Advanced Alloy Systems

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Overview

- Why do we need advanced alloy systems?
  - pushing the limits
  - limitations of current alloy systems
- What are the potential candidate advanced alloy systems that have been explored?
  - Tempered Martensitic Steels - evolutionary
  - Multi-phase V-Ti-Al alloys - revolutionary
  - Nanocomposited Ferritic Alloys - revolutionary
- Where are we going?

Advanced Alloy Systems are Being Explored to Increase Reactor Thermal Efficiencies

- Advanced Alloys
  - Designed to possess specific properties that exceed those of current materials being considered for first wall/blanket structural applications in fusion reactors
- Design Considerations
  - Good heat flux
  - High operating temperatures
    - creep properties (>0.45 T_M under irradiation)
    - long-term dimensional stability (>0.3-0.6 T_M)
  - Corrosion resistance in liquid and gaseous environments
  - Tolerance to radiation hardening and embrittlement (<0.4 T_M)
  - He management - resist He embrittlement (>0.5 T_M)

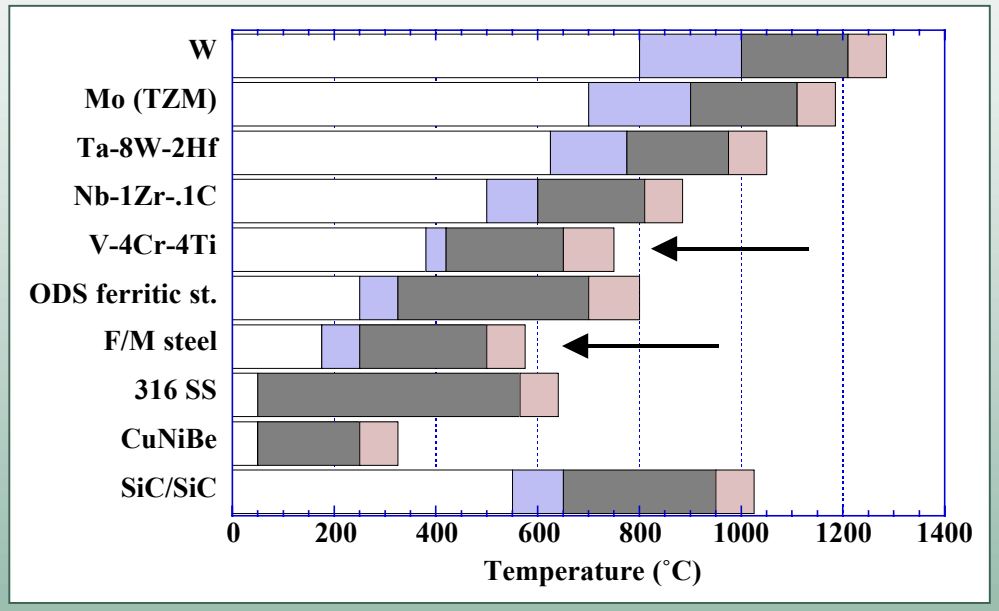
Irradiation Environment for a D-T Fusion Reactor is More Severe Than for a Fission Reactor

- Higher lifetime dose requirements for structure
- Higher He generation rates promotes:
  - He embrittlement of grain boundaries
  - void swelling
- Design microstructures in advanced alloy systems to manage and control He
  - trap He in fine stable configurations
  - particle and particle/matrix interfaces that form deep traps

Current Alloy Systems Have Key Limitations

- V-4Cr-4Ti Alloy
  - low temperature creep limits
  - low temperature radiation hardening
  - possible He embrittlement
  - requires MHD coating
  - poor oxidation resistance
- Ferritic/Martensitic Steels
  - low temperature radiation hardening
  - low temperature creep limits
  - possible He embrittlement
- *Refractory Alloys*

