Processing and Fabrication of V-4Cr-4Ti

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Program Development of V-based Alloys

- A general strategy for developing a material for an application involves:
  - identifying important properties
  - designing appropriate microstructure
  - producing the material
- Reflecting on the US program:
  - focused on *low temperature embrittlement issues*
  - assumed ~20-30 μm grain size and solid solution with lowest possible interstitial content
  - produced two large (500kg and 1200kg) heats of V-4Cr-4Ti and several small heats
- Japanese program followed the same reasoning but has achieved lower interstitial contents

Plate Fabrication Schedule; Teledyne Wah Chang

Machined ingot clad in evacuated SS jacket

↓

Extruded to rectangular billet (63 mm x 200 mm) at 1130-1150°C

↓

Warm-rolled (~400°C) perpendicular to extrusion direction to 23 mm thick

↓

Annealed at ~1150°C, 2h at 10^{-5} torr

↓

Warm-rolled parallel to extruded direction to 12.7 mm thick

↓

Annealed at ~1050°C, 2 h at 10^{-5} torr

↓

Warm-rolled parallel to extruded direction to 6.35 mm thick

↓

Annealed at ~1050°C, 2 h at 10^{-5} torr

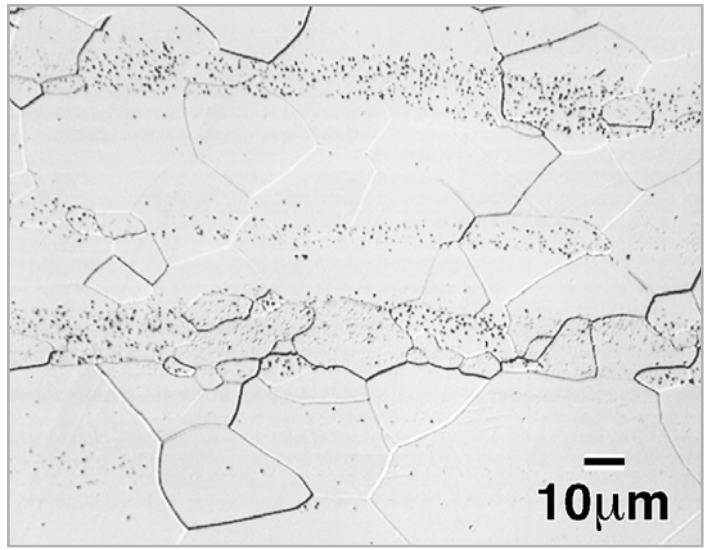
↓

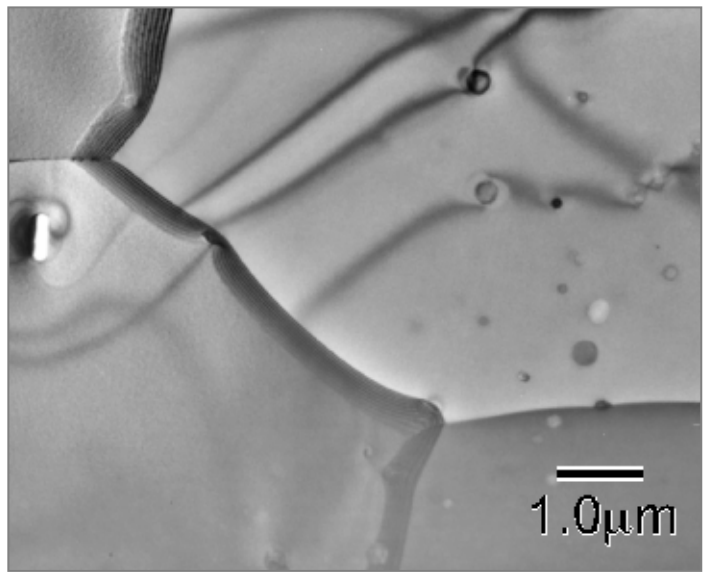
Warm-rolled parallel to extruded direction to 3.81 mm thick

Fully Recrystallized Microstructure Developed for Investigations of V-4Cr-4Ti

Annealing at 1000°C

- equiaxed grains
- typical grain size of 10-30μm
- formation of coarse globular shaped precipitates, referred to as primary Ti(CON)
- 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





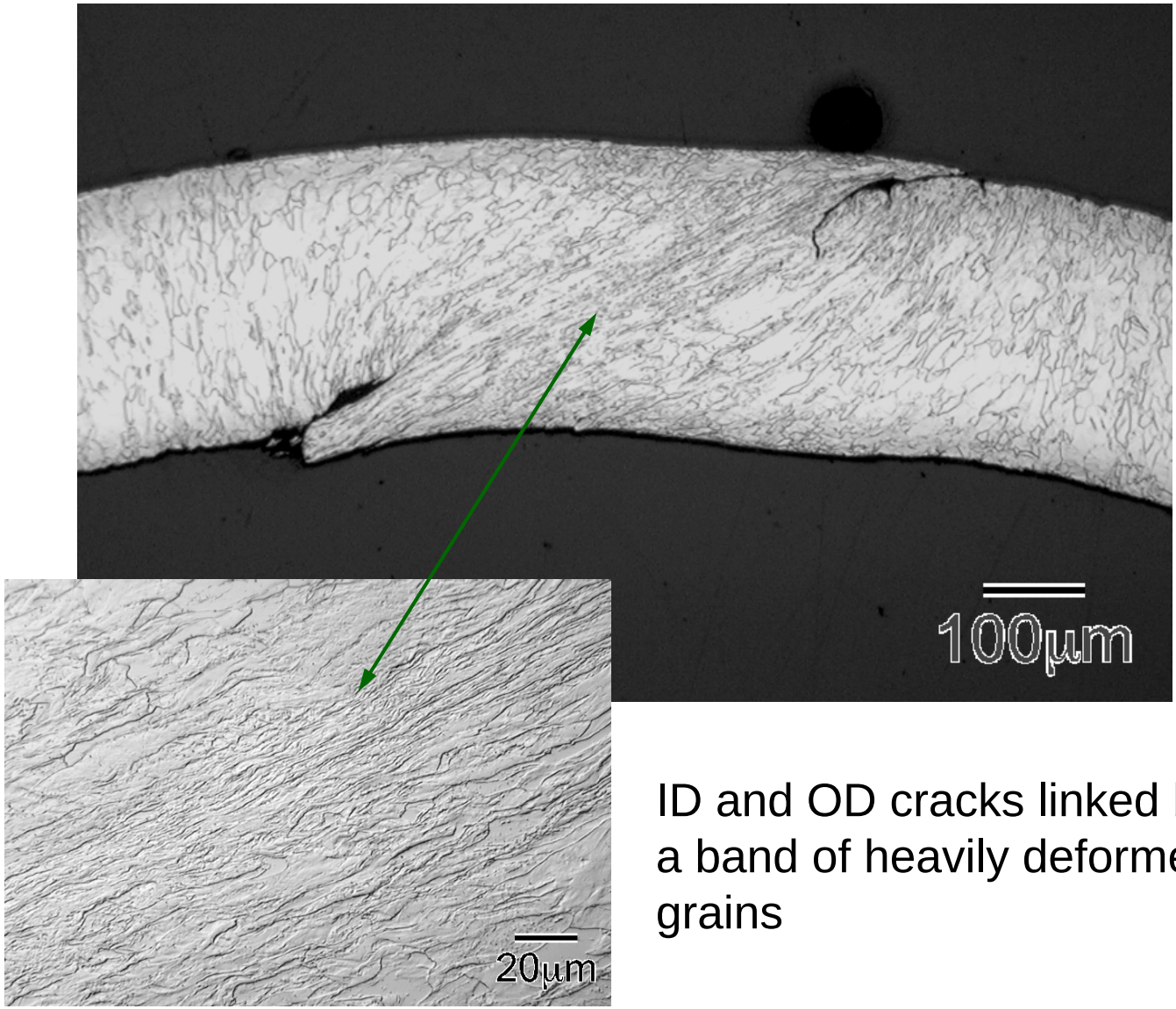
Fabrication of Creep Tubing for JUPITER-II Irradiation Experiments

- First batch of creep tubing from Heat 836625 contained ID and OD cracks (10-200μm deep) frequently linked by a band of heavily deformed grains running at 45 degrees to the through-wall radial direction

