Advanced & Innovative Materials:

Advanced Nanocomposited and Precipitation Strengthened Alloys

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Critical Issues

- Advanced and innovative materials must be developed to meet higher performance goals, which usually implies higher operating temperatures and He management as well as assuming they meet the low, or reduced, activation requirements

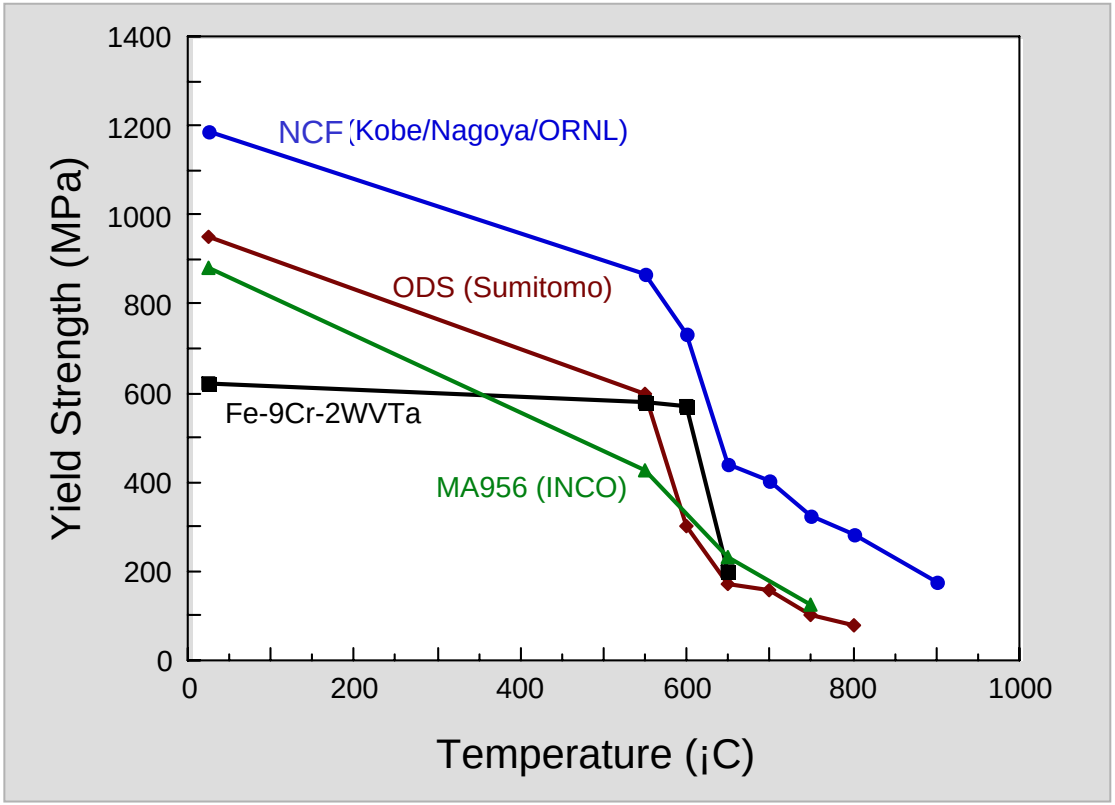
- A second phase particle dispersion in a Cr based ferritic alloy has the potential to satisfy all of these objectives

- But how do we determine when to commit a large research effort to develop these materials? What properties are most essential to make this assessment?

Particle Dispersion is Key to Improving the High Temperature Strength of Fe-based Alloys

- Precipitation strengthened steels
  - adapts well to current physical metallurgy practices
  - precipitation controlled by thermodynamics
  - marginal increase in operating temperatures to 650°C
- Oxide dispersion strengthened (ODS) steels
  - fabricated by mechanical alloying method
  - oxide particles are dispersed in a metal or alloy by ball milling
  - dramatic increase in operating temperatures can be achieved
- Nanocomposited ferritic steels (NFS)
  - superior mechanical properties result from high number density of stable nano-size atomic clusters
  - presents many scientific and technological challenges

Effect of Particle Dispersion on High Temperature Yield Strength Properties



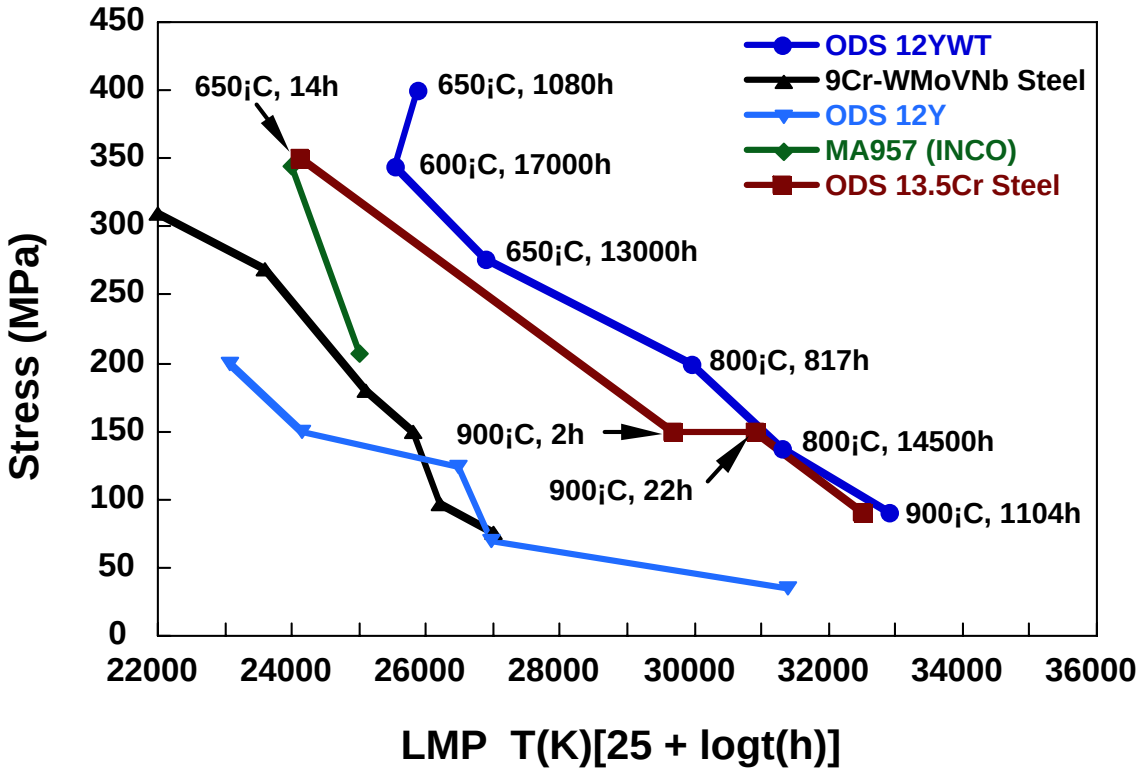
Nanoclusters : NCF alloy (12YWT: MA Fe-12Cr-3W-0.4Ti + Y_2O_3)