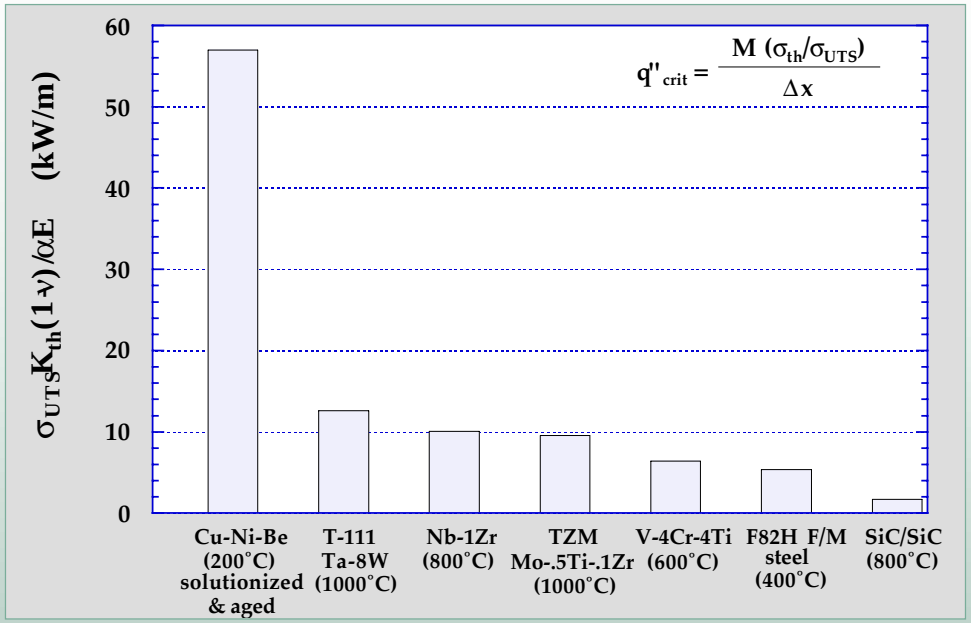
Operating Temperature Windows

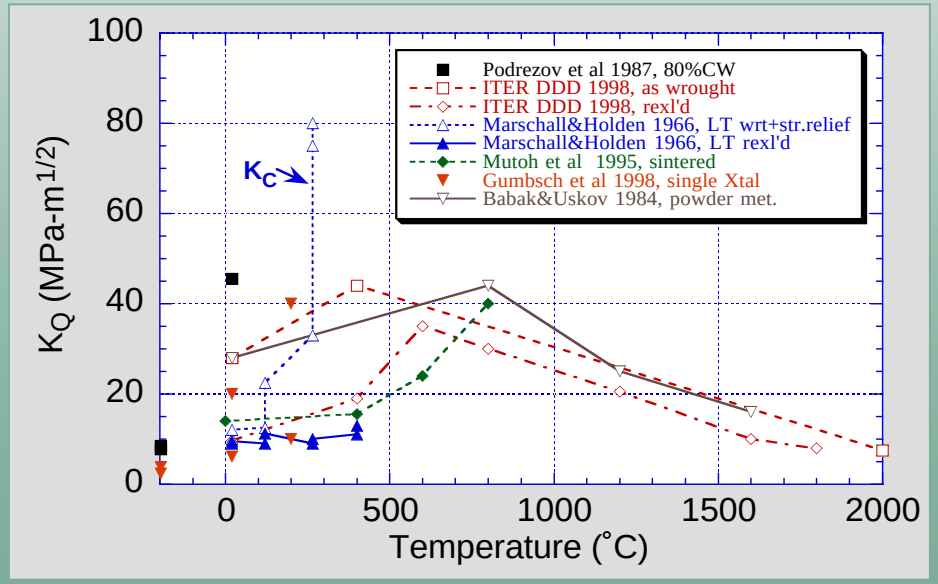


S.J. Zinkle and N.M. Ghoniem (2000)

Refractory Based Alloys

- Attractive Thermal/Physical Properties
  - high temperature capabilities
  - thermal stress figure of merit
  - liquid metal compatibility (Li)





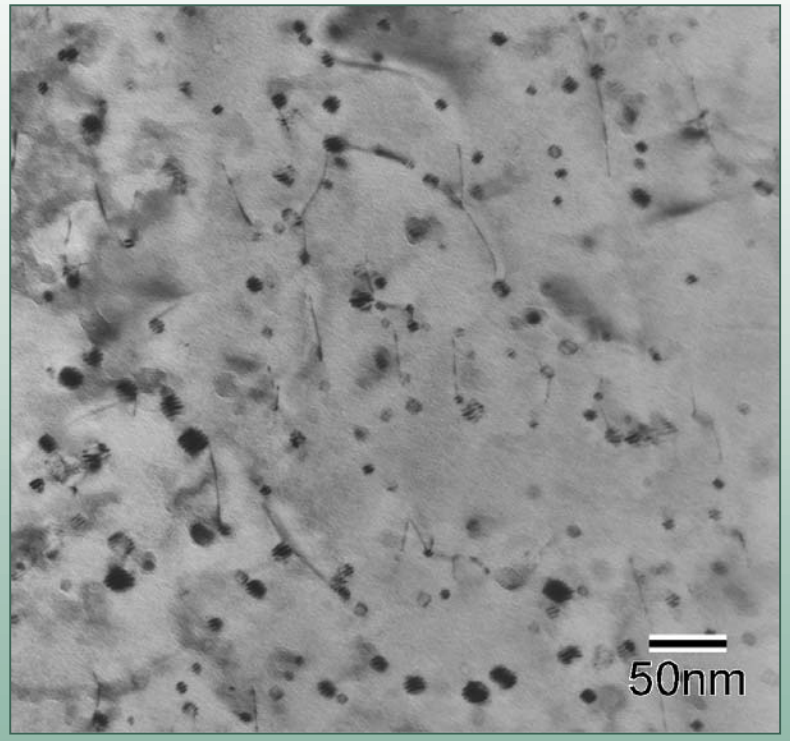
- Main problems
  - low fracture toughness
  - low oxidation resistance

Potential Candidate Advanced Alloy Systems Being Explored

- Age Hardenable Ferritic/Martensitic Steels
  - controlled precipitation in reduced activation Fe-Cr alloys
  - adapts well to current physical metallurgy practices
  - mechanical properties improvements show marginal increase in operating temperatures to 650°C
- V-Ti-Al Alloys
  - multi-phase approach based on γ-TiAl with ductile-second phase
  - potential increase in operating temperature to >700°C
- Mechanically alloyed ODS ferritic/martensitic alloys
  - most promising approach for increasing operating temperature to 800°C
  - presents many challenges to understanding non-equilibrium phenomena in materials science

Potential New Ferritic/Martensitic Alloy

- Dispersion-Strengthened Fe-9.5Cr-3Co-1Ni-0.6Mo-0.3Ti-0.07C steel
  - High number density of nano-size TiC precipitates
- Superior elevated-temperature strength and impact properties compared to conventional 9-12Cr steels
- Advantage over ODS steels: produced by conventional steel processing techniques
- Present composition not for nuclear applications; processing technique applicable to reduced-activation compositions