- Similar cracking problems developed during fabrication of creep tubing from NIFS-HEAT-2 [T. Nagasawa, T. Moroga, San Diego, April 2, 2000]

- Possible factors involved in cracking;
  - oxygen pick-up during annealing (300 to 600 wppm)
  - compression of initial banded Ti(OCN) microstructure during tube reduction
  - carbon pick-up due to inadequate cleaning procedures (80 to 300 wppm)
  - reduction in area too high (45%) in final stages

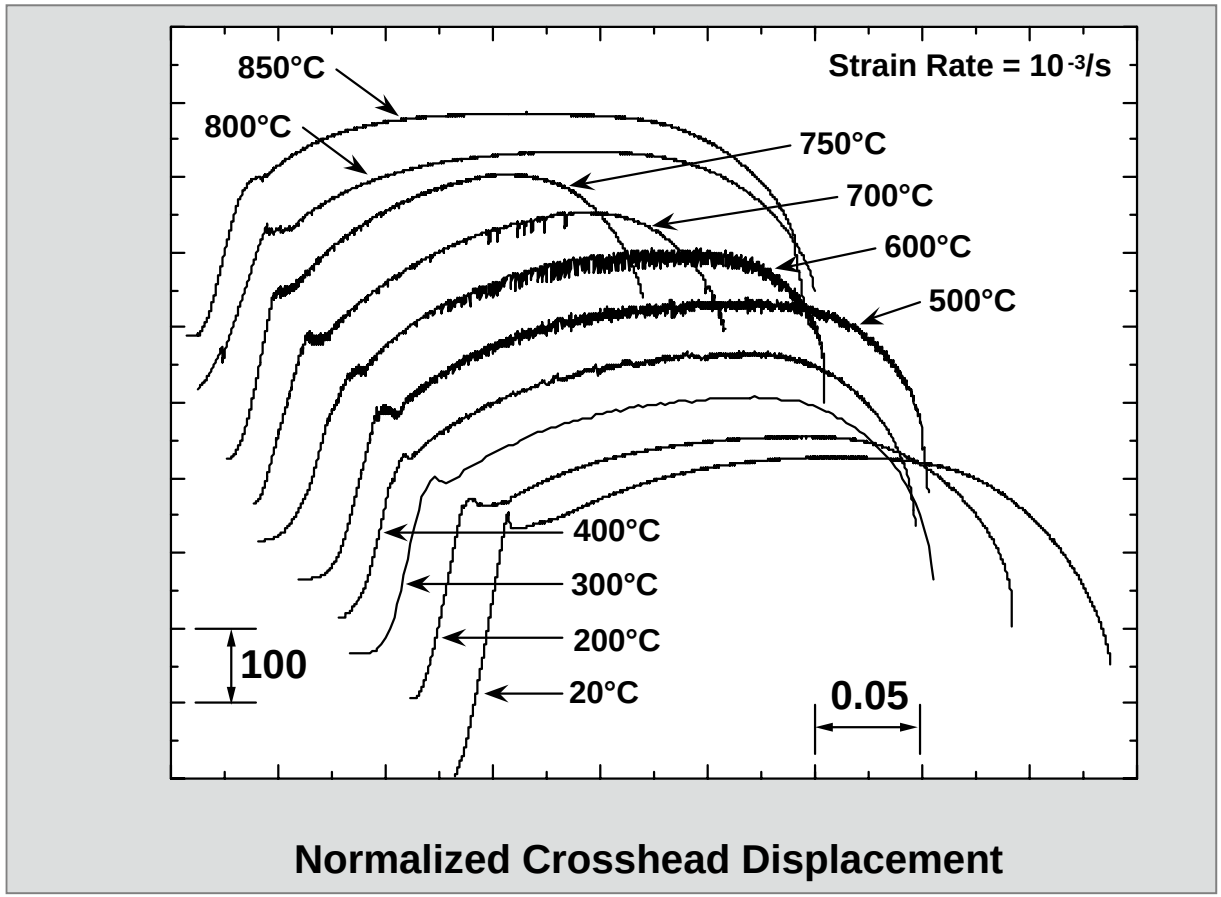
Cracks Observed in Creep Tubing from Heat 836625



ID and OD cracks linked by a band of heavily deformed grains

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

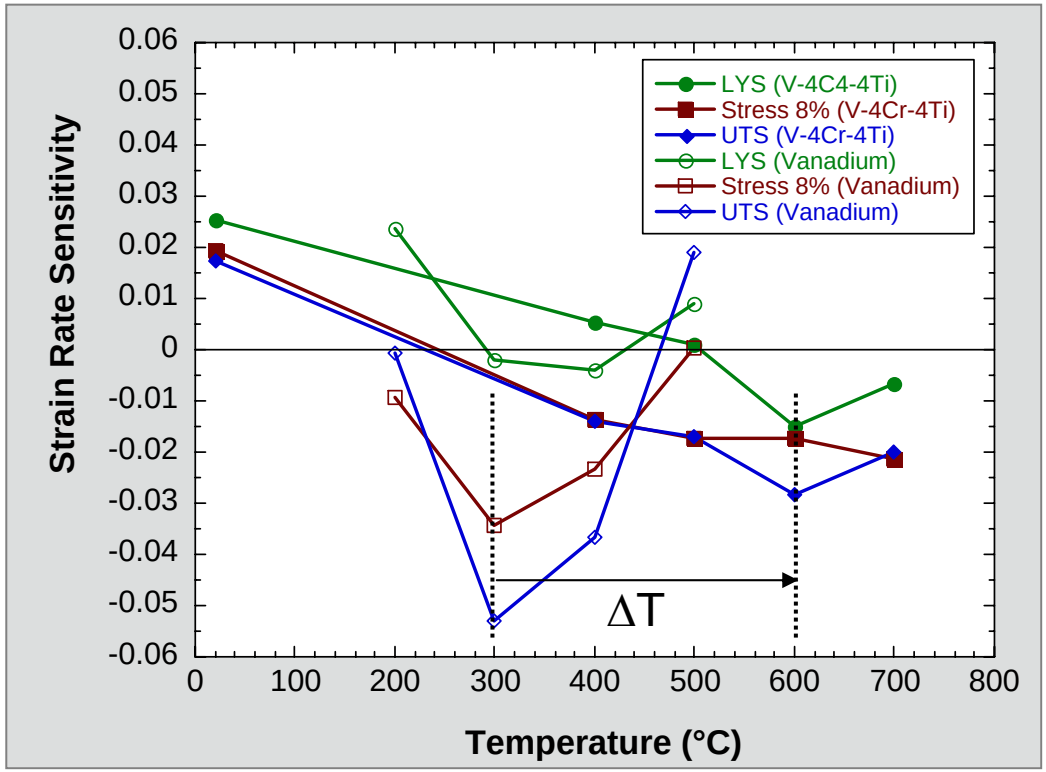
Annealed 1000°C/2h V-4Cr-4Ti



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

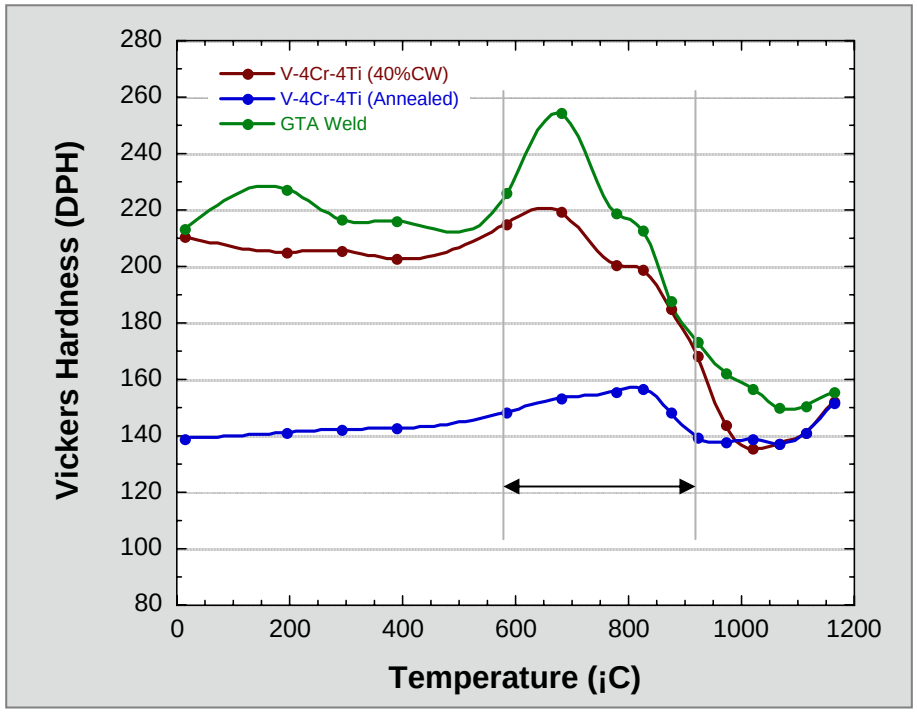
DSA Shows a Strong Interaction Between Ti and Interstitials Solutes

