Development of High-Strength ODS Steels for Nuclear Energy Applications

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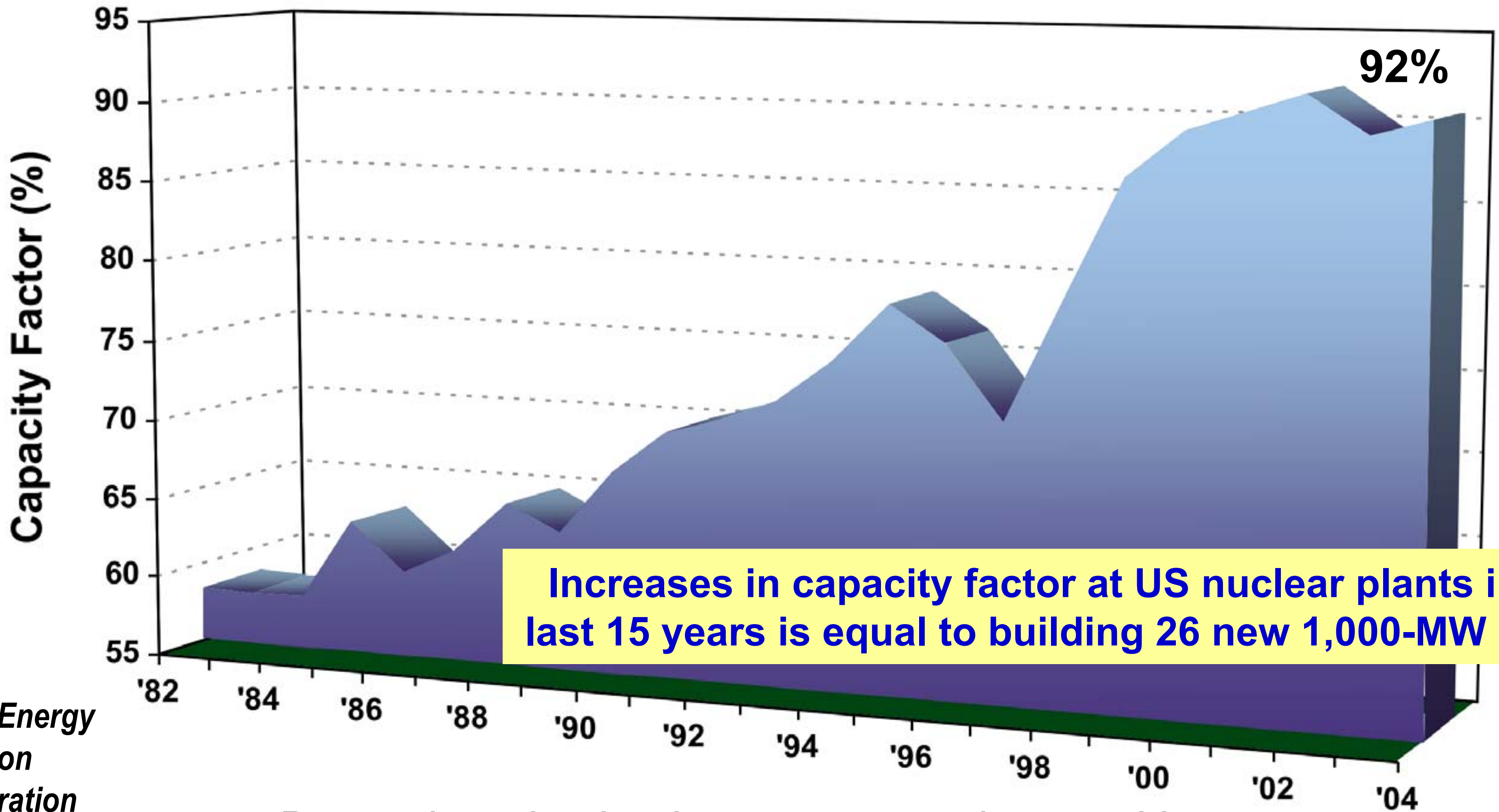
Nuclear power's proven performance

Currently providing 16% of the world's electricity

Average capacity factor for US nuclear power plants has exceeded 90% for the past decade



Increases in capacity factor at US nuclear plants in the last 15 years is equal to building 26 new 1,000-MW plants

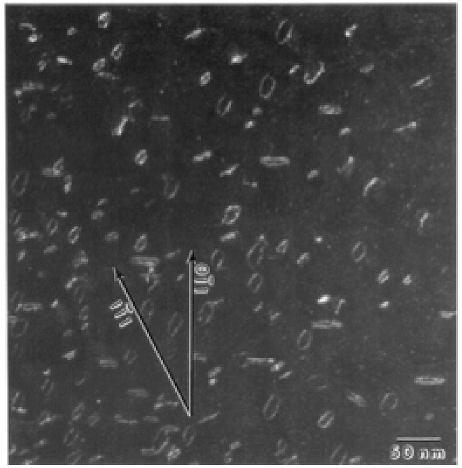
Source: Energy Information Administration

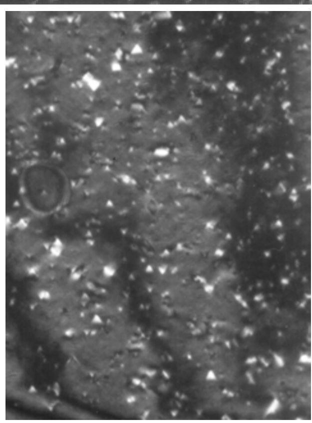
Nuclear Regulatory Commission

Dramatic reduction in stress corrosion cracking issues in steam generators, etc.

