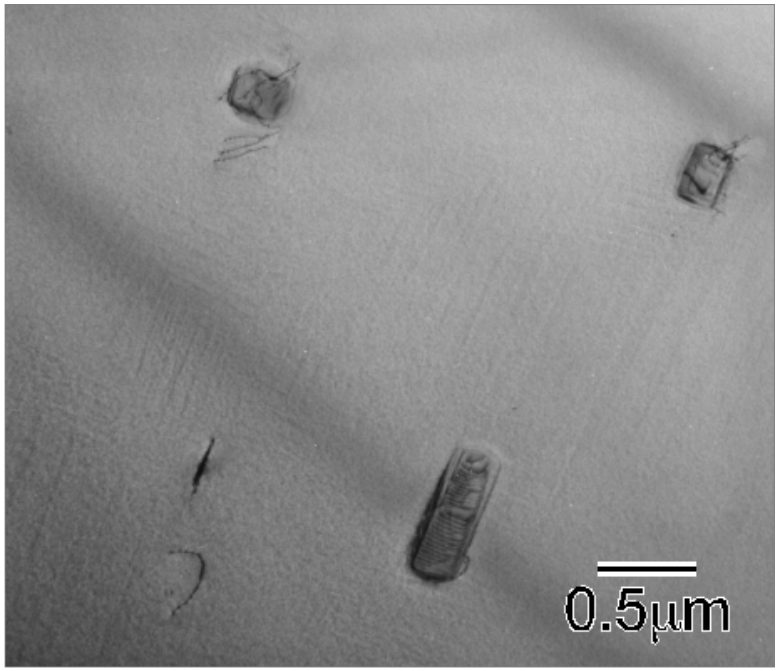
Determination of Solvus for Globular Ti(OCN)

- Previous work
  - 1125°C CVN impact test data of V-4Cr-4Ti
    (Kurtz, Hamilton, and Li, USFMSR, 1997)
  - 1100°C Heat treatments of NIFS-Heat-1 and NIFS-Heat-2
    (Nagasaka et al. 2nd WS on Development V Alloys for Fusion, 2001)

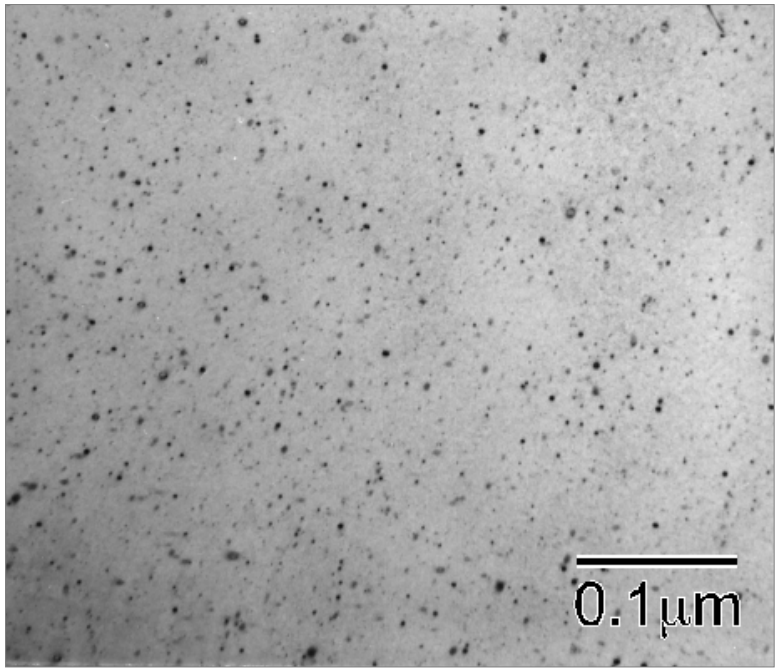
- Current focus
  - Series of high temperature heat treatments
    (1) V-4Cr-4Ti (U.S. 500kg Heat)
    (2) annealed at 1000°C/2h to precipitate globular Ti(OCN)
    (3) then annealed for 2h @ 1150°C, 1175°C, 1200°C and 1300°C

Redistribution of Interstitial (O, C, N) Solutes Occurs Above 1200°C in V-4Cr-4Ti