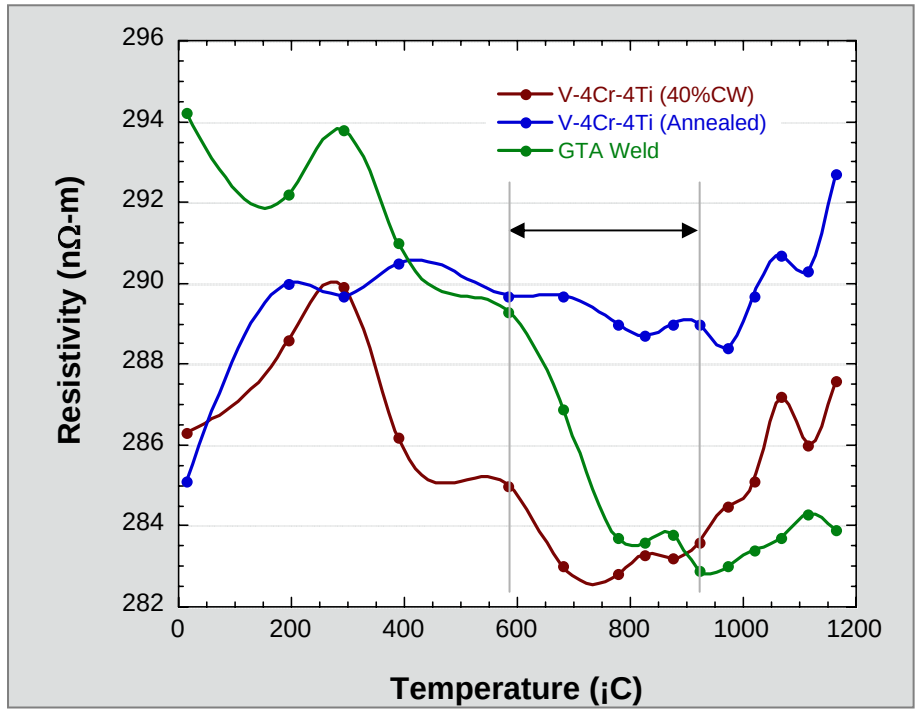
- Segregation of interstitial solutes to dislocations begins at ~200°C in vanadium and ~300°C in V-4Cr-4Ti



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

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

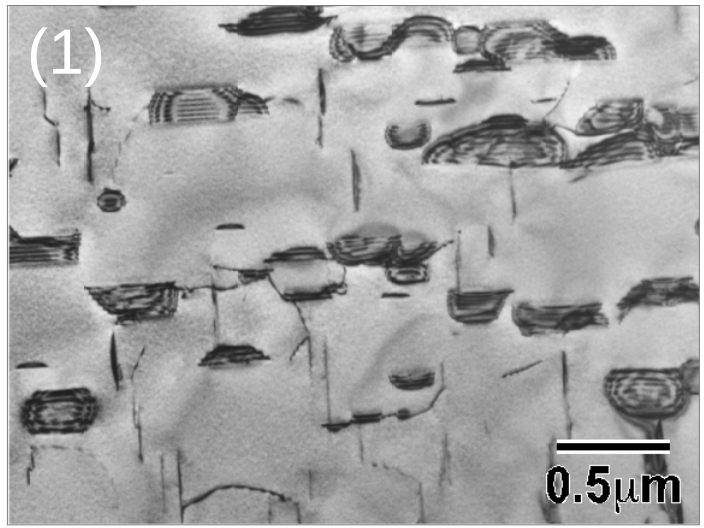
Plate Formation on {001} Habit Occurs in V-4Cr-4Ti at Temperatures <1000°C

Composition (EELS)

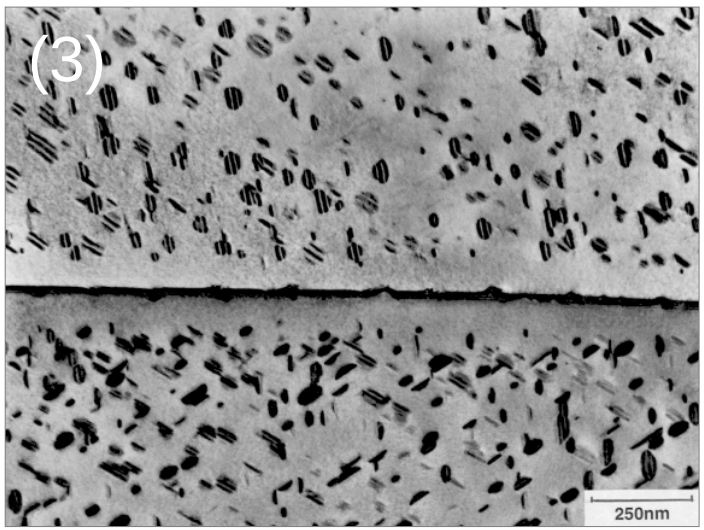
(1) GTA weld..... $Ti_{16}(O_3C_2N_3)$
PWHT 950°C/2h [$Ti_2(C,O,N)_1$ ratio]

(2) Oxidized
- anneal 950°C/1h

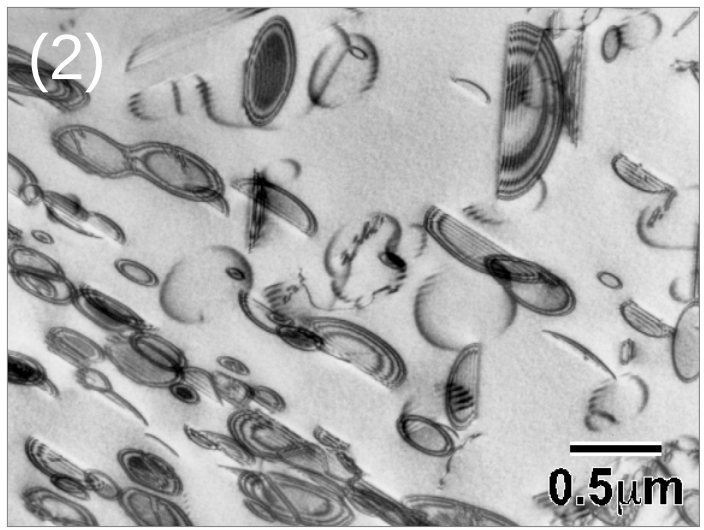
(3) Irradiated..... Ti-rich
- dose of 0.1dpa at 505°C



Grossbeck,Rice, et al.JNM, 1998



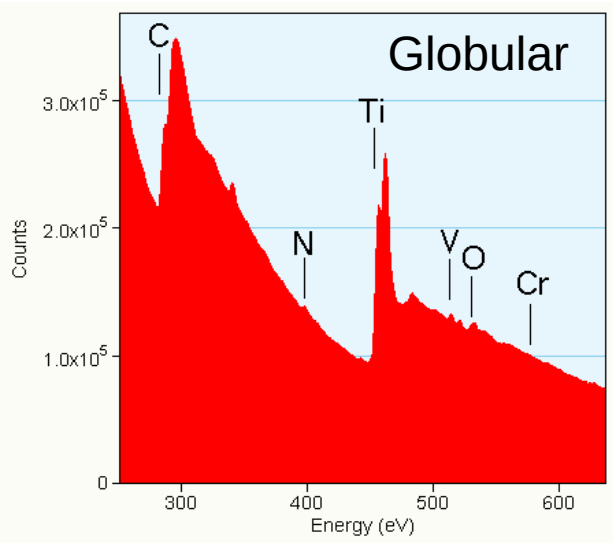
Rice and Zinkle, JNM, 1998



Bentley and Pint, MSA, 2001

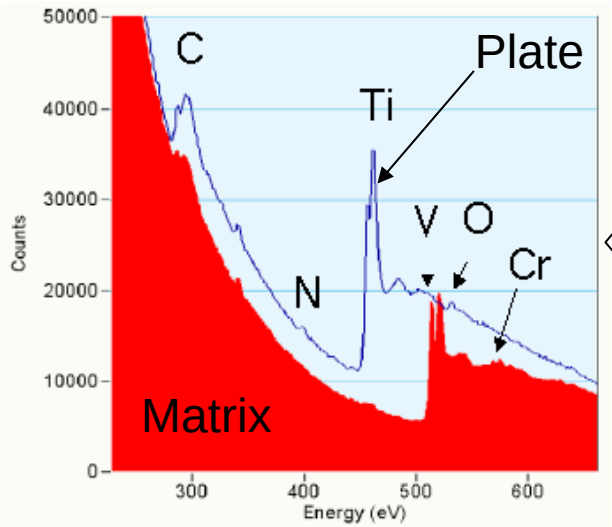
EELS Spectrum Profiles of Precipitates in V-4Cr-4Ti