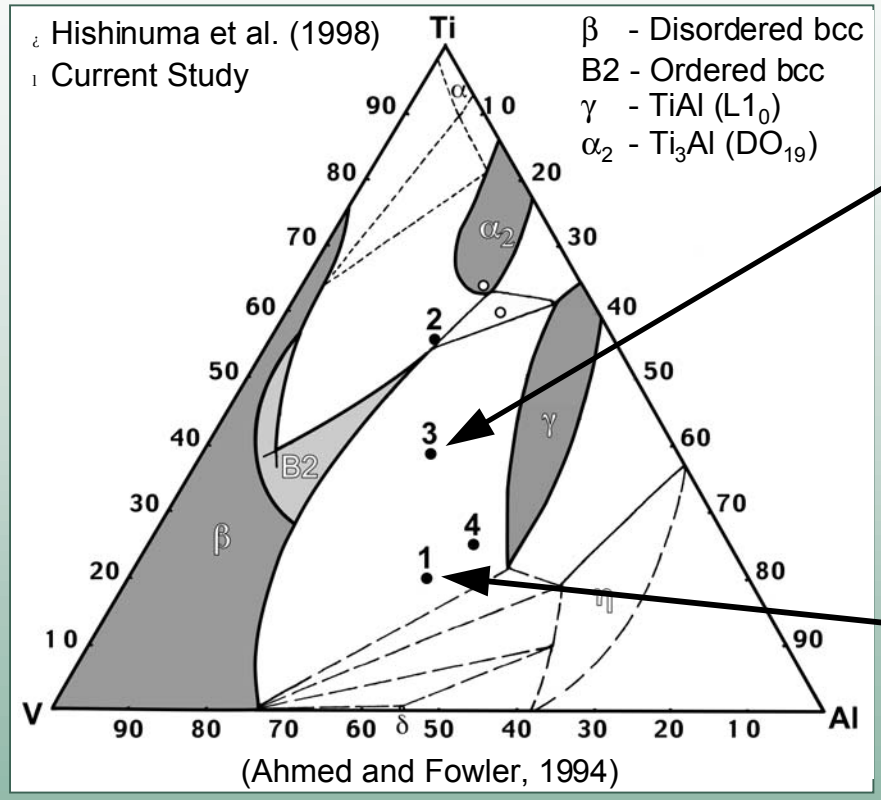


Motivation for Exploring Advanced V-Ti-Al Alloys

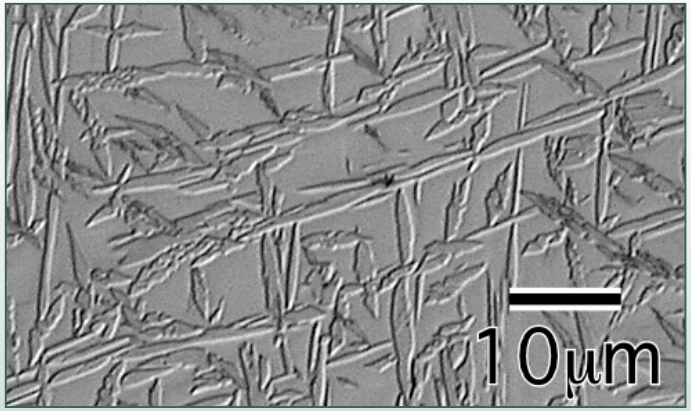
- Objective
  - to develop advanced alloys from the V-Ti-Al system using a multi-phase approach, consisting of either disordered β (bcc) or ordered β (B2-CsCl) and γ-TiAl (ordered $L1_0$) phases, for structural applications at temperatures up to 800°C targeted for He-cooled fusion reactor systems
- Leveraged by scientific and technical knowledge base developed for:
  - γ-TiAl ($L1_0$) intermetallic phase - *aerospace industry*
  - V solid-solution (β) phase - *fusion energy*
- Approach
  - combine phases and control microstructure to achieve attractive properties
    - β
      - low temperature ductility and fracture toughness
      - thermal stress factor
      - low activation
    - B2
      - high temperature strength
    - γ
      - high temperature strength and creep
      - thermal stress factor (similar to the V-4Cr-4Ti alloy)
      - oxidation resistance (alumina scale former)

Two-Phase Alloys Identified in V-Ti-Al System

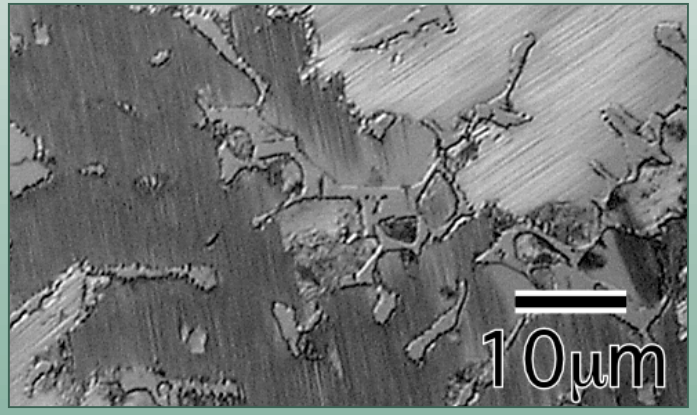
600°C Isotherm



(Ahmed and Fowler, 1994)



γ-Laths in B2 Matrix

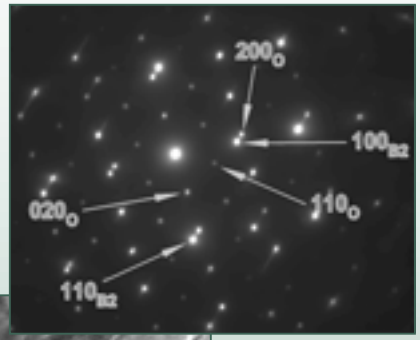


Primary α transforming to γ plates and interdendritic β (retained)

- Extensive Composition Range Exists Between γ-TiAl and β/(B2) Phases

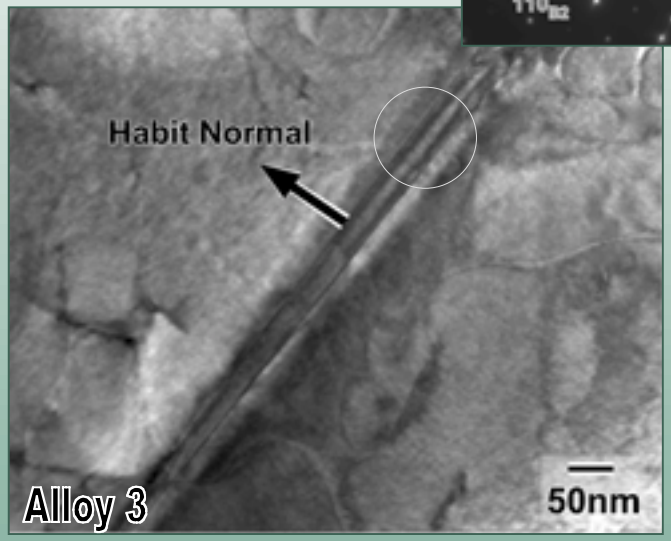
Results Obtained in Feasibility Study are Pertinent to Intermetallics Community

- No structural variants of the ω phase have been observed in the β and B2 phases



$B=[011]_{B2}//[001]_O$

~15° CCW from (211)



No superlattice reflections
$B=[001]_\beta$

- Orthorhombic phase (Cmcm space group) transforms displacively from B2 (#3: 25V-32Ti-43Al)
- Development of a β + γ lamellar microstructure (#1: 31V-16Ti-54Al)

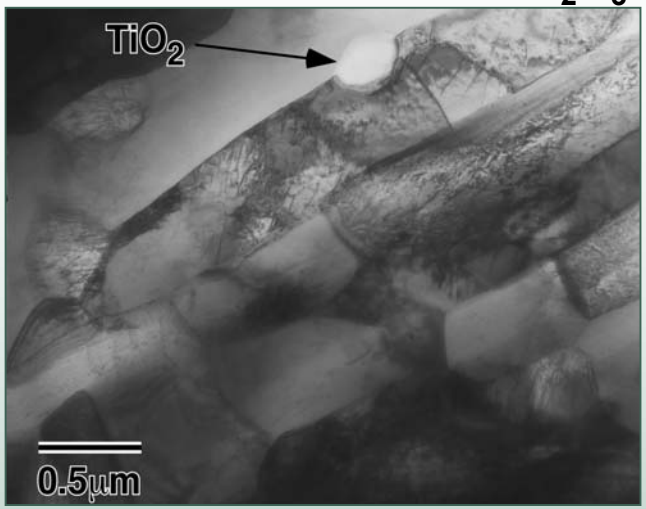
Studies on ODS Ferritic-Martensitic Alloys Have Focused on Processing and Properties Issues