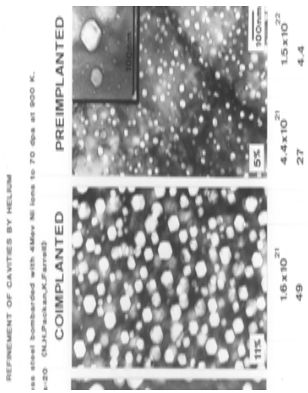
Irradiation Produces Defect Microstructures

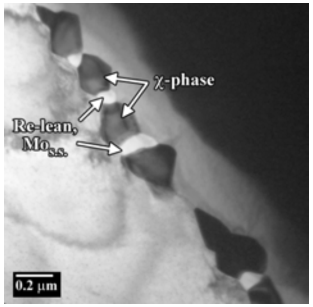
Dislocation loops

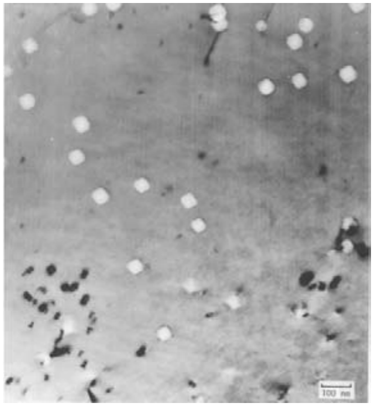


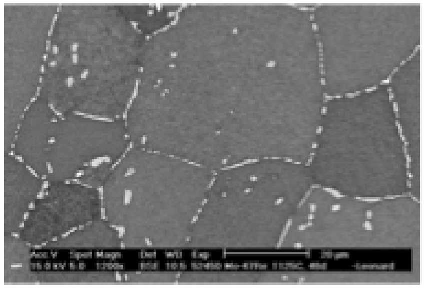


Voids, precipitates, solute segregation

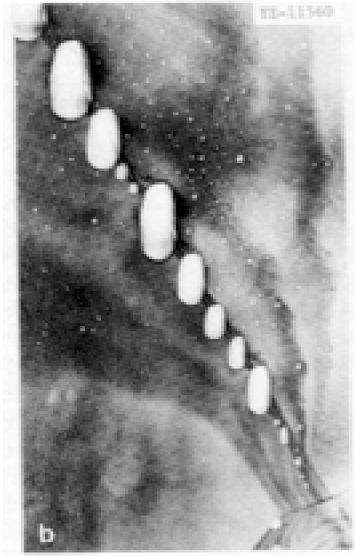








Grain boundary helium cavities

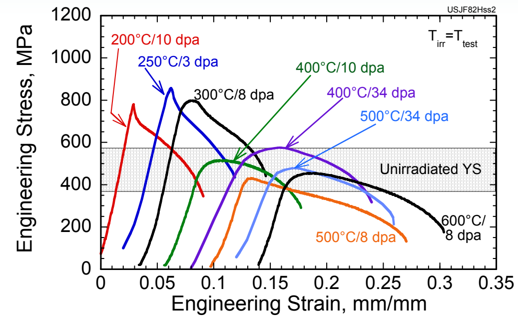


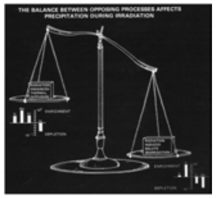
0.2 0.3 0.4 0.5 0.6 0.7

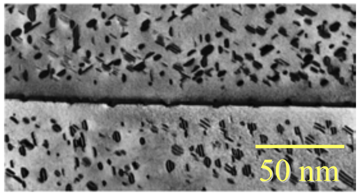
Irradiation Temperature (T/T_M)

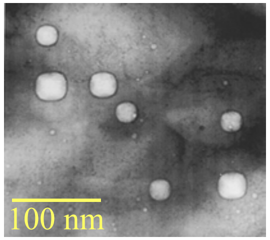
Radiation Damage Can Produce Large Changes in Structural Materials

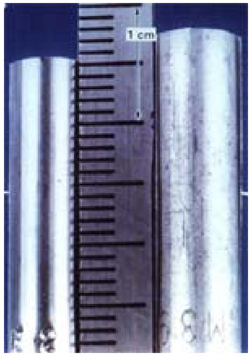
- Radiation hardening and embrittlement
  ($<0.4\ T_M$, >0.1 dpa)
- Phase instabilities from radiation-induced precipitation
  ($0.3\text{-}0.6\ T_M$, >10 dpa)
- Irradiation creep
  ($<0.45\ T_M$, >10 dpa)
- Volumetric swelling from void formation
  ($0.3\text{-}0.6\ T_M$, >10 dpa)
- High temperature He embrittlement
  ($>0.5\ T_M$, >10 dpa)

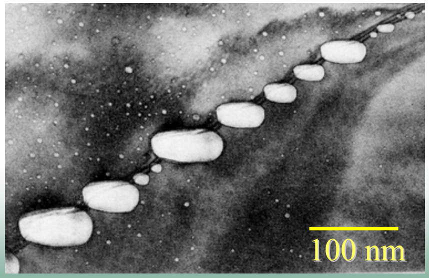












after S.J. Zinkle, Phys. Plasmas 12 (2005) 058101

Gen IV Fission and Fusion Reactors Require the Development of ***Higher Temperature Materials*** *with Adequate* ***Radiation Resistance***