Oxides : Commercial ODS ferritic alloy (INCO MA956)

Oxides : Developmental ODS ferritic alloy (Fe-13Cr-3W-0.4Ti + Y_2O_3)

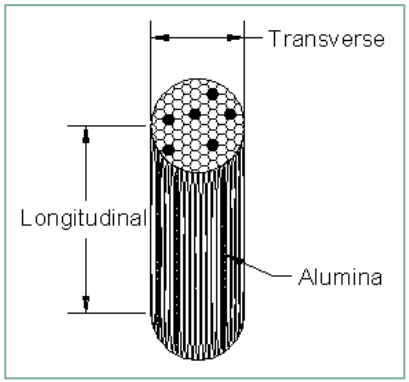
Non-ODS : Advanced ferritic/martensitic steel (Fe-9Cr-2WVTa)

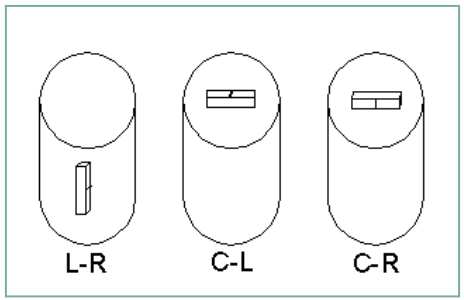
Long-Term, High Temperature Strength of Dispersion Strengthened Ferritic Alloys



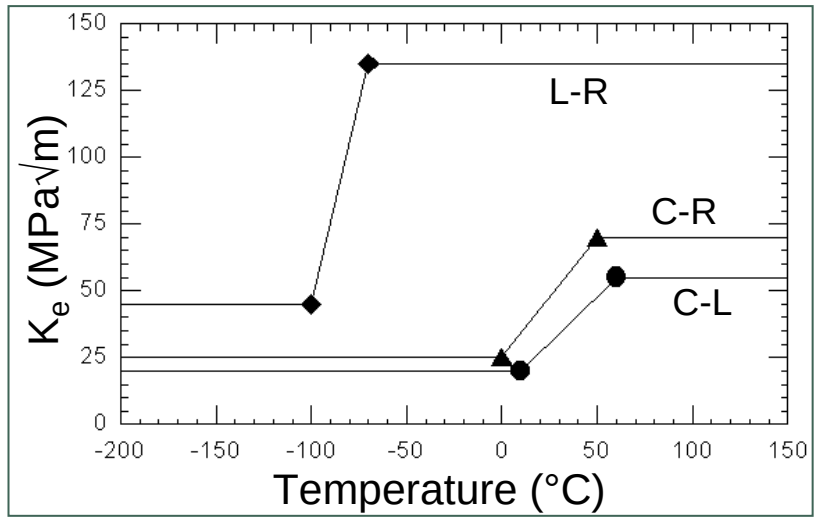
- NCF steel (12YWT)
- Experimentally developed ODS 13.5Cr steel (PNNL, Vista Metal, and U. Idaho)