Unirradiated



Annealed 1000°C

Ti-C rich (Ti-CON)



Annealed 950°C/1h

Ti-C rich (Ti-CON)

12.8 O, 24.1 C, 4.9 N

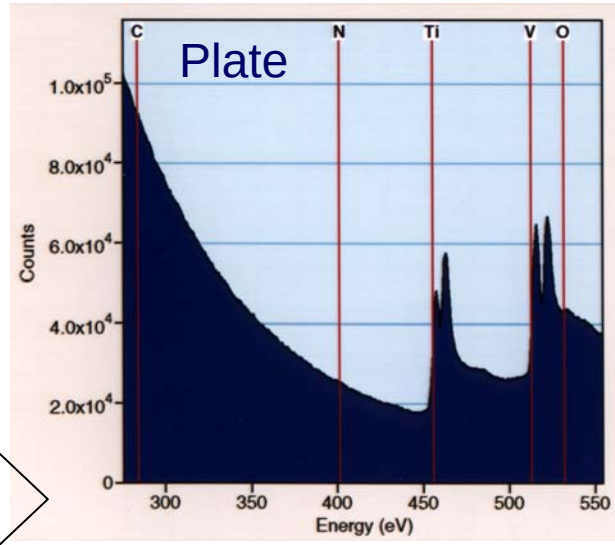
$Ti_{58.2}(CON)_{41.8}$

Irradiated HFIR 13J

4 dpa ; 340/520°C

Ti-rich <10 (O, N at.%)

no C



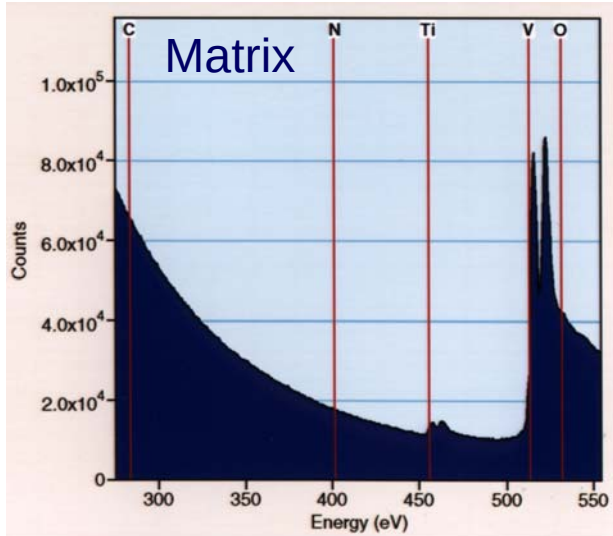
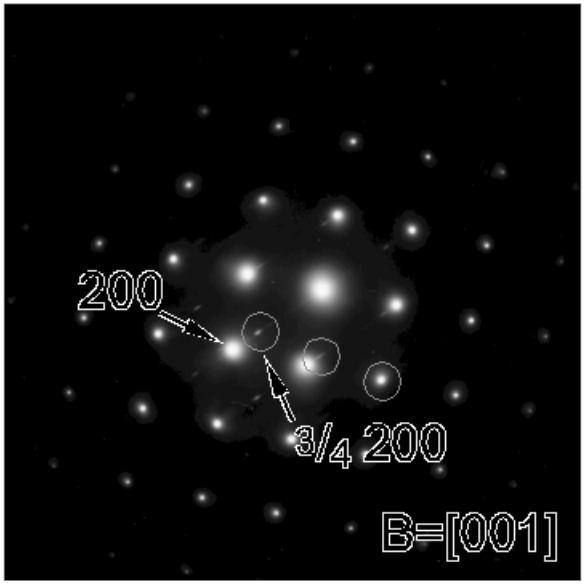
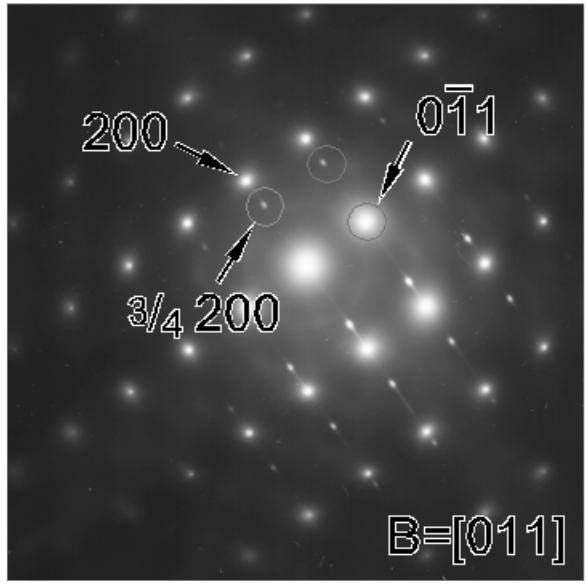
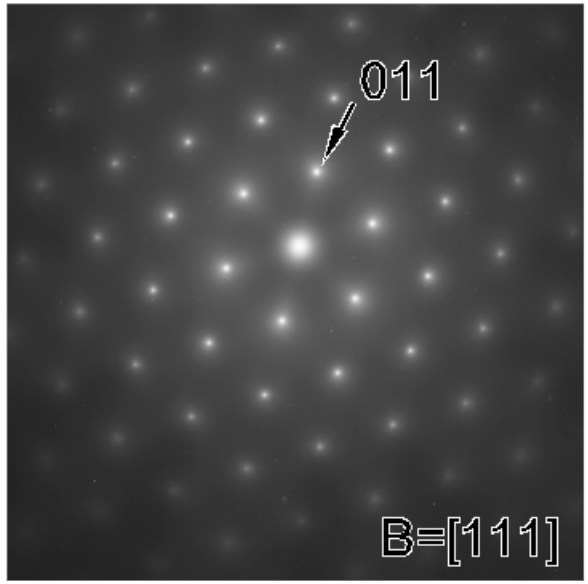
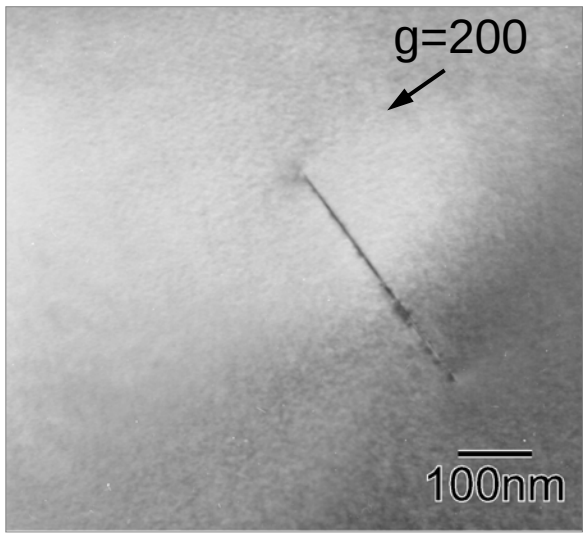