1200°C/2h

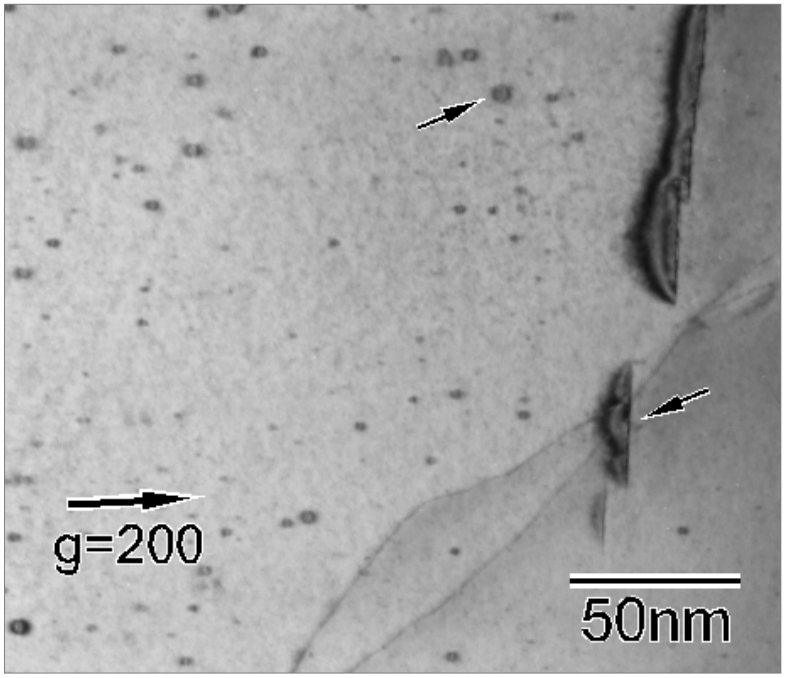


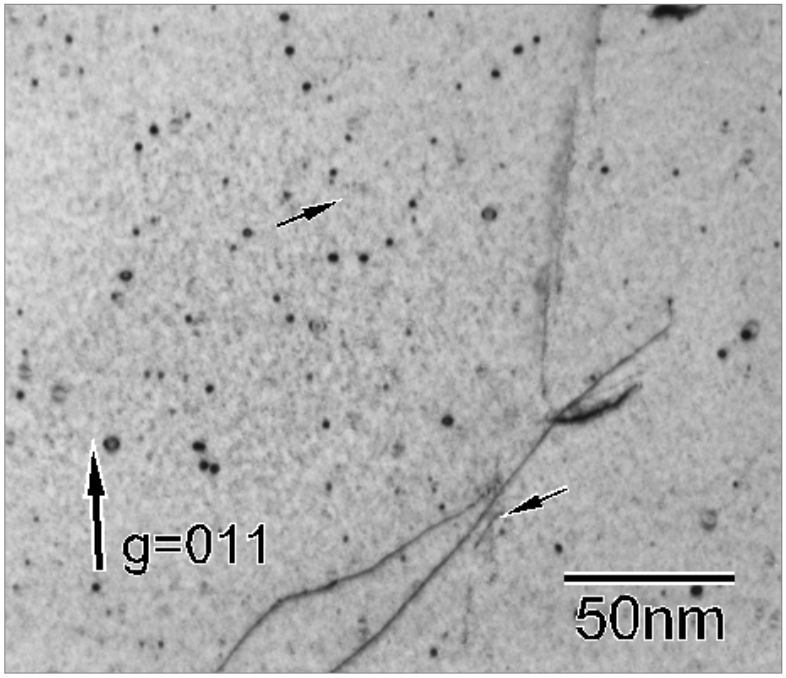
1300°C/2h



- High number density of nano-size precipitates formed at 1300°C
  - primary Ti(OCN) completely dissolved
- Primary Ti(OCN) remains stable at 1200°C
  - changes in crystal form: spherical to tetragonal prism
  - no nano-size precipitates in matrix