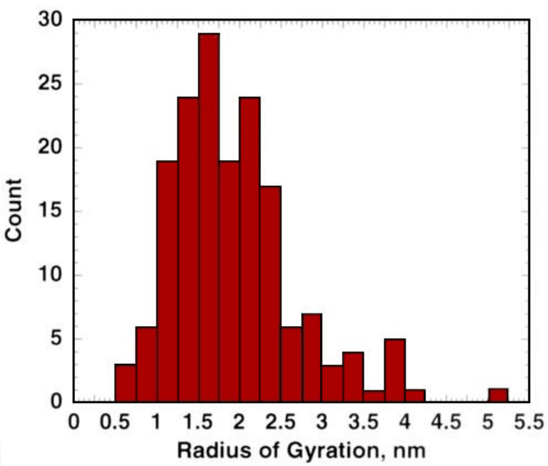
	Fission (Gen. I)	Fission (Gen. IV)	Fusion (Demo)
Structural alloy maximum temperature	<300˚C	500-1000˚C	550-1000˚C
Max dose for core internal structures	~1 dpa	~30-150 dpa	~200 dpa
Max transmutation helium concentration	~0.1 appm	~3-15 appm	~2000 appm (~10000 appm for SiC)
Coolants	H_2O	He, H_2O, Pb-Bi, Na	He, Pb-Li, Li
Structural Materials	Zircaloy, stainless steel	Ferritic steel, SS, superalloys, C-composite	ODS &Ferritic/ martensitic steel, V alloy, SiC composite

Concept for Developing Radiation Tolerant Materials

- High sink strength from internal interfaces
  - *trap vacancies to enhance recombination with self-interstitial atoms*
  - *trap He to suppress bubble formation on grain boundaries*
- Desirable combination of mechanical properties
  - *elevated temperature strength and creep properties*
  - *low temperature fracture toughness*
- Achievable with second phase dispersions
  - *nano-size particles*
  - *high number density*
  - *thermally stable*

Discovery of Oxygen-Enriched Nanoclusters (NC) in Ferritic Alloys Show Promise for Achieving this Goal

- Background
  - Nanoclusters first observed in 12YWT (ORNL)
    - Mechanically alloyed Fe - 12%Cr - 3%W - 0.4%Ti - 0.25%Y_2O_3 ferritic alloy
    - Developed in Japan in late 1990's by Kobe Steel (T. Okuda) and Nagoya University (K. Miyahara and I.S. Kim)
  - Similar oxygen-enriched NC observed in MA957
    - Patented in 1978 by INCO