Plate Shaped Secondary Precipitates





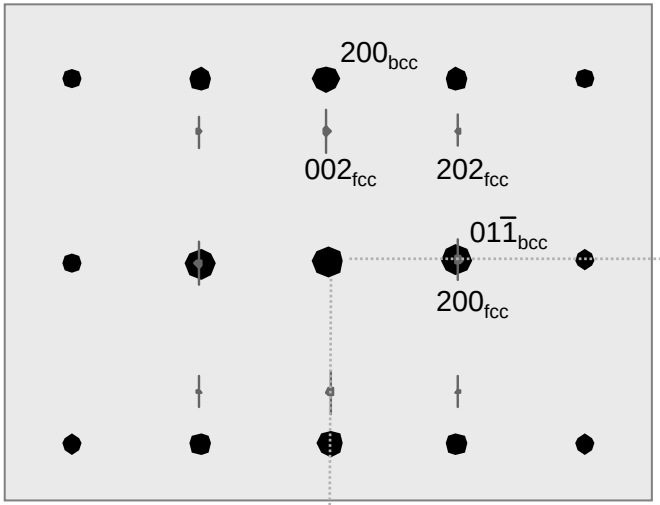




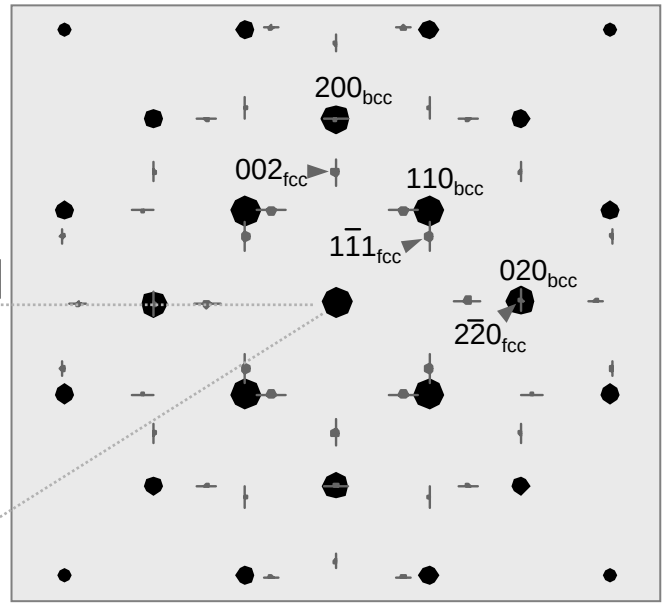
Close to [001]

- {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

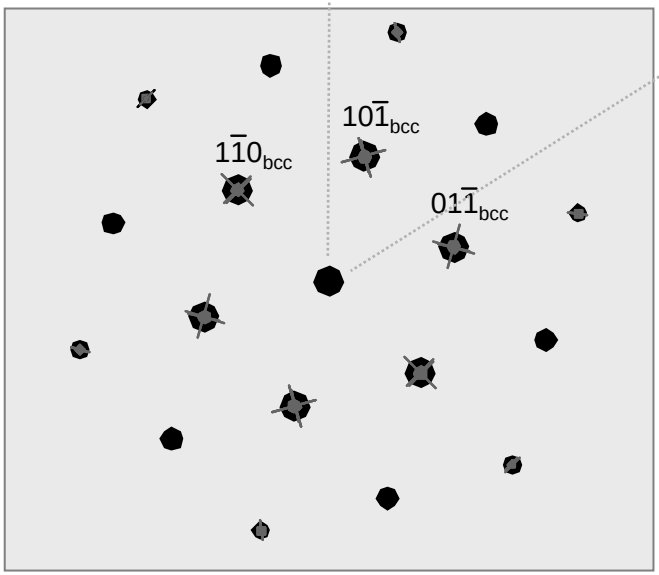
Simulated Electron Diffraction Patterns



[011]



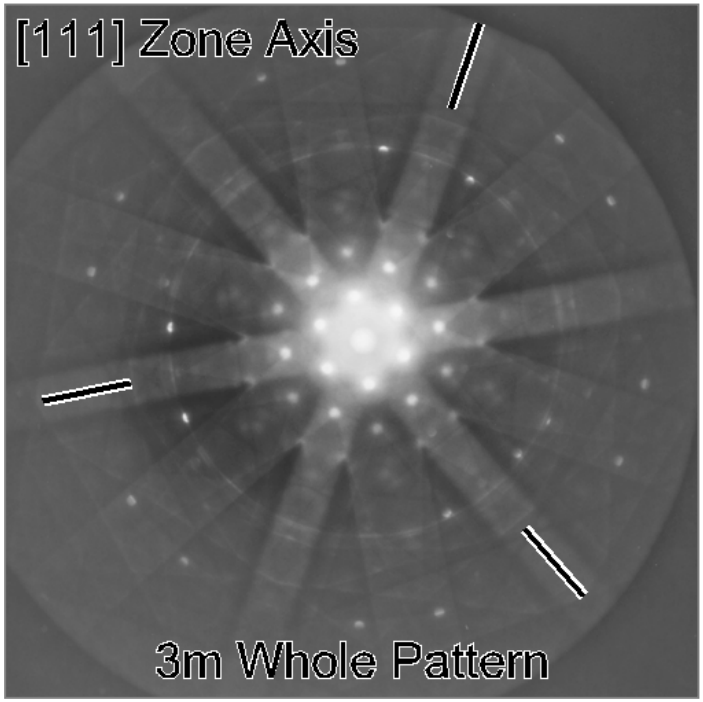
[001]



[111]

- Electron diffraction patterns consistent with fcc Ti(CON)
  - 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

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(CON)
  - 3m [111] and 4mm [100] whole pattern symmetries
  - interplanar angles, d-spacings, and structure factor contained in SAD patterns

Determination of Solvus for Globular Ti(CON)

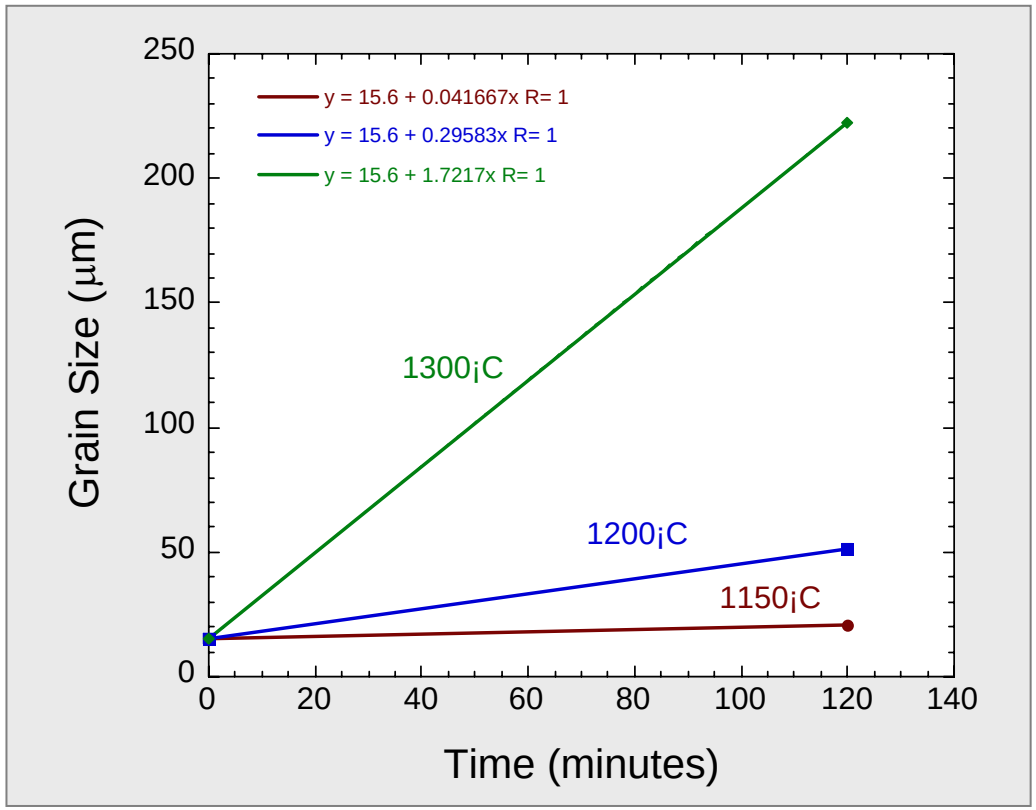
- **Previous work**
  - **1125°C CVN impact test data of V-4Cr-4Ti**
    (Kurtz, Hamilton, and Li, USFMSR, 1997)
  - **1100°C Heat treatments of NIFS-Heat-1 and NIFS-Heat-2**
    (Nagasaka et al. 2nd WS on Development V Alloys for Fusion, 2001)