- Commercially Developed ODS Ferritic Alloy for Breeder Reactor Program
  - INCO MA957 (Fe-14Cr-03.Mo-O.9Ti + 0.25Y_2O_3)
    - deformation and fracture
    - irradiation
- Experimental Nanocomposited Iron Alloys
  - Fe-(8-9)Cr Martensitic Alloys + Y_2O_3-Oxide
    - processing
    - mechanical properties
  - Fe-(12-14)Cr Ferritic Alloys + Y_2O_3-Oxide
    - processing
    - oxidation
    - deformation and fracture
    - thermal creep
    - nanostructural characterization

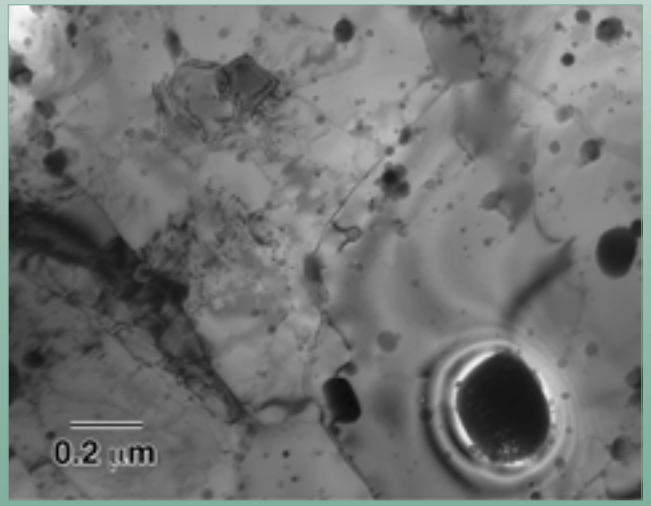
Oxide Dispersion Strengthening Approach

- Perspective
  - +50 year history
- Benefits
  - any desired combination of matrix composition and dispersoid
  - significant improvements in high temperature mechanical properties
- Problems
  - time-consuming & expensive
  - often produces materials with:
    - **anisotropic properties**
    - **coarse particles with non-uniform size and spatial distribution**
  - joining and fabrication
  - lack of understanding - experiment, theory, and modeling

Fe-13Cr-3W-0.4Ti + 0.25Y_2O_3



Fe-9Cr-2W + 0.33TiO_2 + 0.67Y_2O_3



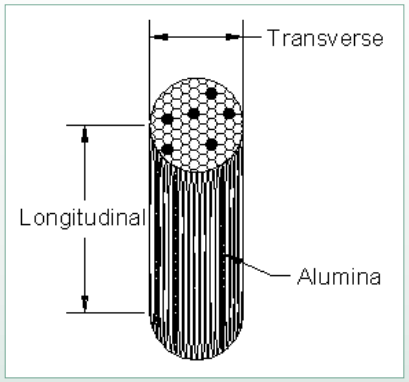
Radiation Behavior of MA957

- FFTF/MOTA irradiation test - 420°C to 200dpa *(peak irradiation swelling temperature)*
  - Encouraging results
    - swelling was similar to or less than optimized M steels (HT-9 & T91)
    - tensile strengths unaffected & elongation slightly degraded
    - oxide dispersoids are resistant to radiation damage

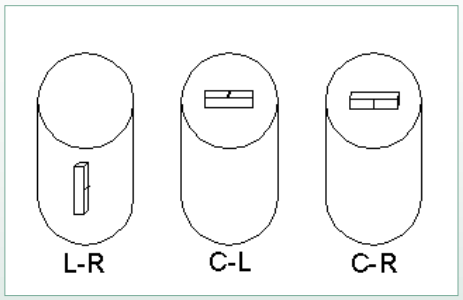
Alloy	Composition (wt.%)	Swelling (% density change)	Highest Swelling (%)	Mean Void Size (nm)	Void Density ($^{\#}/cm^3$)
T91	Fe-8.43Cr-0.89Mo-0.24V-0.37Mn	1.76	5.0	21.4	4.8×10^{15}
MA957	Fe-13.8Cr-0.26Mo-0.90Ti + $0.26Y_2O_3$	1.75	3.73	6.1	9.2×10^{14}
MA957	Fe-13.1Cr-0.27Mo-0.95Ti + $0.25Y_2O_3$	0.25	3.5	35.4	8.6×10^{14}

  - Alloy design issues
    - void swelling restricted to prior recrystallized grains
    - precipitation of phase separated α' phase
    - heat-to-heat variations in properties behavior
- HFIR irradiation completed - ~800°C to 5dpa
  - Post-irradiation testing beginning

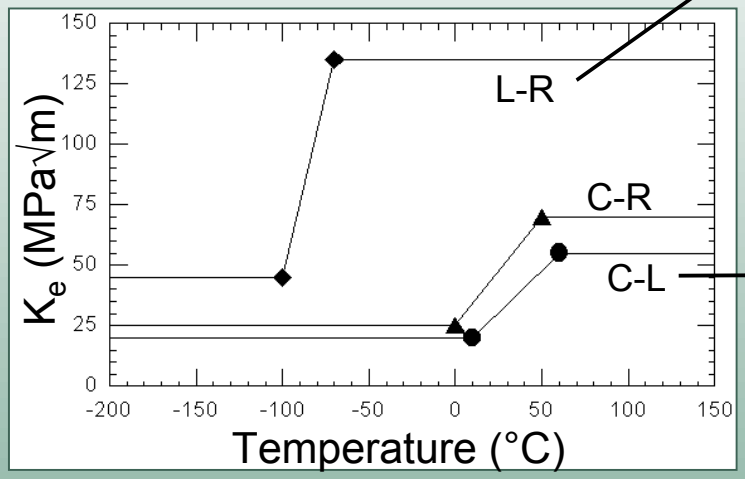
Low Temperature Toughness Behavior in MA957