Characteristics

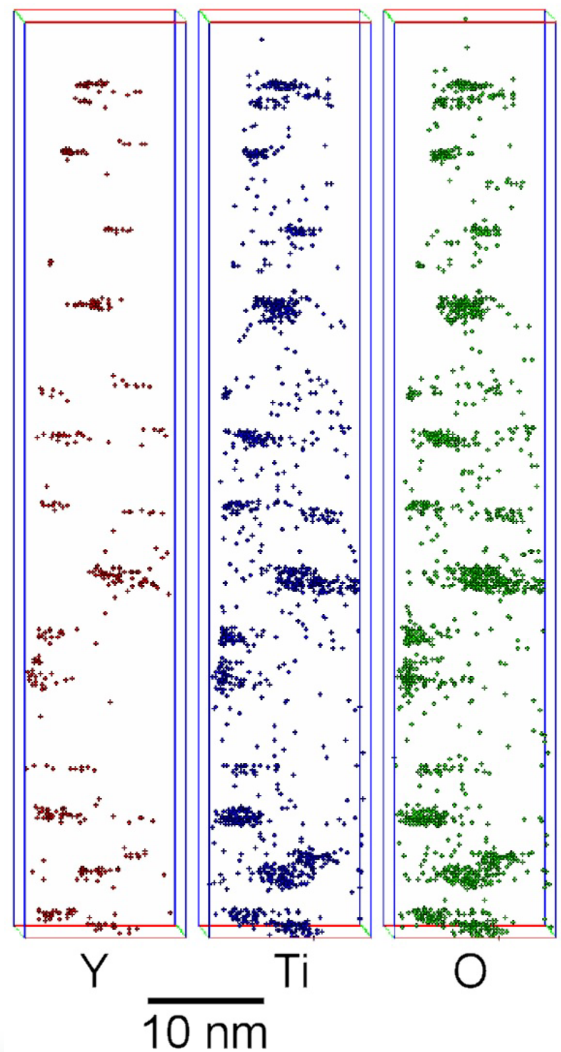
Radius: 2.0 ± 0.8 nm

Number density: $1.4 \times 10^{24}\ m^{-3}$

Composition: 8.1 ± 5.2 %Y

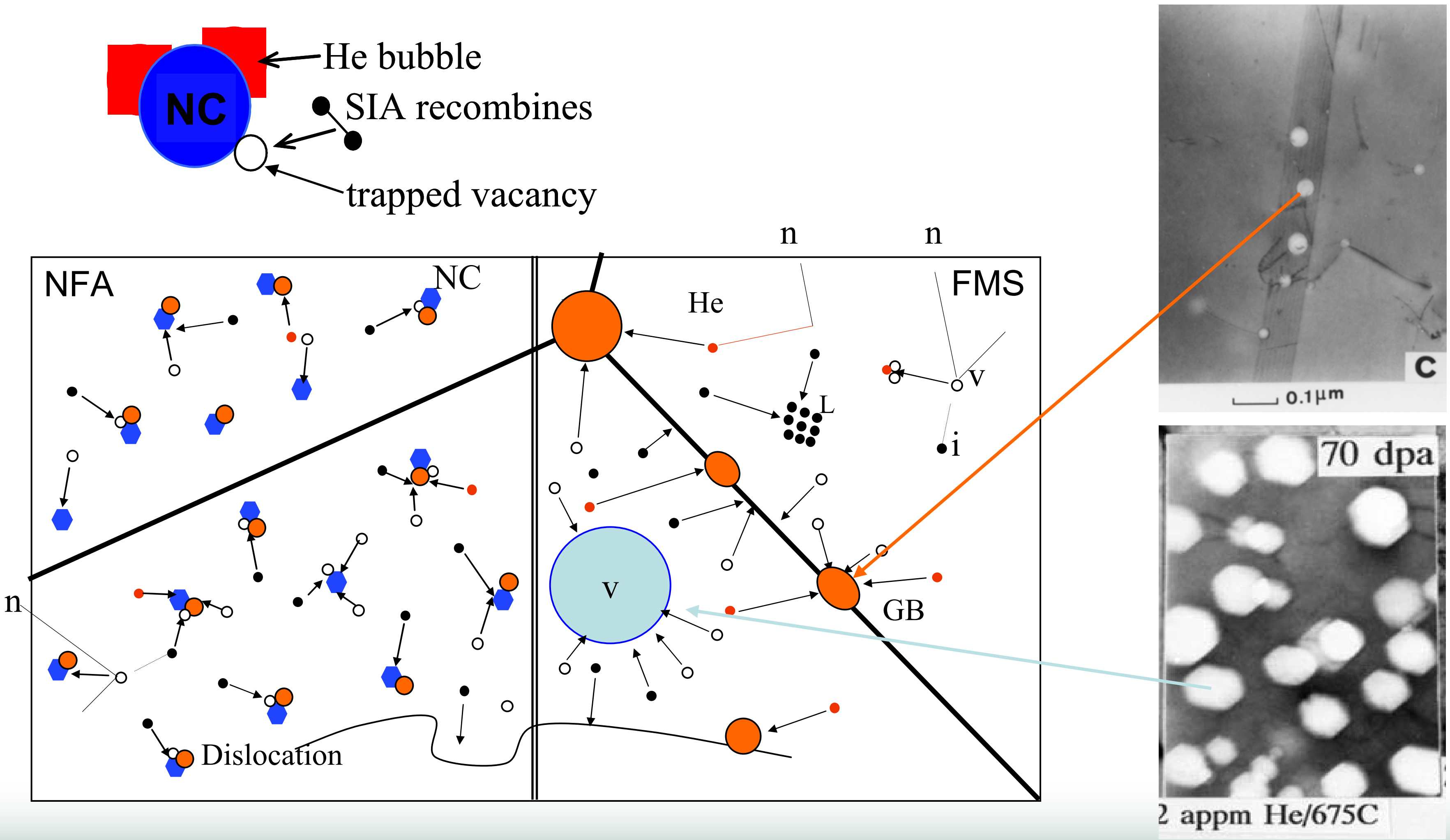
42.1 ± 5.6 %Ti

44.4 ± 8.2 %O



Mitigating Neutron Irradiation Damage

Nanoclusters have a high sink strength and trap (getter) both He (in fine bubbles) and vacancies (to enhance self-healing of damage by recombination with self-interstitial atoms, SIA)



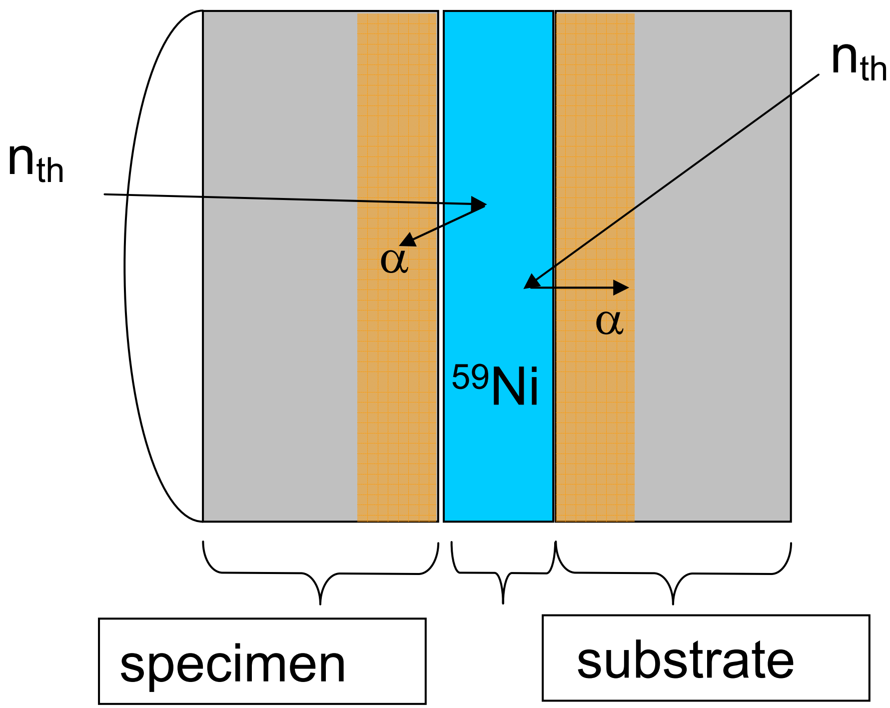
Thanks to Bob Odette, UCSB

Proof of Concept: Results of In-Situ Neutron + He Implantation of MA957 (JP26: 9 dpa at 500°C in HFIR)