- **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

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

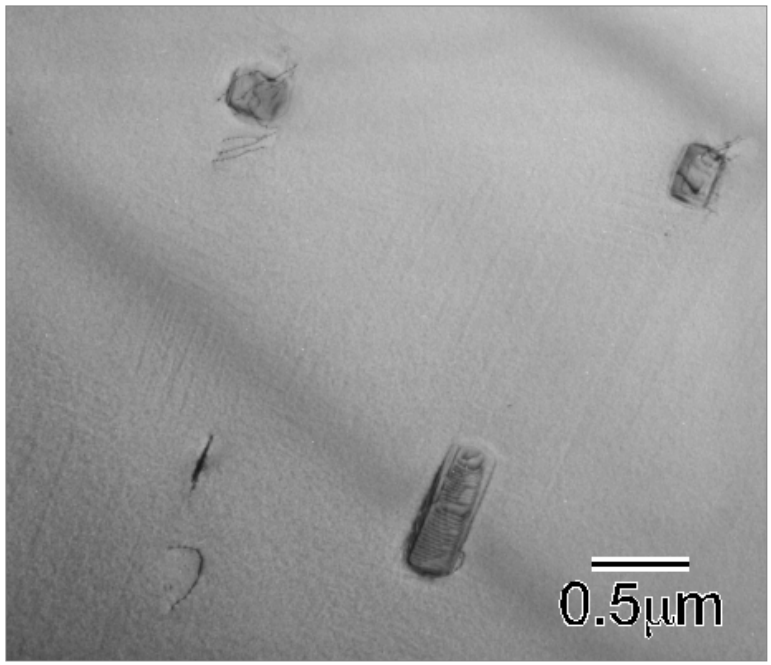
Temperature (¡C)	Grain Size (μm)
1150	20.6
1200	51.1
1300	222.2



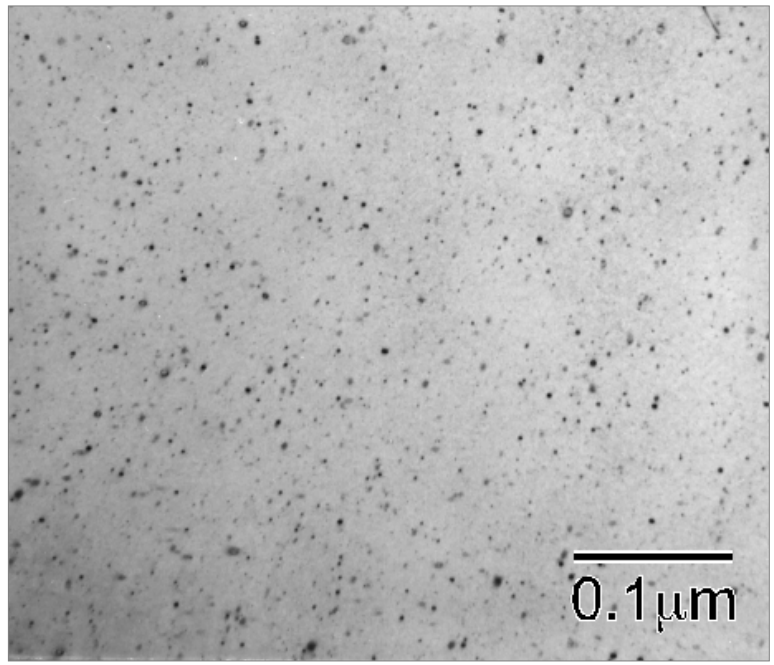
- Grain size does not change significantly below 1150°C
- Rapid increase in grain size occurs above 1200°C
  - possible correlation with dissolution of globular Ti(OCN)