Low Temperature Toughness Behavior in MA957





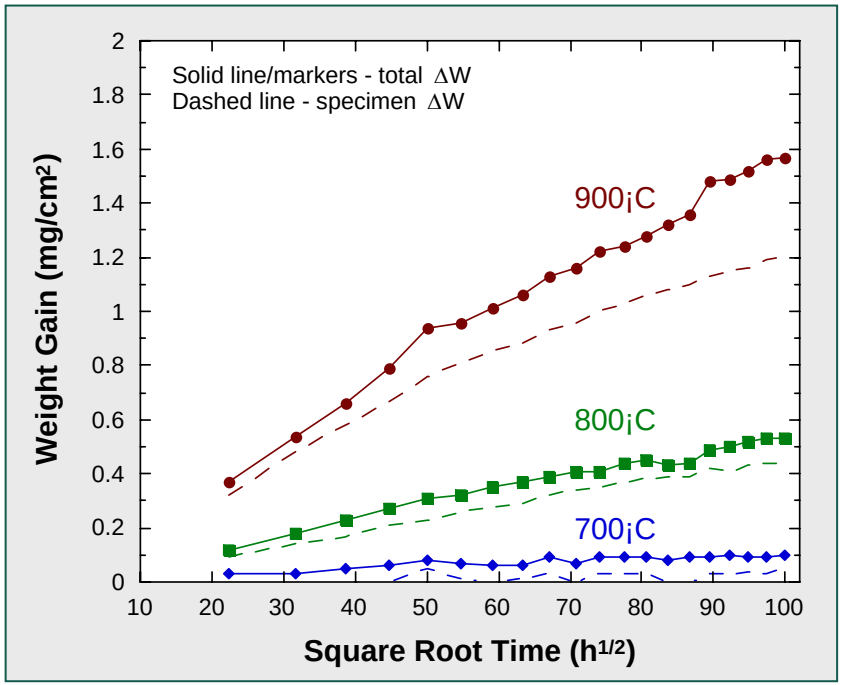
1/3-sized Charpy Specimens

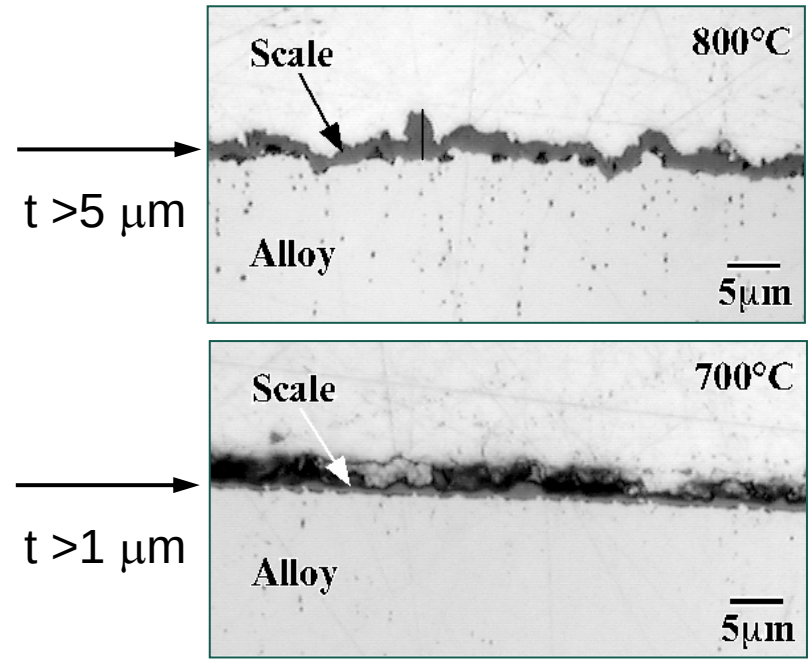


- Fracture toughness trends reflect the microstructural anisotropy in the longitudinal direction *(parallel to extrusion direction)*
  - correlated with 10:1 aspect ratio of grain size and Al_2O_3 stringers
  - highest toughness is achieved when the crack propagates orthogonal to elongated grains and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

(Odette, Alinger: UCSB)

Oxidation Resistance Increased 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

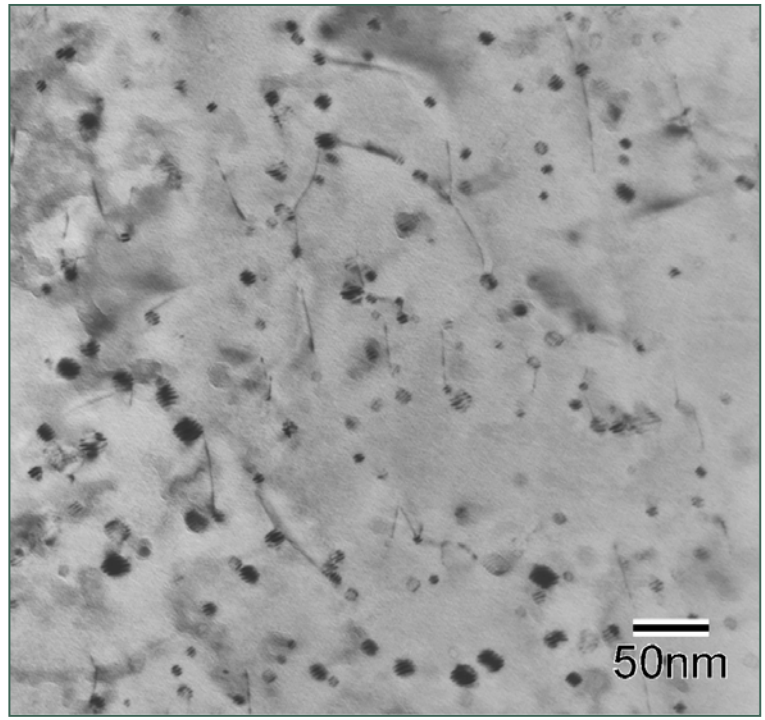
(Partly funded by Fossil Energy AR&TD Materials Program)

(Sumitomo, Kobe, & ORNL)*

Precipitation Strengthened Ferritic/Martensitic Steel

A-21steel (Fe-9.5Cr-3Co-1Ni-0.6Mo-0.3Ti-0.07C)

- High temperature strength and impact properties are better than conventional 9-12Cr steels
- Conventional practice of creating a supersaturation of C by solutionizing (austenitizing), followed by thermomechanical processing to control the precipitation
- Alloying modifications needed