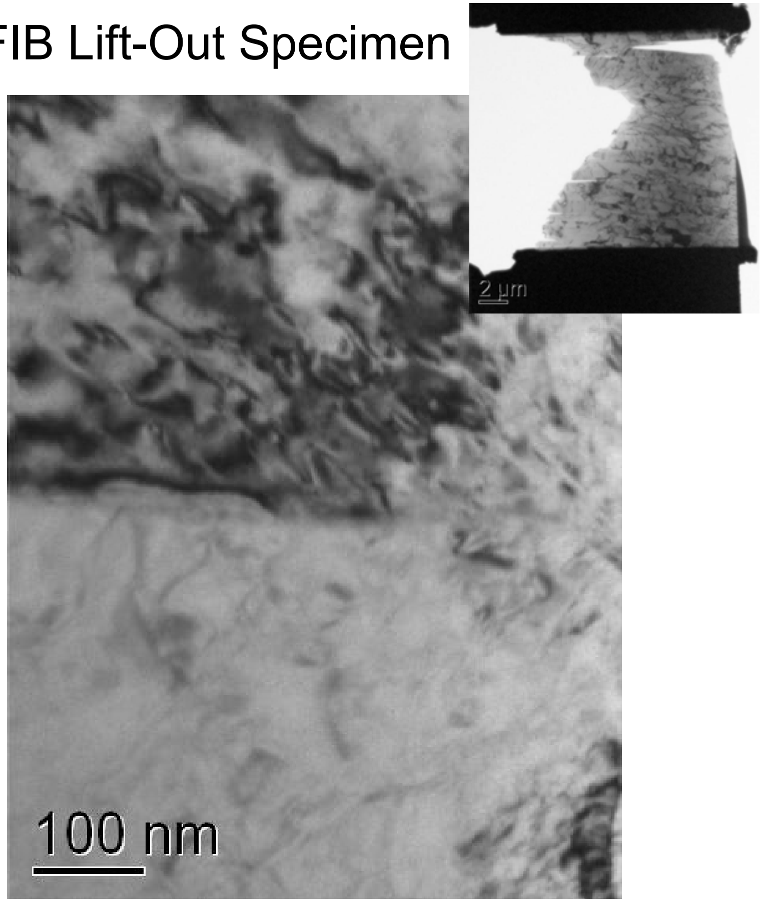
4-μm thick NiAl layer generates ~380 appm He in adjacent 6 μm of MA957