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

1200°C/2h

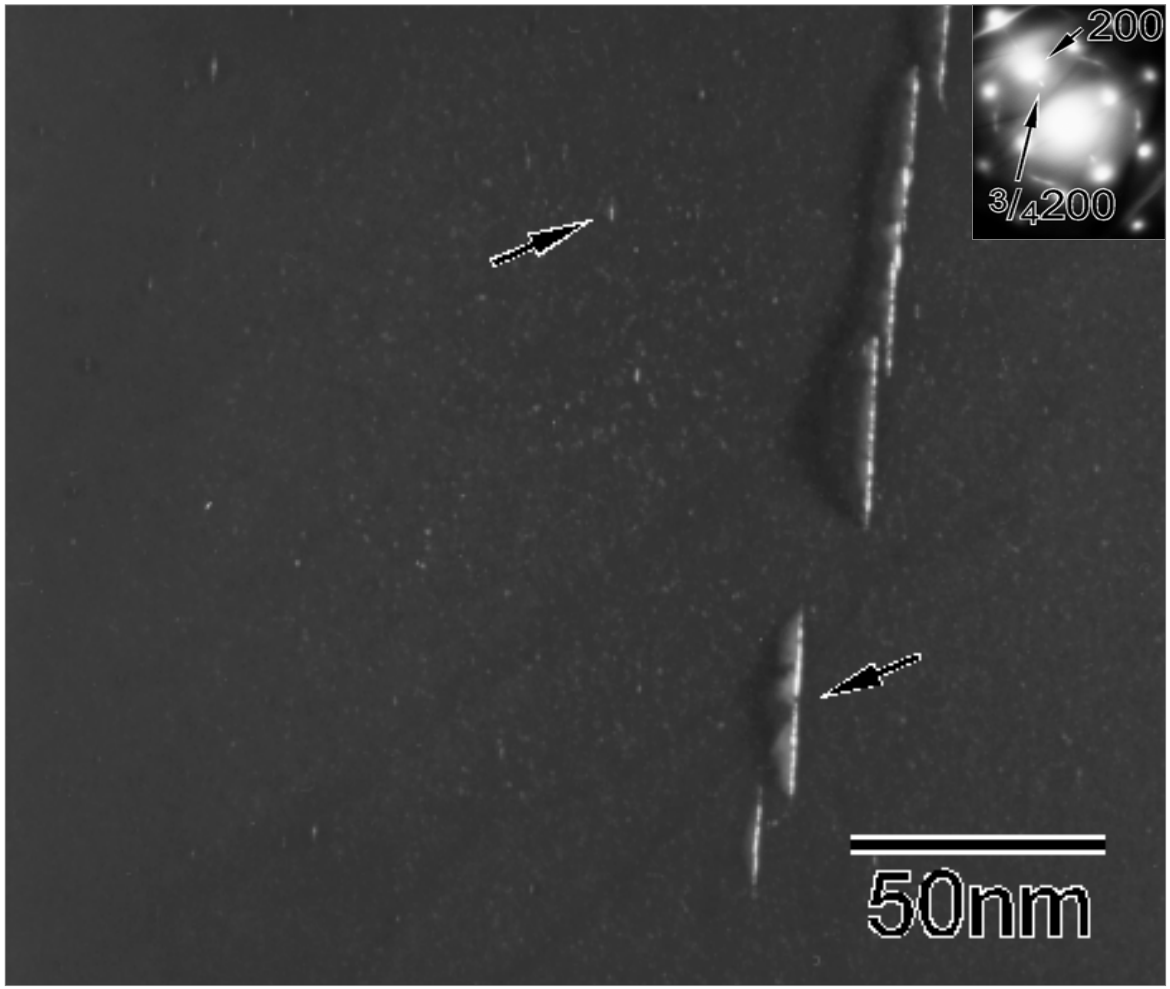


1300°C/2h



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

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



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

Summary

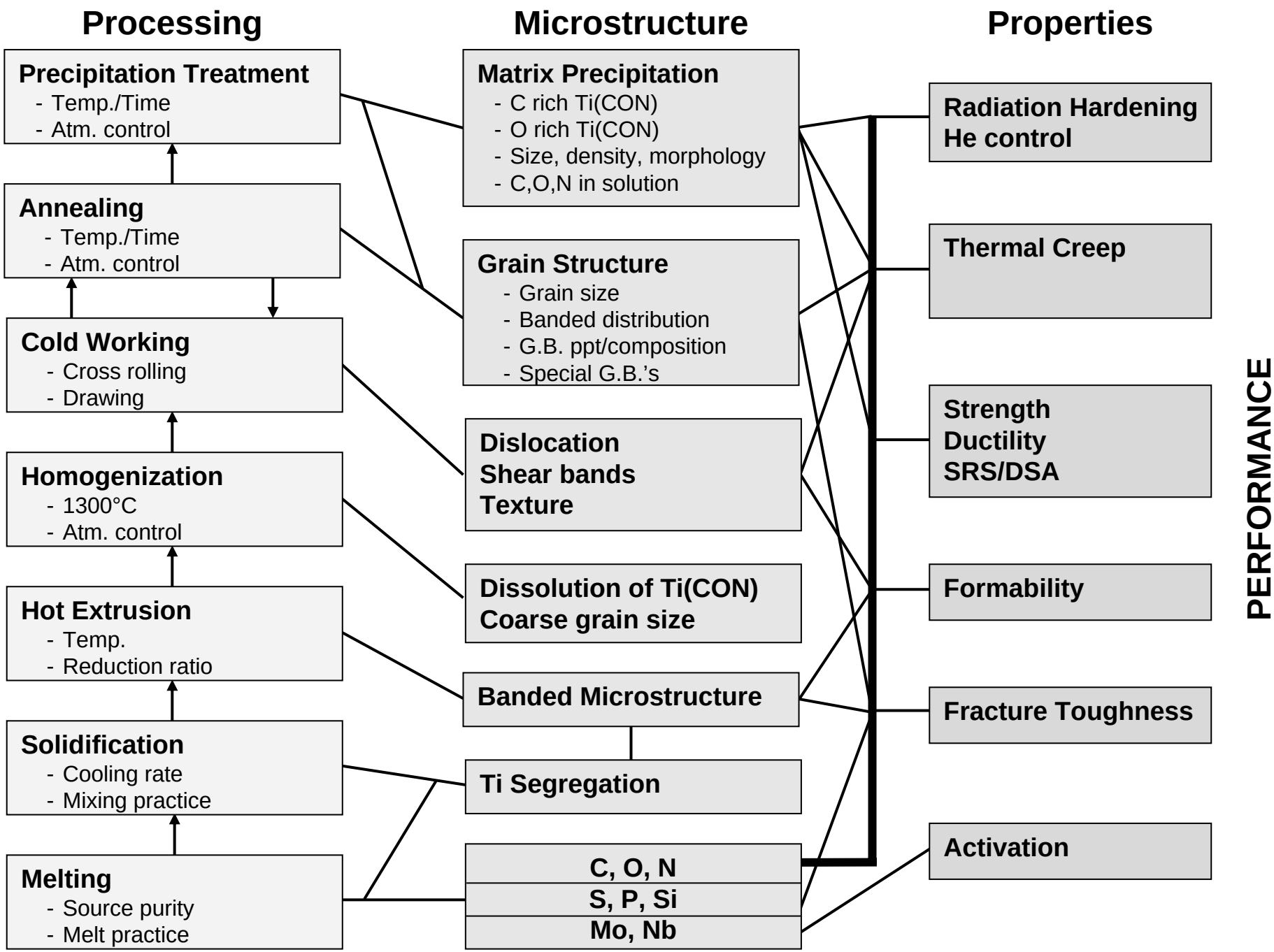
- Solute Ti interacts with interstitial (O,C, N) impurities by:
  - lowering the mobility of interstitial solutes
  - increasing the barrier strength, impeding dislocation motion
  - shifting the maximum negative SRS by ~300ºC (static and dynamic strain aging)
  - forming {100} plate Ti(CON) precipitates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

Key Issues

- Need a better understanding of the physical metallurgy of the V-Cr-Ti system
  - solubility and diffusion data of interstitial solutes in the alloy
  - development of TTT diagrams for controlling the precipitation behavior
- The formation and structure of precipitiates in V-4Cr-4Ti has improved, but requires further work
  - composition variations of plates
  - relationship between precipitate morphologies: do different interstitial solutes control the nucleation of globular & plates ppt.
  - investigate the thermal stability of the nano-size Ti(CON) plates
- Need to understand the origin of the banded grain structure and whether it is the cause of problems in tube fabrication
  - do we incorporate a high T solutionizing treatment during processing

Future Issues

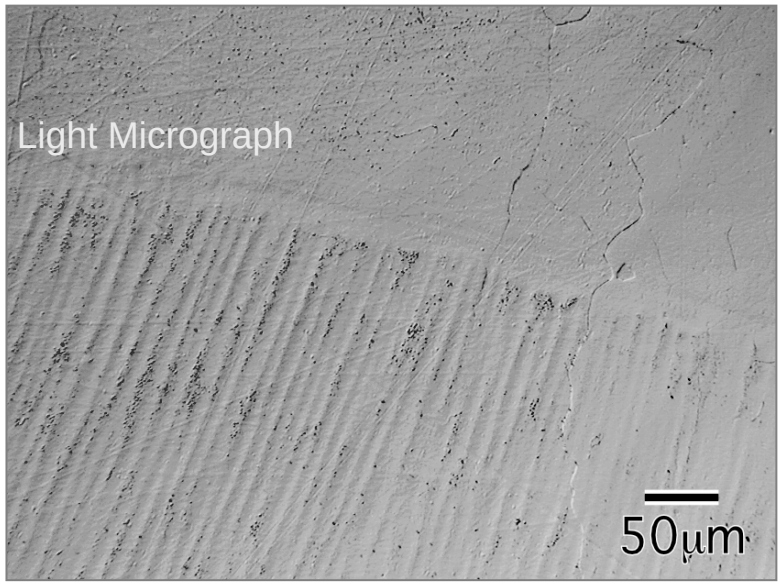
- Development of V-based alloys for improved high temperature strength:
  - beyond V-4Cr-4Ti compositions to optimize Ti-(CON) ppt.
  - alternative alloying to promote stable compounds, i.e. Al, Si, Y, Zr
  - beyond V-Cr-Ti system: activation issues

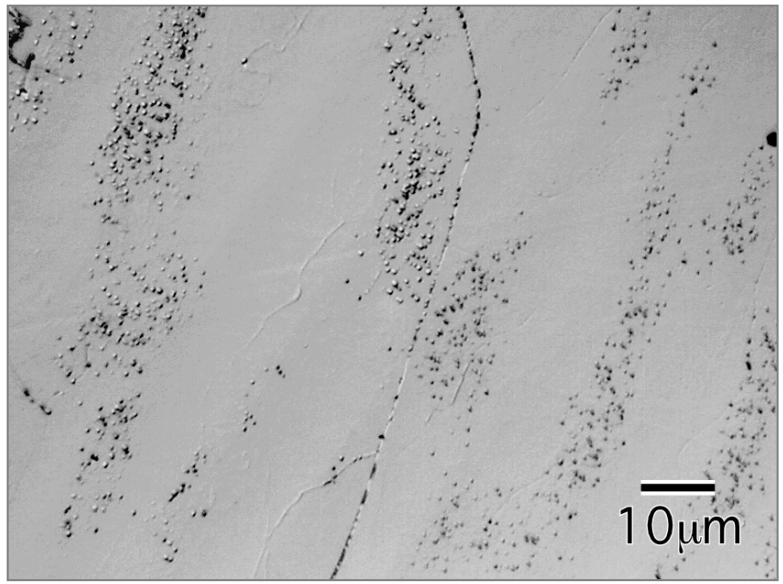

Processing
Microstructure
Properties
Precipitation Treatment
- Temp./Time
- Atm. control
Annealing
- Temp./Time
- Atm. control
Cold Working
- Cross rolling
- Drawing
Homogenization
- 1300°C
- Atm. control
Hot Extrusion
- Temp.
- Reduction ratio
Solidification
- Cooling rate
- Mixing practice
Melting
- Source purity
- Melt practice
Matrix Precipitation
- C rich Ti(CON)
- O rich Ti(CON)
- Size, density, morphology
- C,O,N in solution
Grain Structure
- Grain size
- Banded distribution
- G.B. ppt/composition
- Special G.B.'s
Dislocation
Shear bands
Texture
Dissolution of Ti(CON)
Coarse grain size
Banded Microstructure
Ti Segregation
C, O, N
S, P, Si
Mo, Nb
Radiation Hardening
He control
Thermal Creep
Strength
Ductility
SRS/DSA
Formability
Fracture Toughness
Activation
PERFORMANCE

Recent Focus is on Segregation of Solute Atoms

Isochronal annealing from RT to 1200°C

(1hr at either 50°C or 100°C increments - 14 total)