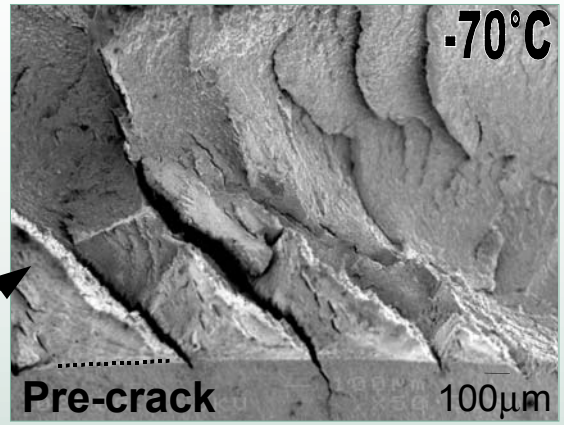


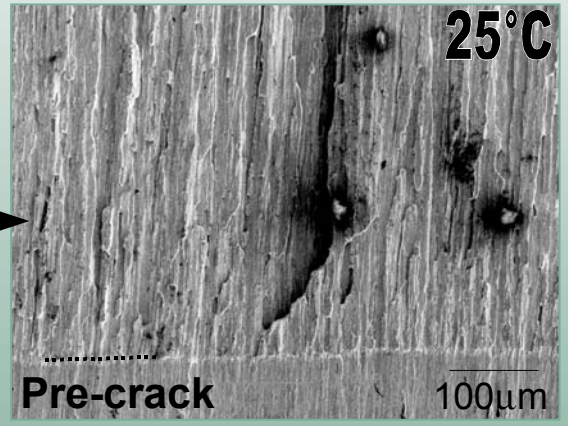
1/3-sized Charpy Specimens



Summary



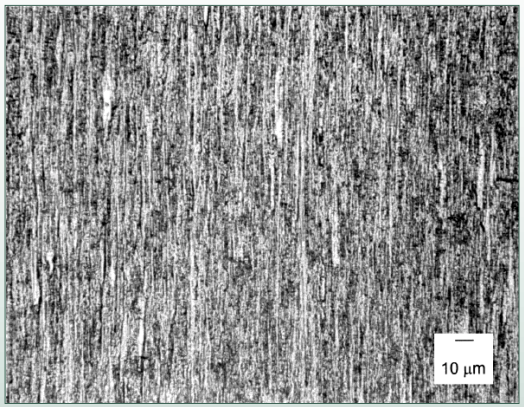




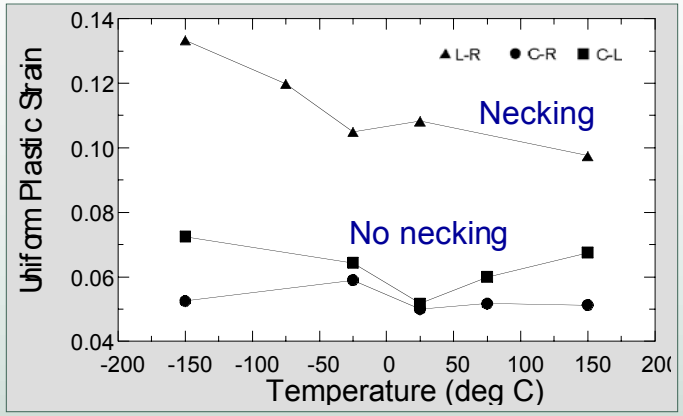
Crack Direction

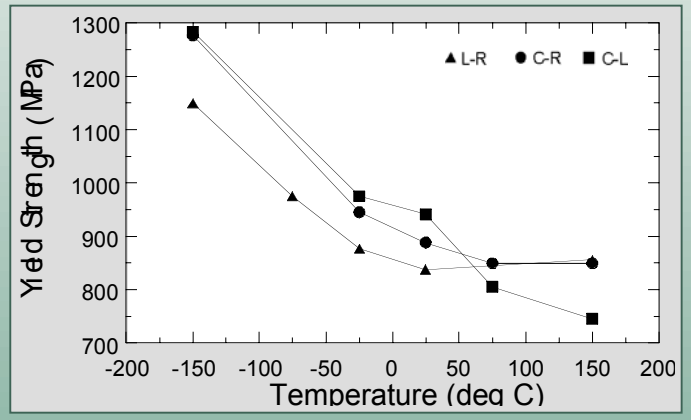
- Fracture toughness trends reflect the microstructural anisotropy in the longitudinal direction *(parallel to extrusion direction)*
  - correlated with 10:1 aspect ratio of grain size and Al_2O_3 stringers
  - highest toughness is achieved when the crack propagates orthogonal to elongated grains and Al_2O_3 stringers - (*L-R orientation)*

Anisotropic Tensile Properties Measured at Low Temperatures in MA957

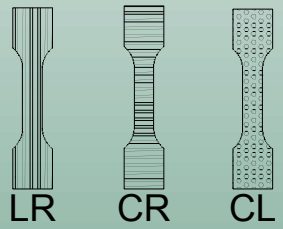


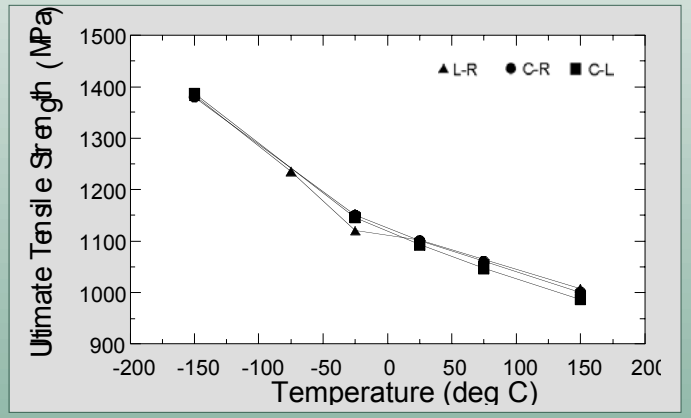
- Anisotropic structures
  - elongated grains (10:1 aspect ratio)
  - Al_2O_3 stringers
- Parallel to extrusion direction