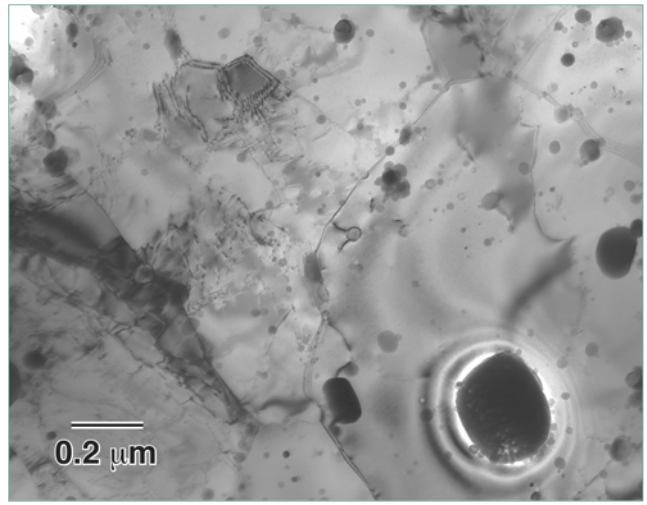


- nano-size TiC precipitates
- high number density

ODS Ferritic and Ferritic/Martensitic Alloys

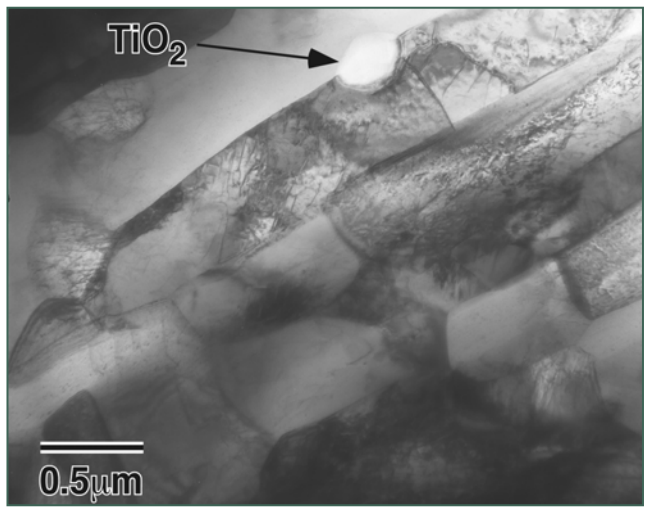
- Composition Issue Unresolved
  - low Cr ferritic/martensitic : equiaxed grain morphology
  - high Cr ferritic : phase stability and Cr scale formation
- Problematic Mechanical Alloying Processing Method
  - time-consuming & expensive
  - microstructural non-uniformities
  - impurities in powder and contamination during MA can influence microstructural development
- Commercially produced (ex. INCO MA956 and MA957)
  - Joining and fabrication are feasible
  - Irradiation behavior is good

ODS F/M Steel



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

ODS Ferritic Steel

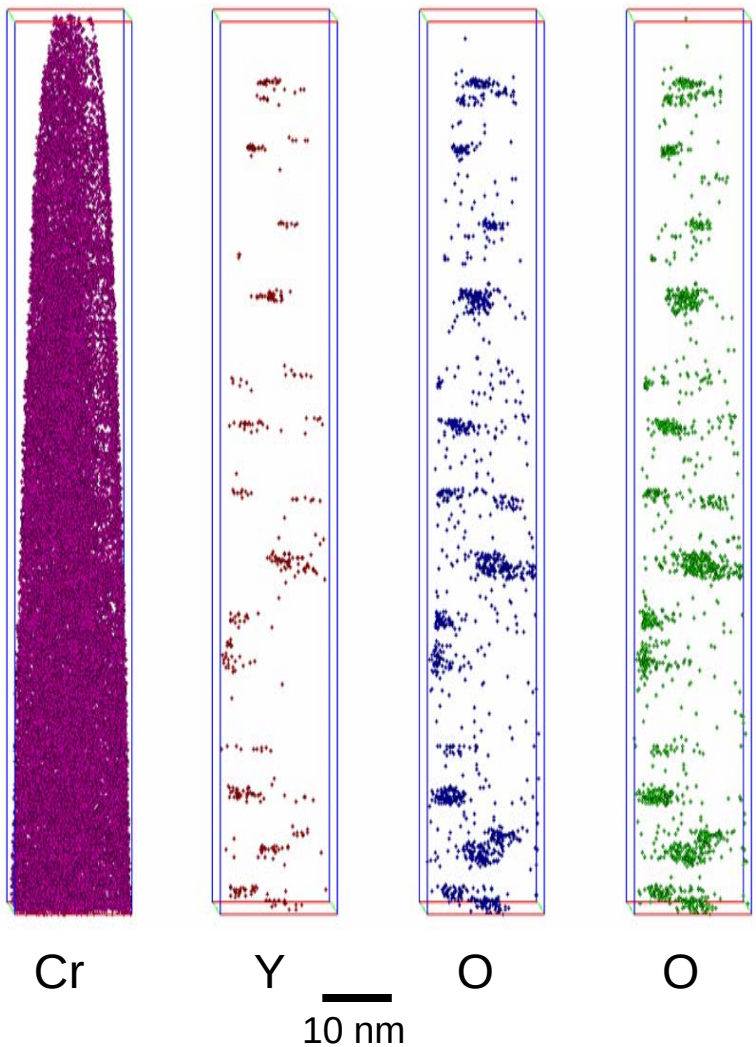


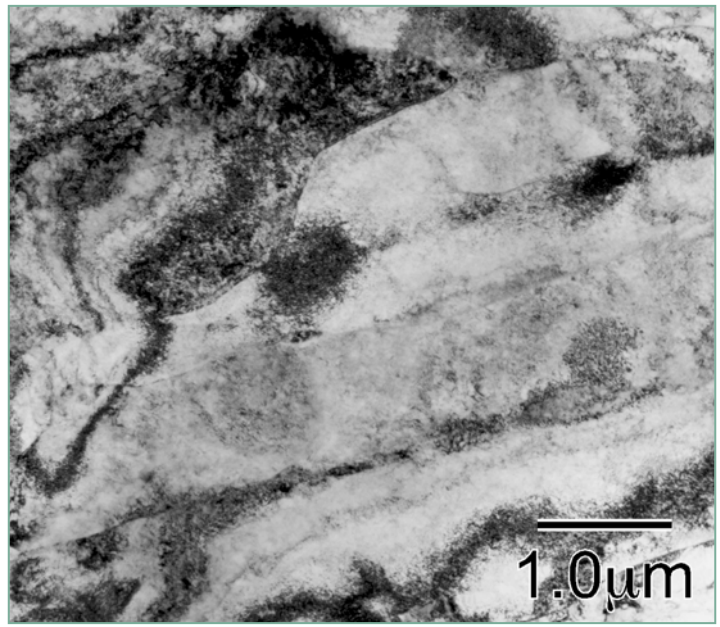
Fe-13Cr-3W-0.4Ti + 0.25Y_2O_3

Nanocomposited Ferritic (NCF) Steel

(MA Fe-12Cr-3W-0.4Ti + 0.25Y_2O_3 : 12YWT)