$^{58}Ni + n_{th} \rightarrow {}^{59}Ni + \gamma$

$^{59}Ni + n_{th} \rightarrow {}^{56}Fe + {}^{4}He\ (4.76\ MeV)$



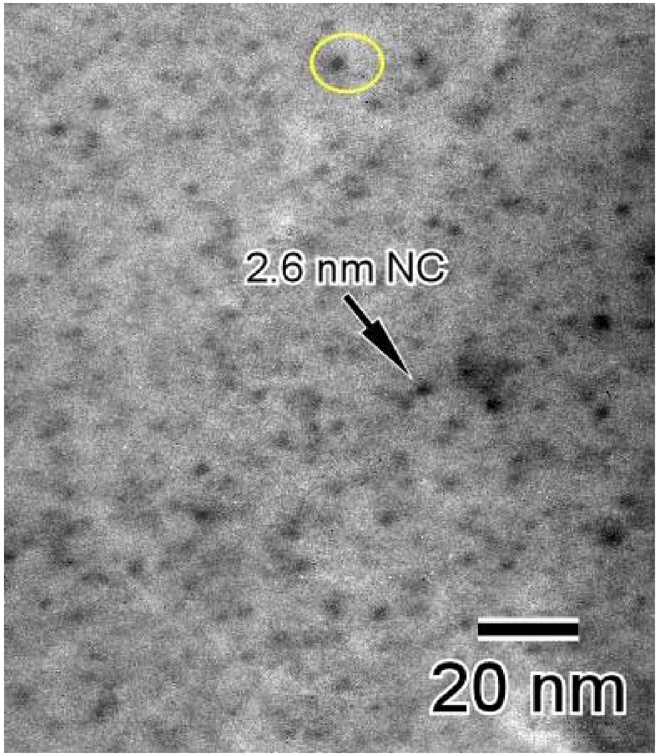
FIB Lift-Out Specimen



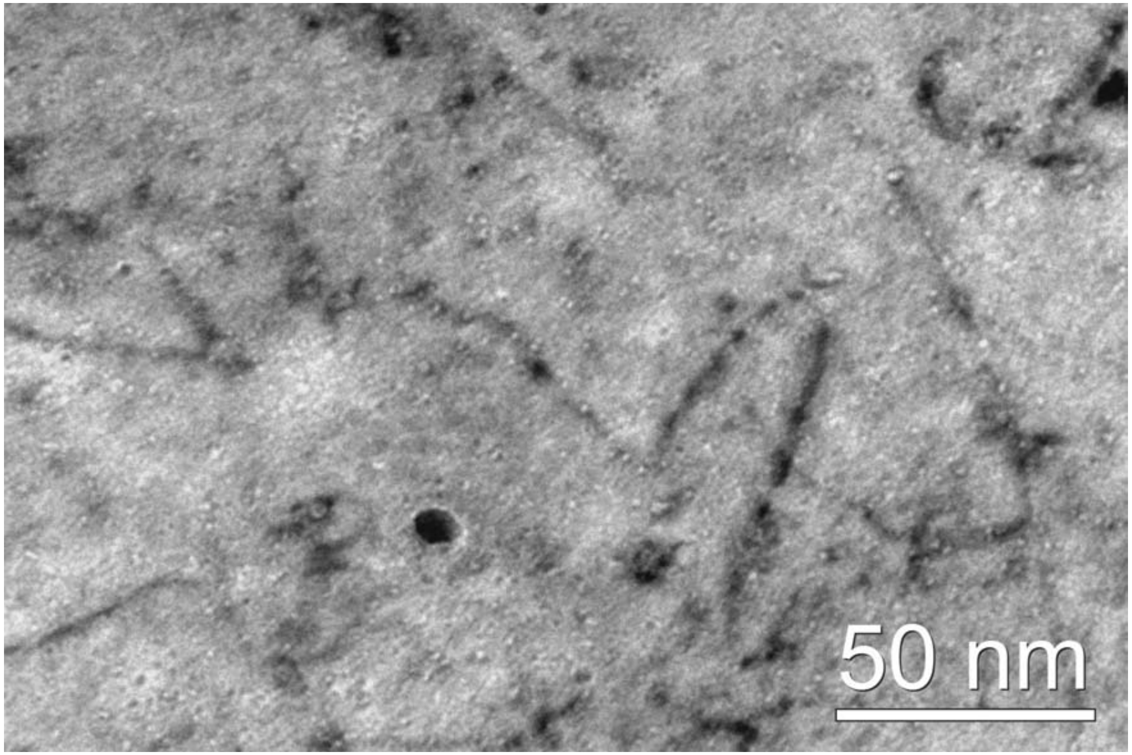
"The transport and fate of helium in nanostructured ferritic alloys at fusion relevant He/dpa ratios and dpa rates"
T. Yamamoto, G.R. Odette, P. Miao, D.T. Hoelzer, J. Bentley, N. Hashimoto, H. Tanigawa, R.J. Kurtz
J Nucl Mater 367-370 (2007) 399-412

Survival of NC and He Trapping in MA957

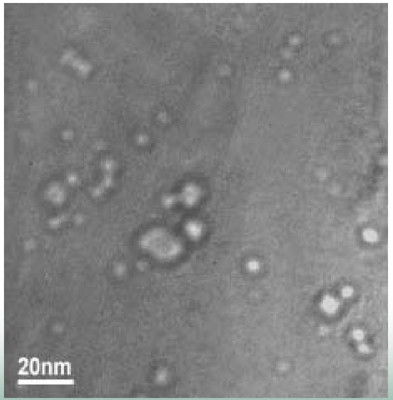
EFTEM Fe M Jump Ratio



-512 nm Under Focus



- Compared to Eurofer 97, the results indicate that NC play an important role in mitigating the accumulation of point defects as well as trapping He in ~1-2 nm bubbles



Eurofer 97

Development of Advanced ODS 14YWT Ferritic Alloy

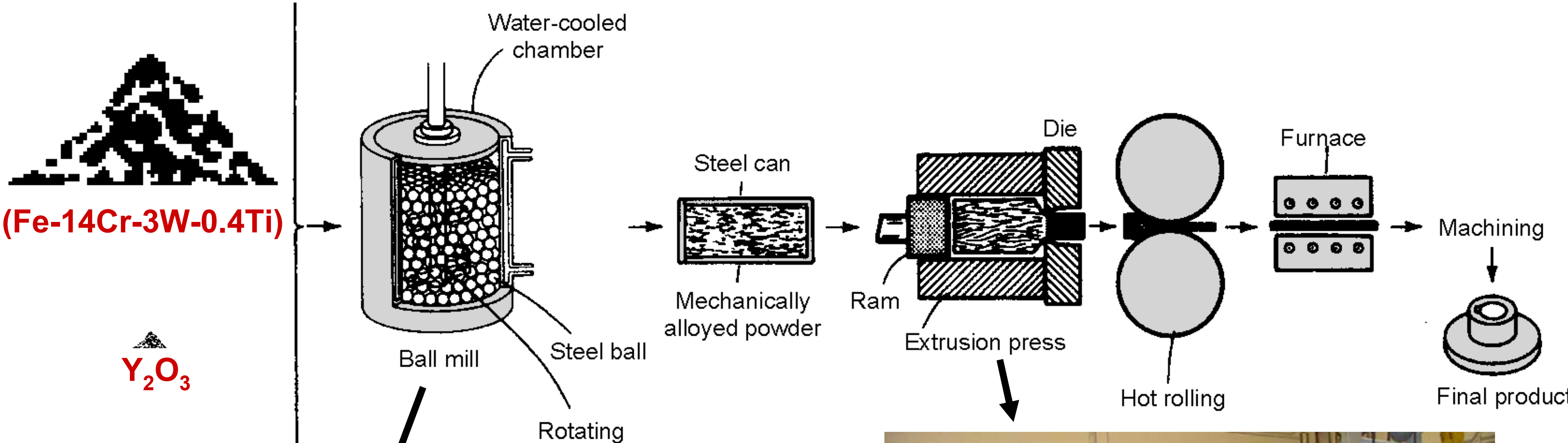
- The development of 14YWT began in 2001 since MA957 was discontinued by INCO and 12YWT was produced once
- Numerous small heats have been produced over 9 years