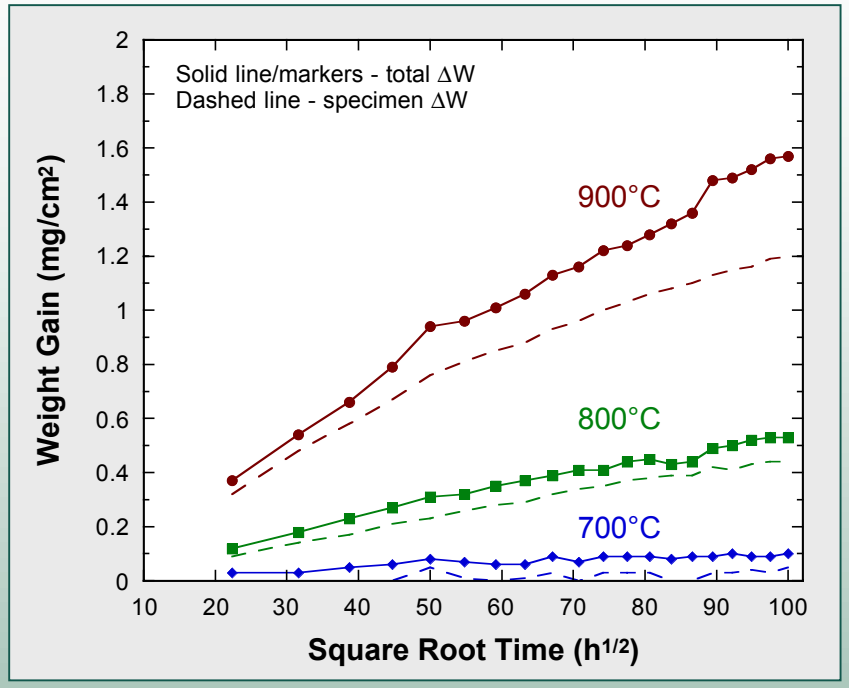
Tensile specimens oriented relative to extrusion direction

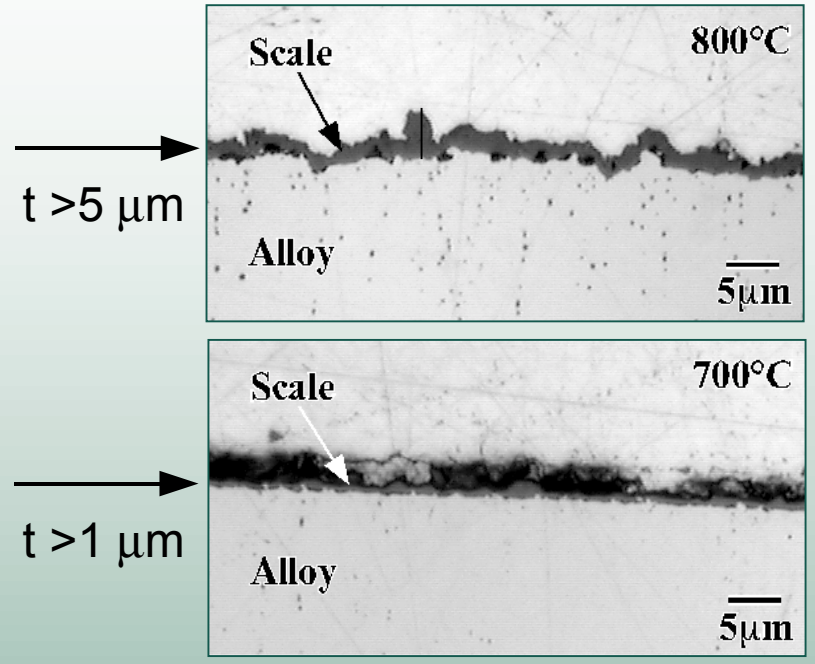




- For each orientation, yield strengths vary slightly and ultimate tensile strengths are equivalent
- The L-R orientation has the greatest capacity for strain accumulation

Oxidation Kinetics Decreased Significantly in ODS Fe-13Cr* Alloy



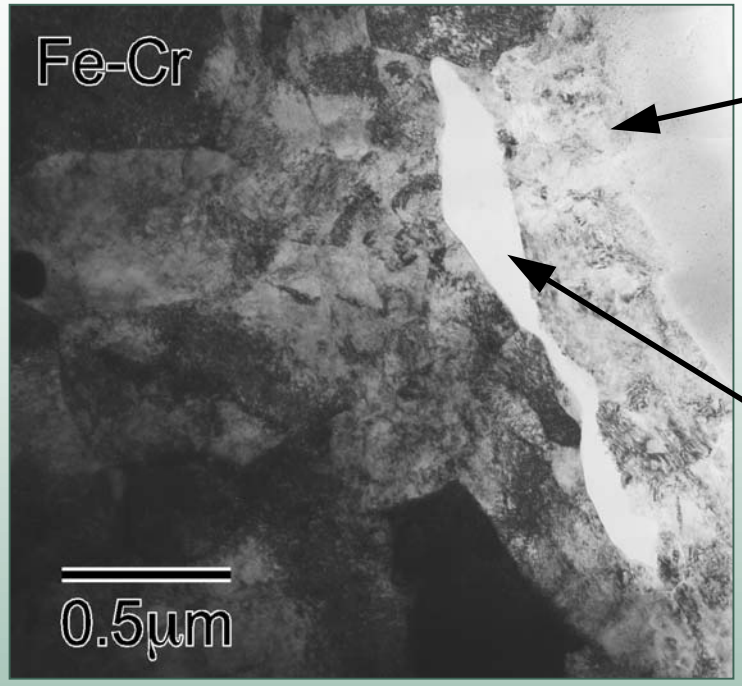


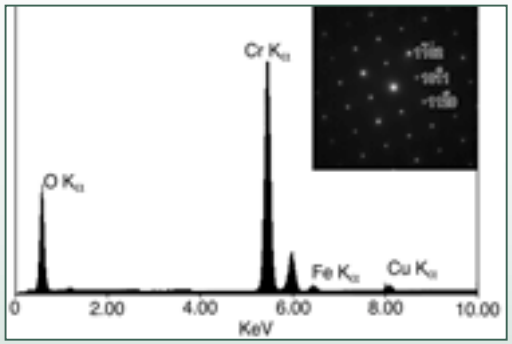
Material	Temperature (°C)	Time (h)	Parabolic Rate Constant (x $10^{-16} g^2 cm^{-4} s^{-1}$)
MA Fe-13Cr-3W-0.4Ti + 0.25Y_2O_3	700	10,000	1.9
MA Fe-13Cr-3W-0.4Ti + 0.25Y_2O_3	800	10,000	71
MA Fe-13Cr-3W-0.4Ti + 0.25Y_2O_3	900	10,000	630
Fe-25Cr	700	100	370

(Partly funded by Fossil Energy AR&TD Materials Program)