3-D Atom Probe Tomography

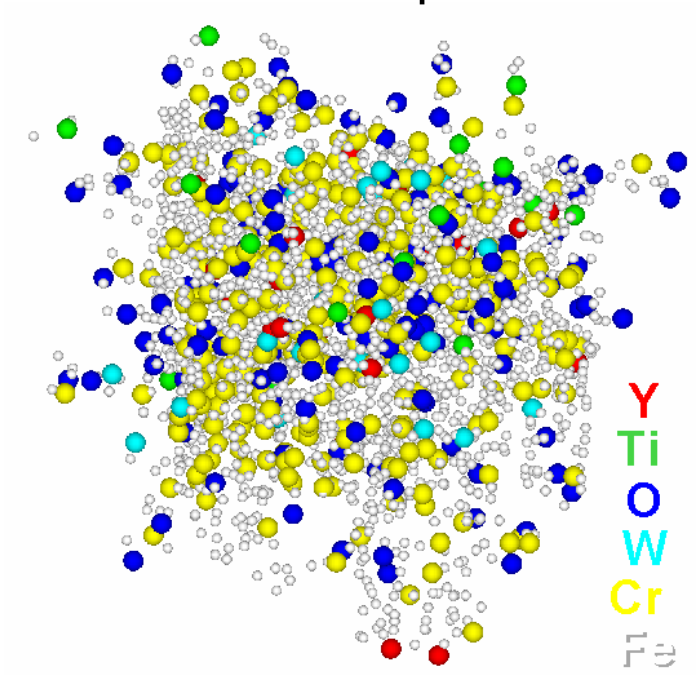


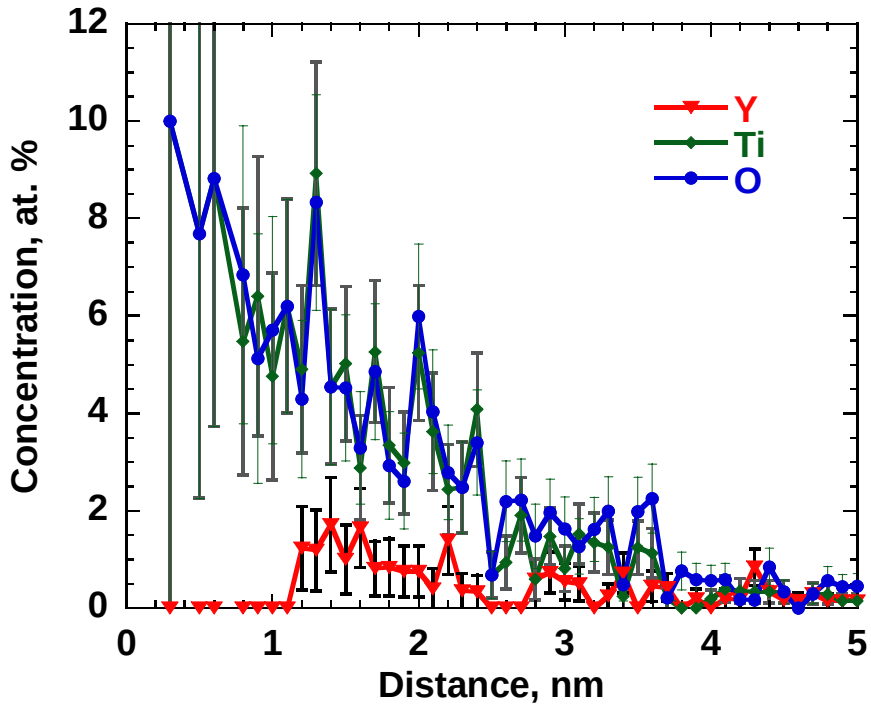


- very high number density of ~10^{24}/m of uniformly distributed nanoclusters
  - site occupancy on bcc Fe lattice
  - average size r_g = 2.0 (+/- 0.8) nm
- elongated grains containing high dislocation number density (TEM)