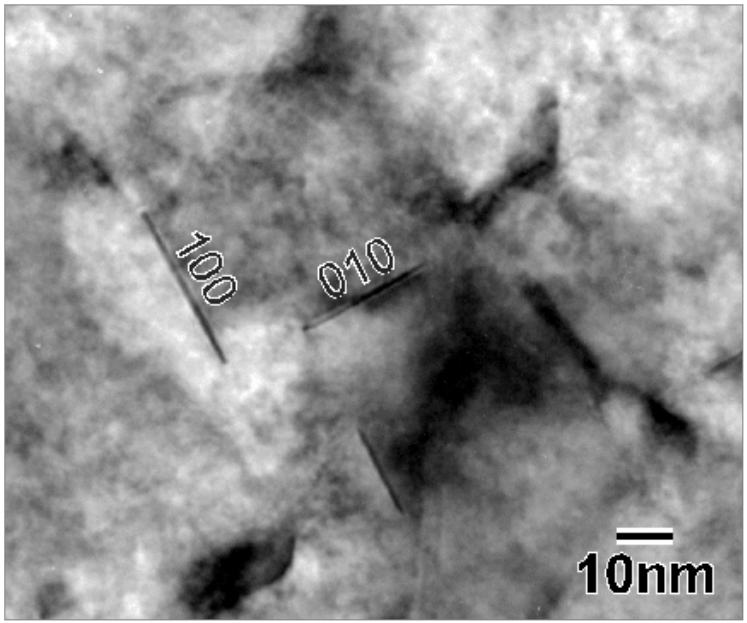


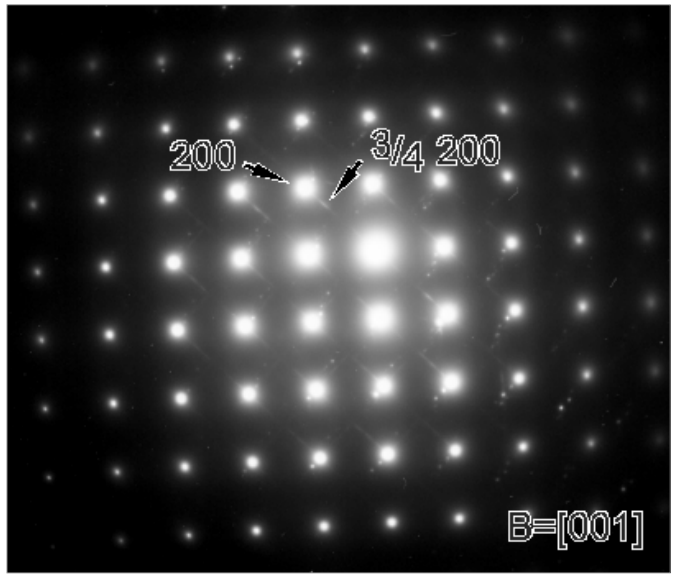


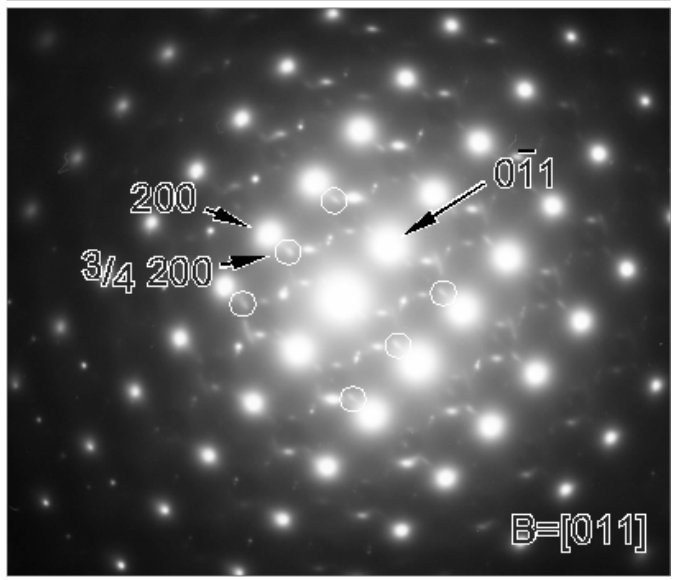
- **Evidence suggests that Ti segregates during solidification in GTA weld fusion zone**
  - **globular Ti(OCN) forms preferentially in Ti-rich regions during the isochronal annealings**

- **Also, from microprobe analysis of ingots prepared in RF**
  - **composition modulations in Ti; λ = ~55μm *(M.M. Potapenko et al. 1999)***

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

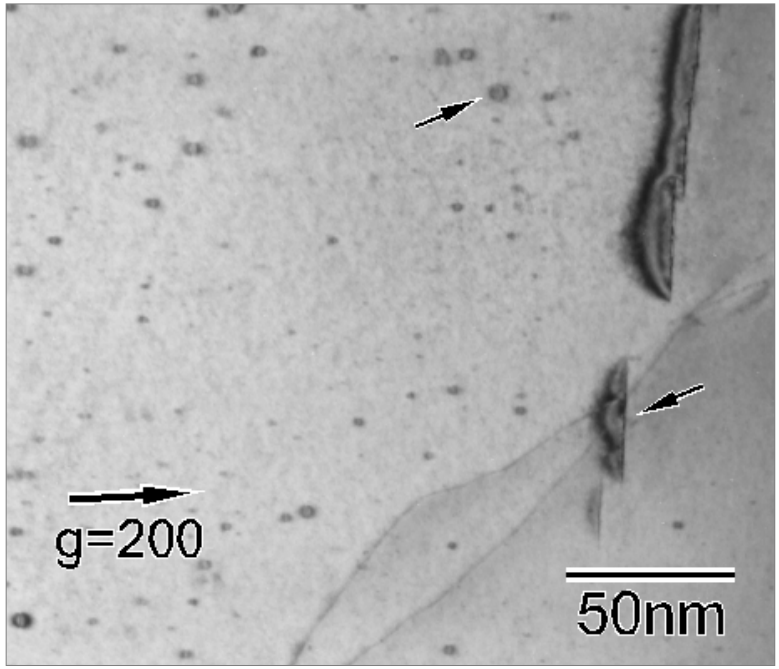
Structural Analysis of Ti(CON) Phase

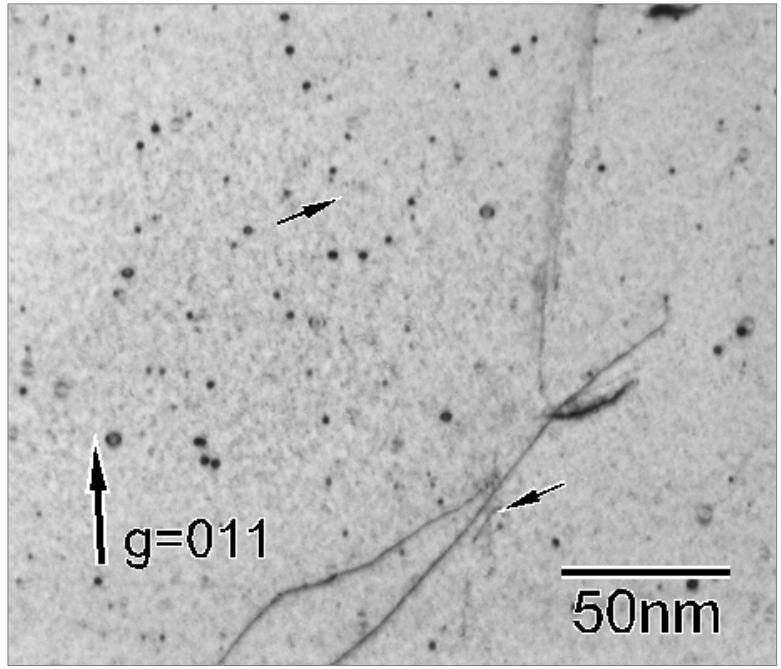
- Lattice parameters from JCPDS and composition ranges

Phase	Composition (at.% x)	Space Group	Lattice Parameter	PDF Number
γ-TiO_x	34.9 to 55.5	Fm3m	4.177	8-0177
TiN_x	28 to > 50	Fm3m	4.256	6-642
TiC_x	32 to 48.8	Fm3m	4.3285	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: 0.419 +/-0.01 nm
  - best agreement with TiO
- Temperature may be an additional factor

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**