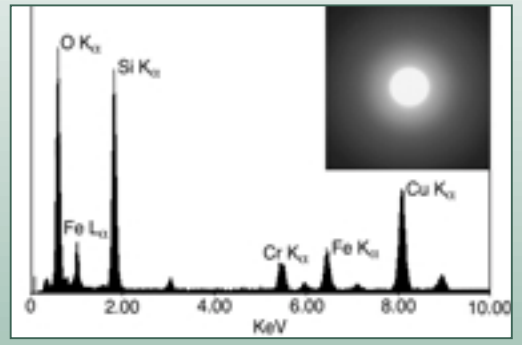
(Sumitomo, Kobe, & ORNL)*

Excellent Oxidation Behavior Attributed to Continuous Cr-oxide Surface Scale





Surface Cr_2O_3 Scale

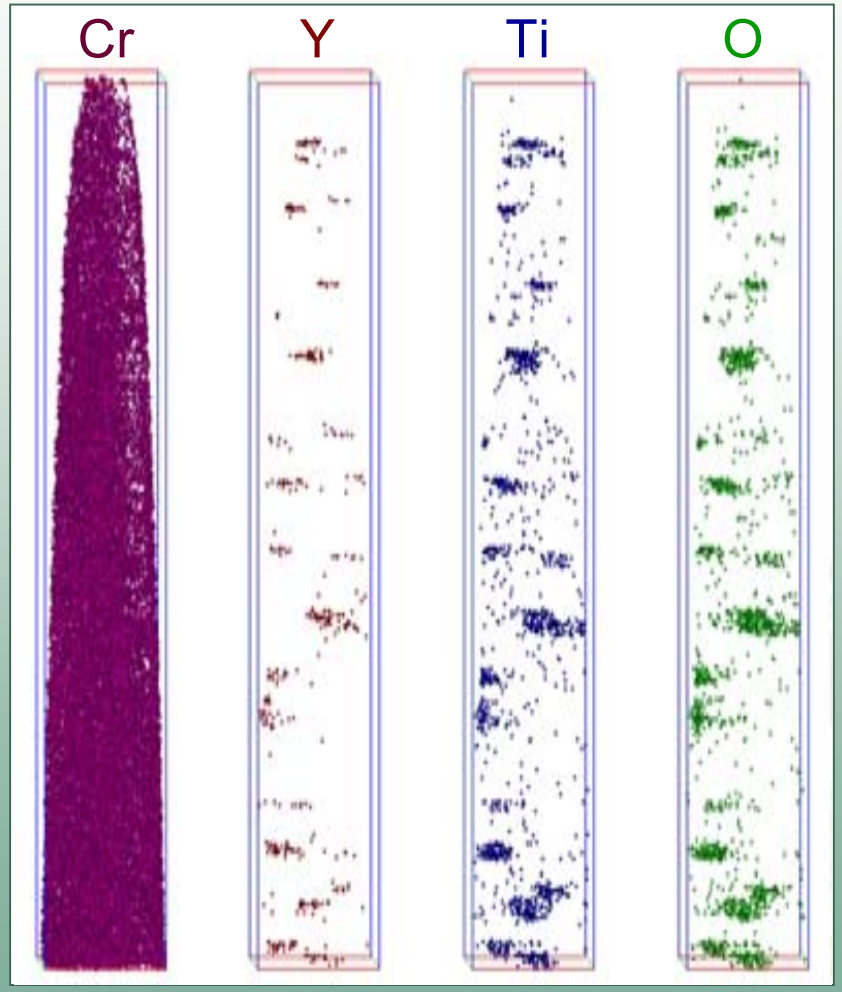


Amorphous SiO_2 Sublayer

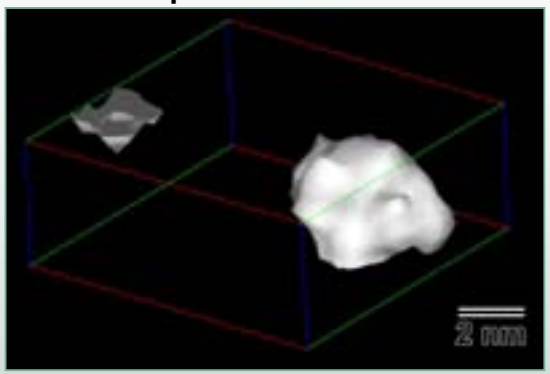
- Unexpected result
  - nominal 13%Cr in alloy is near the minimum Cr content to form a continuous protective scale
- Two additional factors contributed to low oxidation rate
  - Y_2O_3 dispersion reduces grain size and promotes Cr transport to surface
  - SiO_2 sublayer acts as diffusion barrier - even though only 0.05wt.%Si in alloy