Radial Concentration Profile from the Center of Mass of a Nanocluster Particle

3-D APT Composite

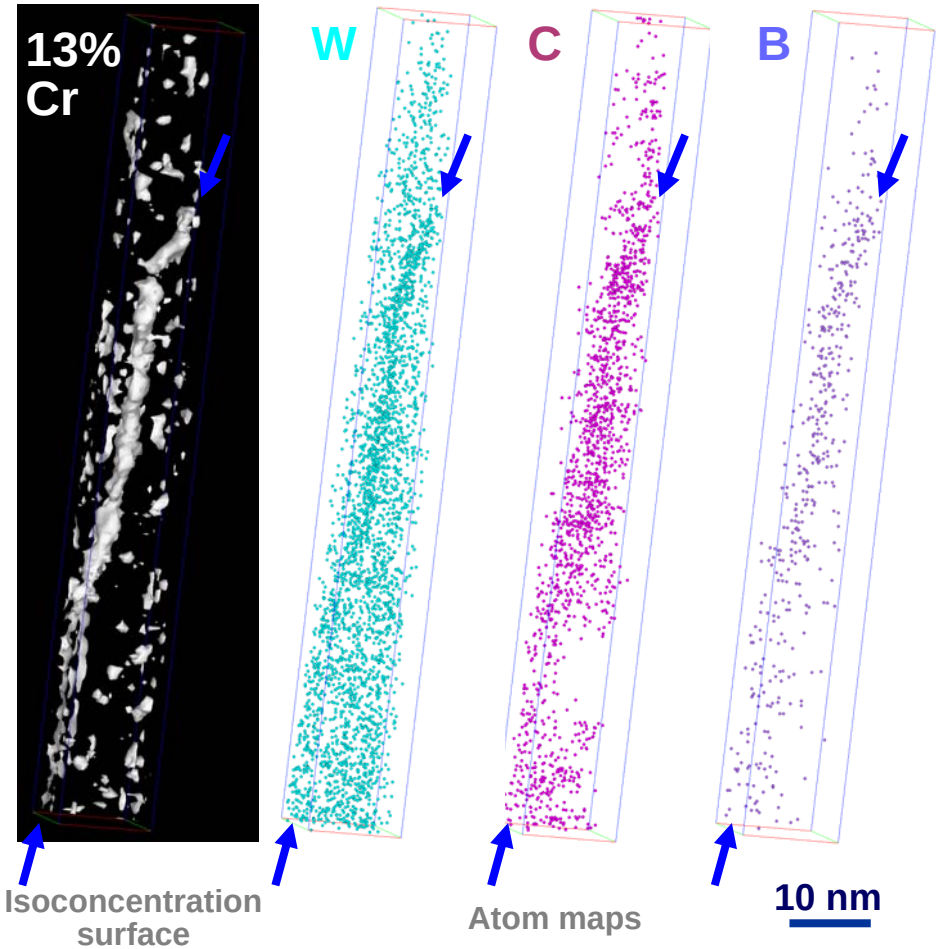




- Some evidence of a yttrium depletion at the core and an enrichment at the particle-matrix interface
- Diffuse interface structure

M.K. Miller, LDRD 2002

Dislocation Pinning by Solute Atmosphere May Contribute to High Temperature Strengthening