Heat	Extrusion Date	Mass (g)	Temp. (ºC)	Dispersion	History
OE14YWT-SM1	29-Apr-02	200	850	NC	Bi-Modal GS: SANS
OE14YWT-SM2	08-Feb-04	200	850	NC	Poor milling condition
OE14YWT-SM3	17-Mar-04	200	850	NC	SANS; Pb and super critical water corrosion tests
OE14YWT-SM4	18-Mar-04	200	850	NC	Tensile test; Steam corrosion test
OE14YWT-SM5	17-Sep-04	200	850	NC	Navy ATR irradiation experiement
OE14YWT-SM6	28-Jan-05	800	850	NC	Fracture toughness, tensile; HFIR Rabbit; Matrix I
OE14YWT-SM7	03-Aug-05	1000	850	NC	Navy ATR irradiation experiement
OE14YWT-SM8	03-Aug-05	1000	850	NC	Given to BES Project
OE14YWT-SM9	03-Aug-05	200	850	NC	10 h milling test
OE14YWT-SM10	27-Jun-07	1200	850	NC	INERI testing; Matrix II
OE14YWT-CR1	18-Sep-01	200	1175	Oxide	High temperature extrusion
OE14YWT-CR2	Fall, 2001	200	1175	Oxide	Tensile test
OE14YWT-CR3	29-Apr-02	200	850	NC	Bi-Modal GS; SINQ
OE14YWT-CR4	17-Mar-04	200	850	NC	Tensile test; SANS
OE14YWT-CR5	17-Sep-04	200	850	NC	Coarse particle study; Bi-Modal GS

- A major focus was to reduce the grain size
  - increase the strength and improve other properties, i.e. fracture
  - increase the sink strength for radiation tolerance

The NFA 14YWT is produced by Mechanical Alloying

Atomized Fe-alloy powder is ball milled with Y_2O_3 powder



Zoz Attritor Mills

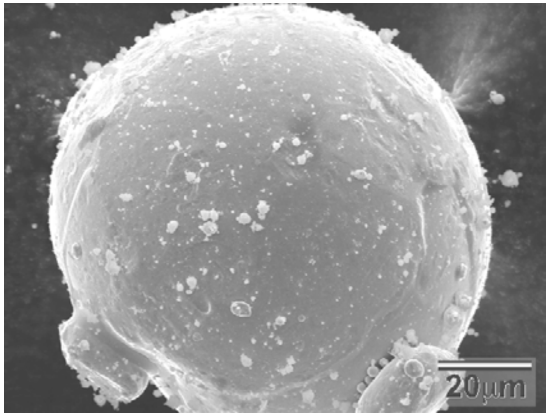
Watson-Stillman Co. (Roselle, NJ) unit with total capacity of 1,250 tons (2.5×10^6 lbf)

Ball milling is critical in mechanical alloying (MA)

(1) Must uniformly disperse Y_2O_3 in each Fe alloy particle

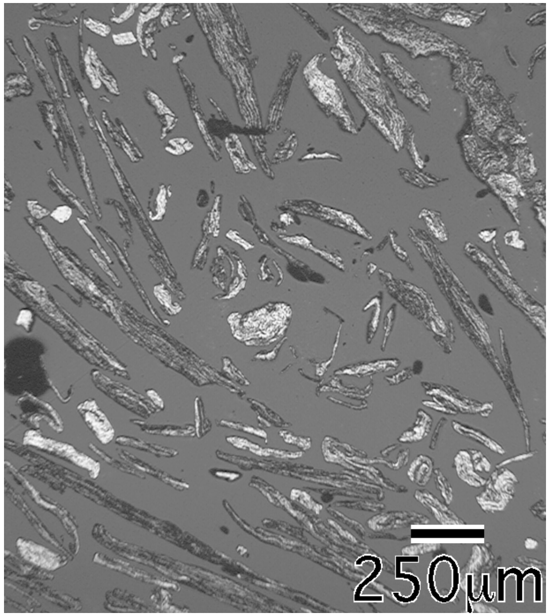
(2) Must force Y_2O_3 into solution in the bcc Fe lattice