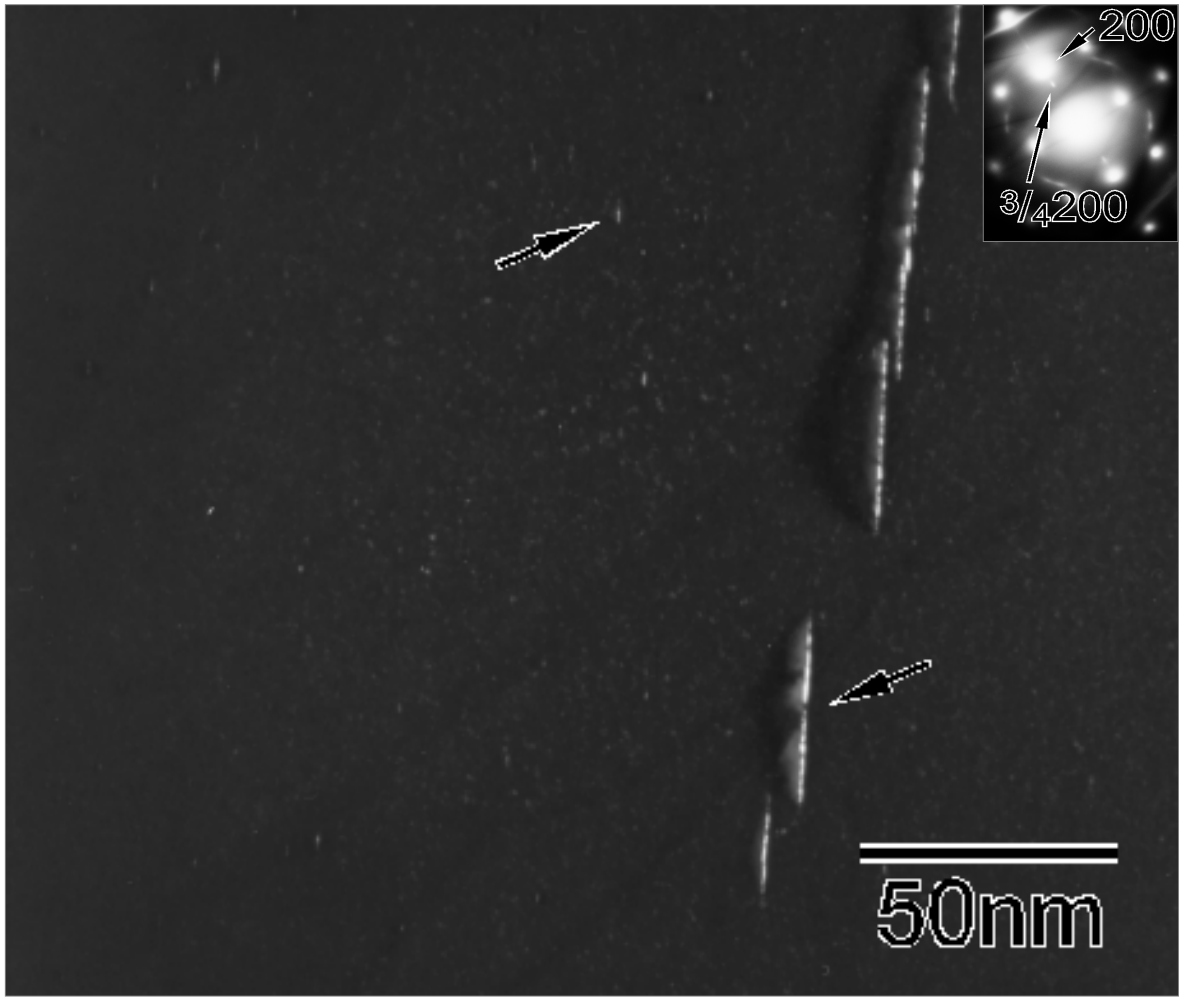
Determination of Solvus for Globular Ti(OCN)





- Precipitates show g•b = 0 invisibilities with g=011 and g=200
  - b = a<100>
  - large strain field
- Inside-outside contrast behavior using ±g (s>0)
- Coarse precipitates formed on dislocations
  - precipitate formation occurred during cooling from 1300°C

Nano-Size Precipitates are Consistent with Plate Shaped Ti(OCN)



- Dark field TEM image using 3/4<200> reflection
- Plates in the matrix are ~1nm thick

Summary

- Solute Ti interacts with interstitial (O,C, N) impurities by:
  - lowering the mobility of interstitial solutes
  - increasing the barrier strength, impeding dislocation motion
  - shifting the maximum negative SRS by ~300ºC (static and dynamic strain aging)
  - forming {100} plate Ti(OCN) precipitates
    - > ~600°C (thermal)
    - > ~300°C (neutron irradiation)
  - forming globular Ti(OCN) precipitates above ~1000°C
- Structural analysis of the Ti(OCN) phase
  - fcc crystal structure for both {100} plate and globular morphology
  - interstitial content varies considerably for {100} plates
- Established solvus of globular Ti(OCN)
  - 1200°C < T < 1300°C