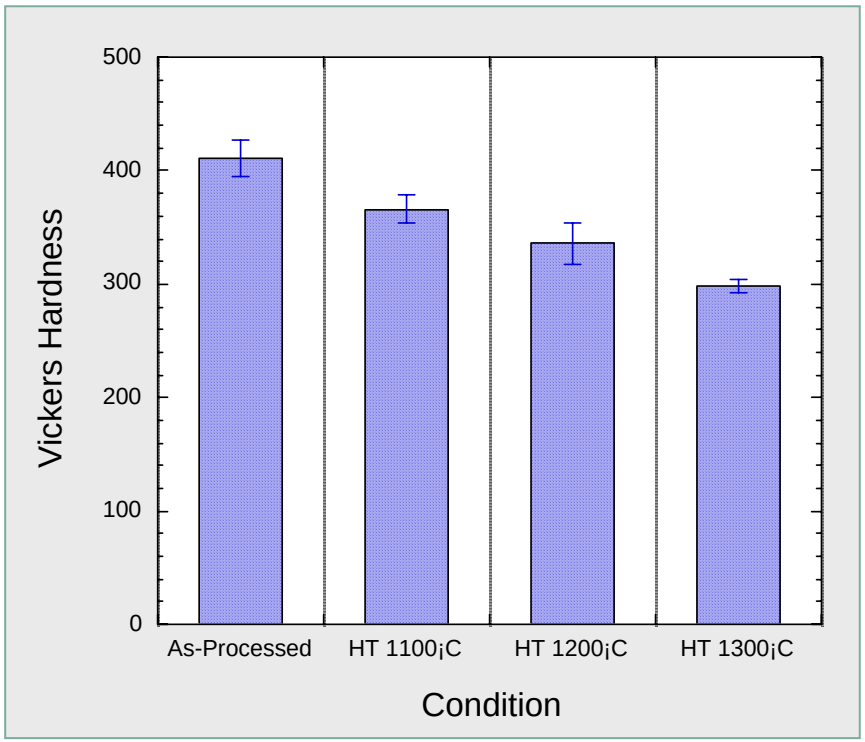


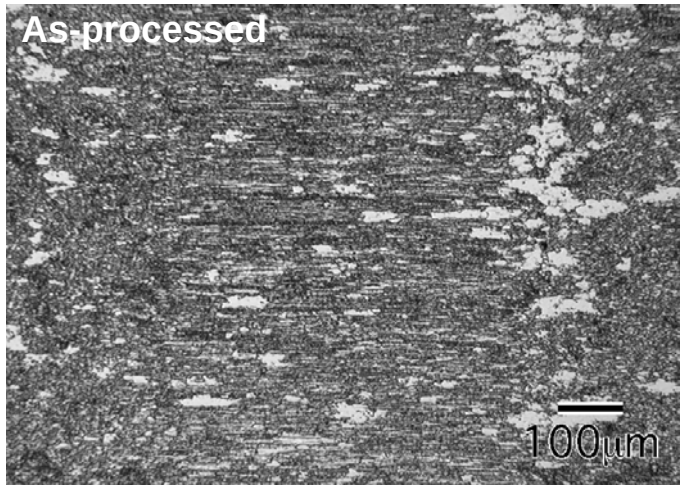
COMPOSITION OF SOLUTE-ENRICHED REGION AROUND DISLOCATION

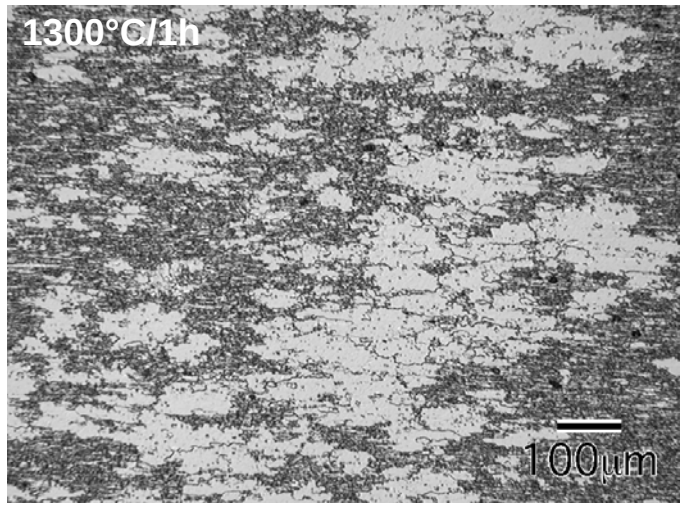
analysis volume defined by a C + B atom maximum separation of 1.5 nm

	Alloy	Ferrite	Dislocation
Cr	13.3	12.3	15.9 ± 0.16
W	0.92	0.71	1.21 ± 0.05
Ti	0.46	0.08	0.44 ± 0.03
Y	0.13	0.01	0.16 ± 0.02
O	0.19	0.11	0.53 ± 0.03
C	trace	0.18	1.38 ± 0.05
B	trace	0.05	0.44 ± 0.03
N	trace	0.15	0.17 ± 0.02

Microstructural Stability Observed in 12YWT Alloy with Short Term Exposure at Very High Temperatures







- Softening is not significant
- ~50% of the microstructure has recrystallized after annealing for 1h at ~86% T_{MP}(~1520°C)

Summary

- Precipitation strengthened steels offer marginal increases in temperature, but should be pursued based on high feasibility
- NCF steels offer the best combination of properties at high temperature
  - processing conditions that produce nanoclusters is not understood
  - stability issues during neutron irradiation have not been addressed
- Are properties of NCF attractive enough to offset the high R/D costs needed to develop the experimental and theoretical understanding of nanoclusters

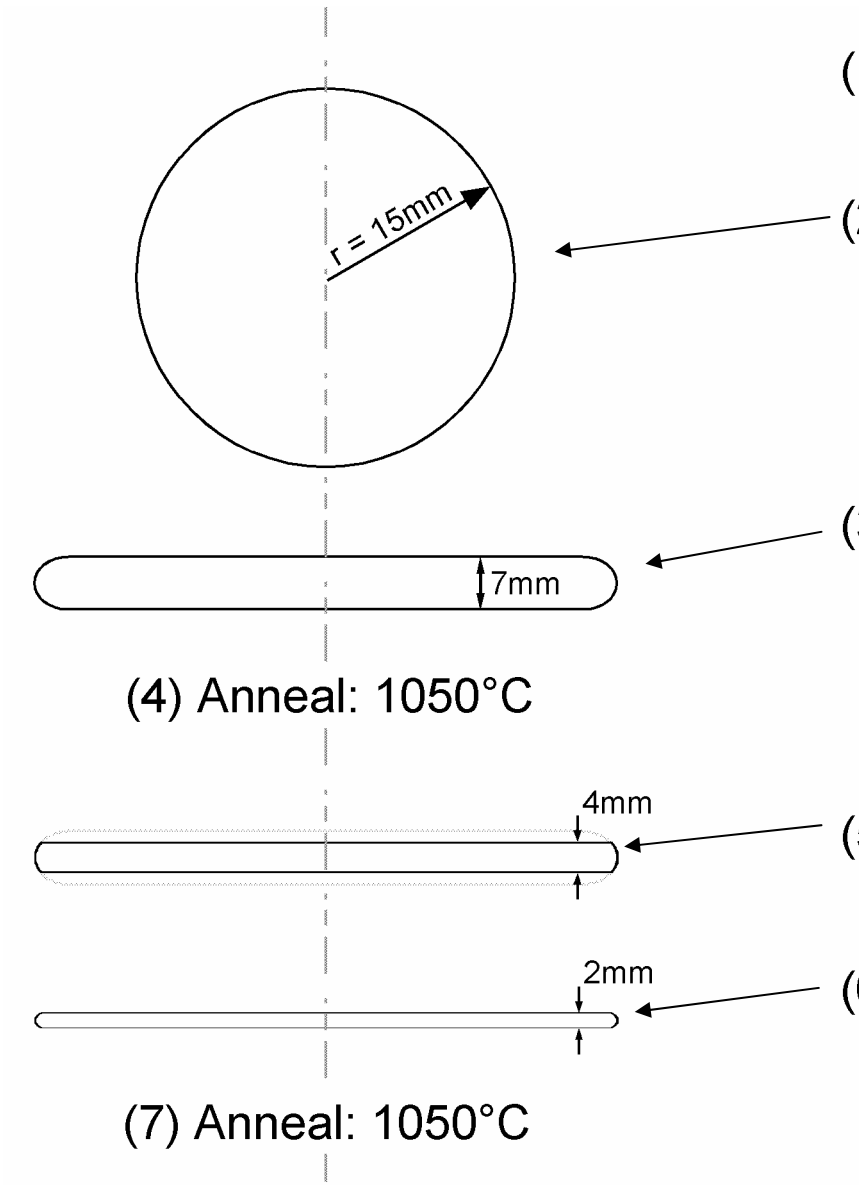
Key Issues of ODS Ferritic and F/M Steels

- Greater database of processing, properties, and structure exists for ODS alloys
- Fabricability issues have been investigated
  - fabrication procedure is sensitive to grain anisotropy and impurity stringers
  - successful fabrication schedule for tube production was developed for MA957 (Westinghouse Hanford Co., Carpenter Technology, Inc., and Superior Tube Co.)
- A joining method has been demonstrated
  - Welding by traditional fusion methods creates difficulties
    - porosity and slag formation
    - inherently weak weld metal caused by removal of dispersoid
  - Pulsed magnetic welding method
- Stability of oxides during high temperature neutron irradiation