Atom Probe Reveals the Presence of Nanoclusters in the MA ODS 12YWT* Alloy

3-DAP Atomic Coordinates



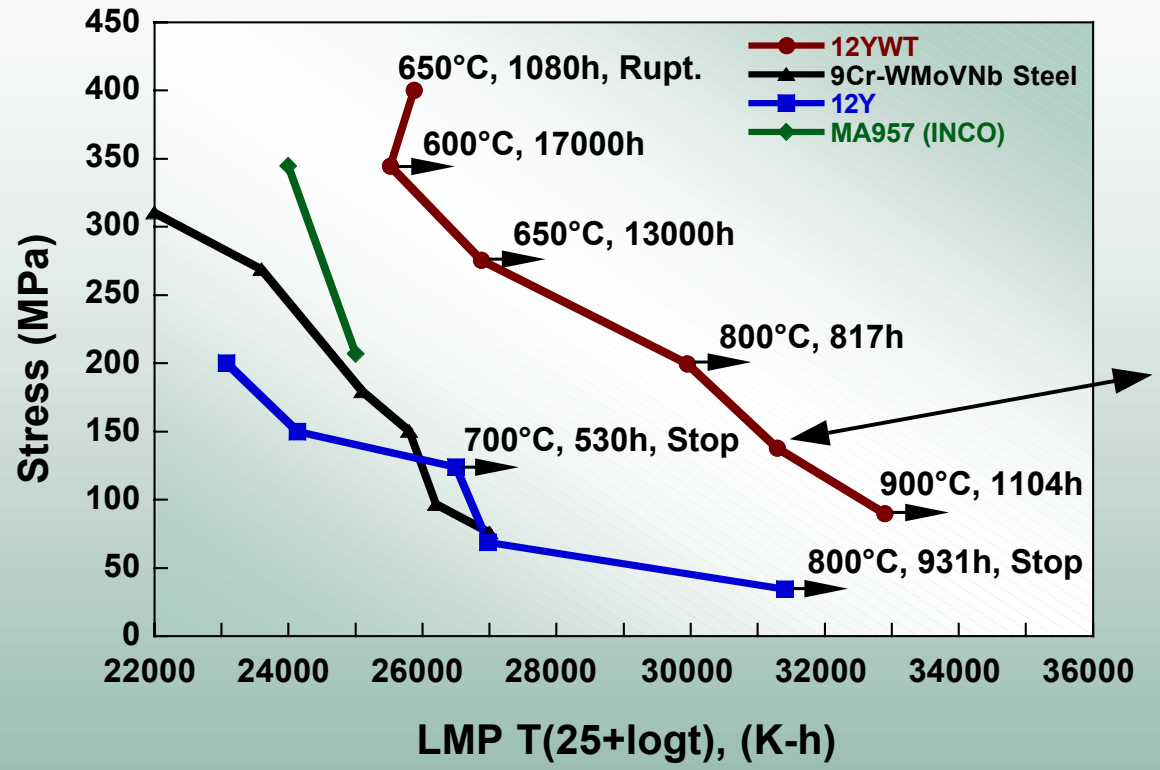
Isocompositional Surface

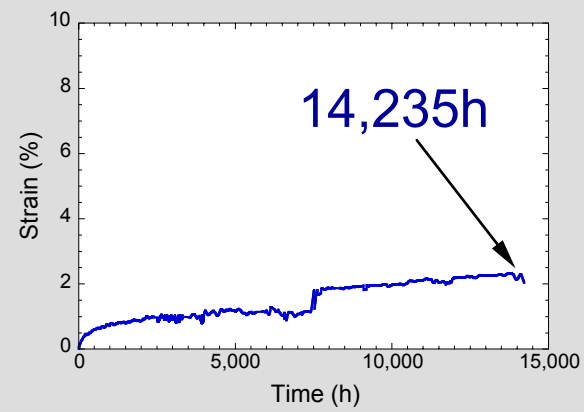


- Nano-size clusters
  - Average composition (at.%) :
    - O - 23.6 $\pm$ 10.6
    - Ti - 19.9 $\pm$ 8.7
    - Y - 9.2 $\pm$ 7.8
  - Size : $r_g = 2.0 \pm 0.8$ nm
  - Number Density : $n_v = 1.4 \times 10^{24}/m^3$
- Nanoclusters not present in ODS Fe-13Cr + $0.25Y_2O_3$ alloy

(Partly funded by ORNL LDRD Seed Money Fund)

MA ODS 12YWT Alloy Exhibits Excellent High Temperature Creep Strength



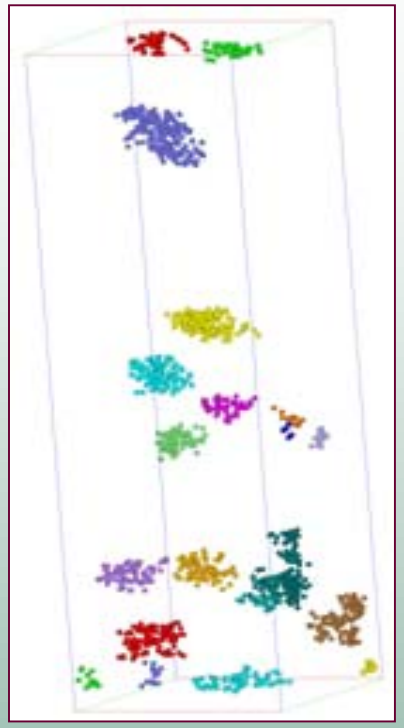


800°C and 138 MPa

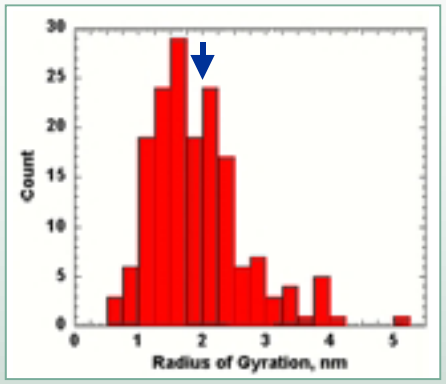
- minimum creep rate
  $2.13 \times 10^{-10} s^{-1}$
- total strain
  2.03%

- Time to failure is increased by several orders of magnitude
- Potential for increasing the upper operating temperature of iron based alloys by ~200°C

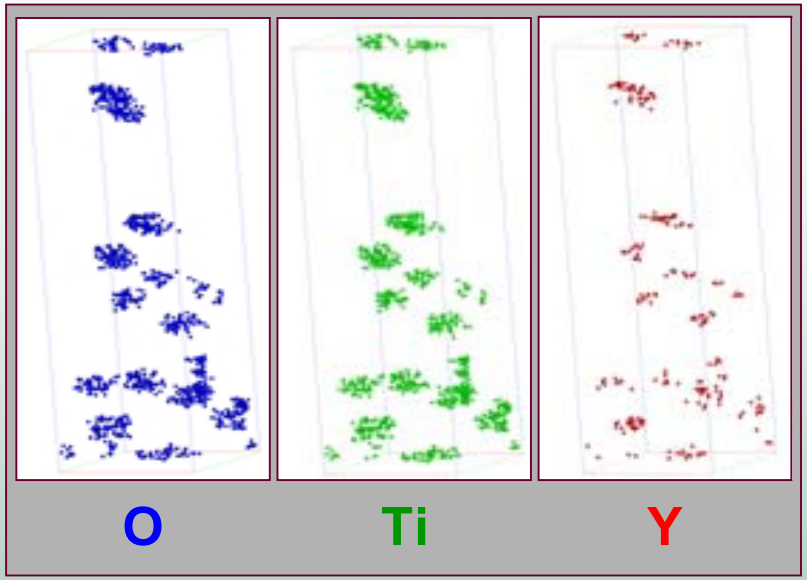
Recent Work Challenges Our Understanding of Thermodynamics at the Nanoscale



Volume = 22 x 21 x 73 nm



- R_g = 2.0 nm
- N_v = $1.4 \times 10^{24}/m^3$
- same as before thermal creep test



Average Composition of Nano-Particles (at.%)			
O	Ti	Y	Balance
28.1 +/- 9.8	24.6 +/- 8.5	7.9 +/- 4.9	Fe + ~5.6Cr

- These nanoclusters remain stable at 800°C and 138 MPa for >14,000h
- Understanding this phenomena will require theory and modeling
  - thermodynamic factors such as diffusivity, solubility and critical size
  - structural factors such as defect stabilization and interface

Future Directions

- Goal
  - to identify advanced material systems based on functionality and to provide experimental and theoretical insights for understanding processing, structures, and properties in advanced materials to achieve the desired function

- Other Interests
  - alternative processing paths for making nanostructures
    - internal oxidation
    - consolidation
  - nanocomposited vanadium alloys
  - functionally graded alloys
  - layered and coated systems