Critical Assessment of NCF steels

- Formation of nanoclusters has not been duplicated
  - most significant barrier to their development
  - define important processing and alloying variables
- Structure needs to be more fully understood
  - probes of atomic bonding
  - matrix/cluster interface
  - lattice strains
- Stability
  - understanding the mechanism for stability can help identify important processing and alloy composition parameters
  - experimental results have led the theoretical work, but this is an important area for theory
- High temperature strengthening mechanisms
  - what role does the solute atmosphere on dislocation density, solute atmosphere, high number density of nanoclusters, and grain size

Mechanical Alloying and Fabrication of NCF Steel



(1) Ball Milling
- 48 h in Ar

(2) Hot Extruded
- mild steel can
- 1150°C
- 5:1 reduction in area
  > 67mm to 30mm dia.

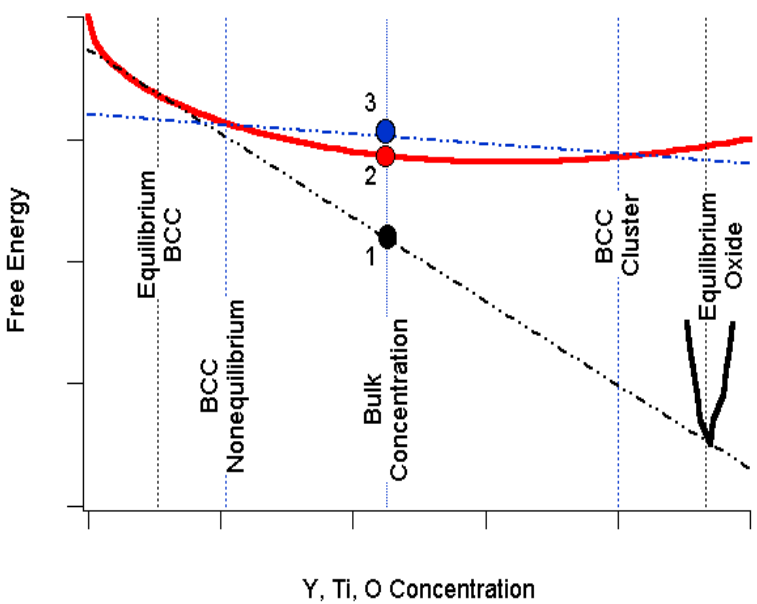
(3) Hot Rolled
- 1150°C
- 30mm dia. to 7mm thick plate
- gradient in reduction
  > 77% maximum reduction in thickness at center
  > 0% reduction at 7mm thickness

(5) Machine
- Remove 1.5mm from top and bottom surfaces

(6) Warm Roll
- 600°C
- 50% reduction in thickness

Are Alternative Processing Methods to MA Possible?

- Thermodynamic calculations for an assumed microstructural evolution



(1) start with an equilibrium condition between the alloy bcc phase and Y_2O_3 oxide phase

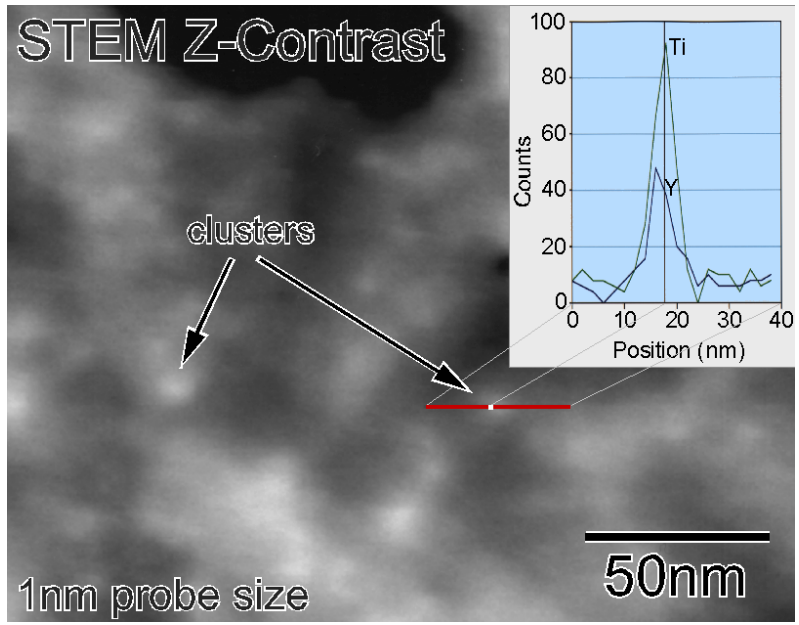
(2) establishment of a non-equilibrium solid solution of Y and O in the bcc matrix

(3) changes associated with forming Y, Ti, O rich clusters in the bcc matrix

- The free energy of the system *must always increase*
- Increases in free energy occurs during high energy ball milling

Irradiation Environment for a D-T Fusion Reactor

- High lifetime dose requirements for structure
- High He generation rates promotes:
  - He embrittlement of grain boundaries
  - void swelling
- Design microstructures to manage and control He
  - trap He in fine stable configurations
  - particle and particle/matrix interfaces that form deep trap
- Particle dispersion concept needs to be investigated

Critical Assessment of NCF steels

- Nano-size length dimension of cluster particles creates many difficulties and hinders our ability to understand their structure
  - nanoclusters have only been detected using APT and high resolution Z-contrast STEM
  - XRD, synchrotron and anomalous X-ray diffraction methods have not produced any meaningful results
  - other advanced analytical methods and approaches are needed, ex. EXAFS