As-Received

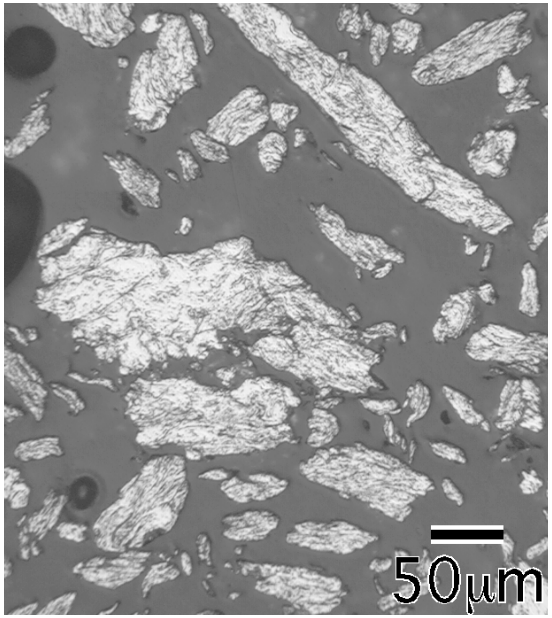


Up to 5 μm Y_2O_3 agglomerates on surface of Fe alloy sphere

Milled 5h



Milled 80h



- Spherical particles undergo extensive plastic deformation during early stages of ball milling and rapidly develop into large mm size flakes
- Flakes become brittle due to work hardening and simply fracture into smaller particles during latter stages of ball milling

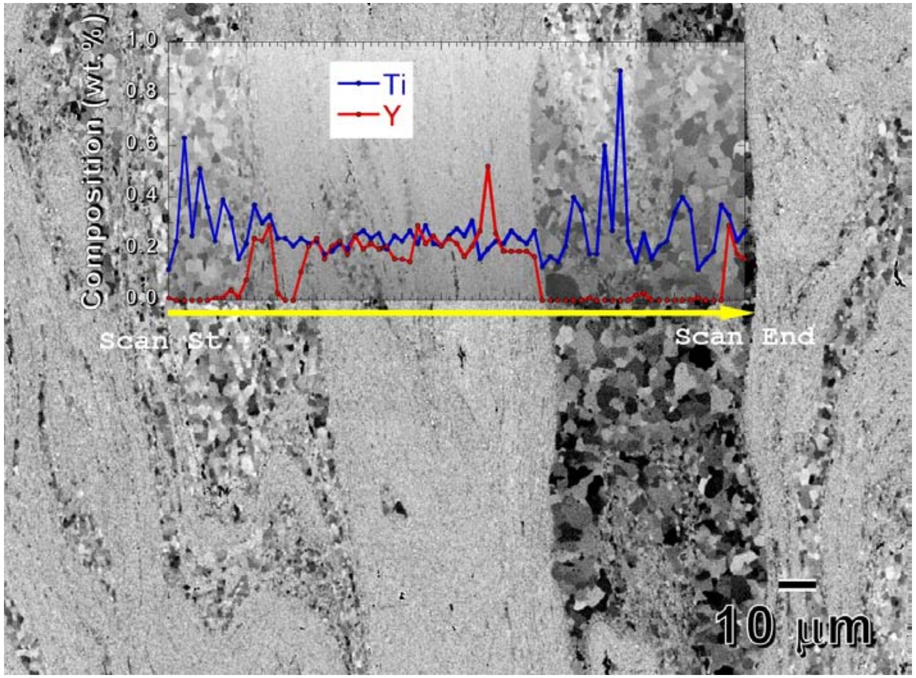
Oak Ridge National Laboratory

When ball milling does not distribute Y effectively

14YWT ball milled for 40 h and extruded at 850ºC

Poor milling conditions

Y not dispersed uniformly

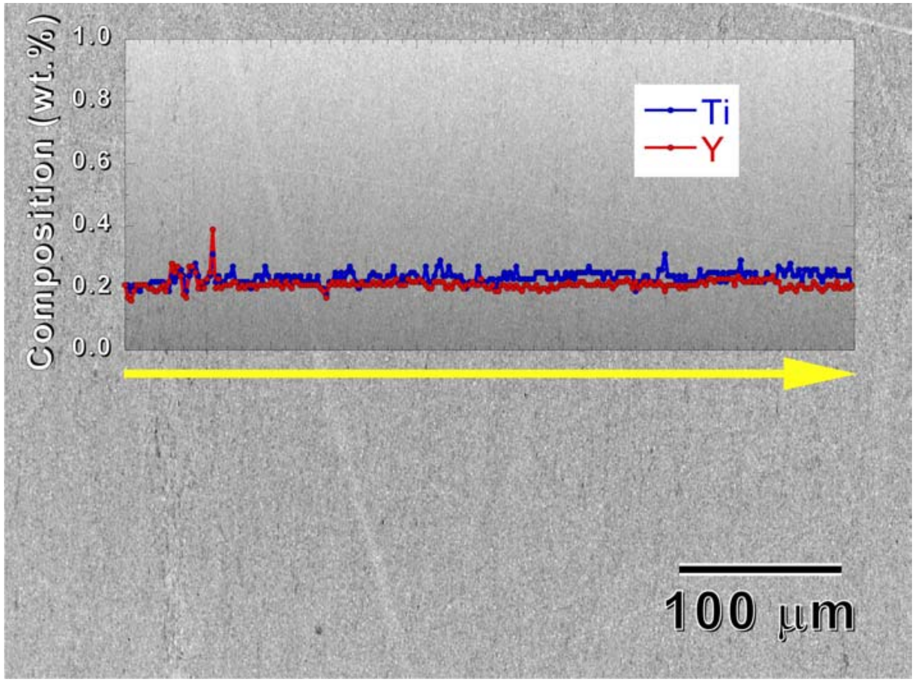


Bi-Modal grain size

NC present only in Y-rich regions

Optimized milling conditions

Y dispersed uniformly

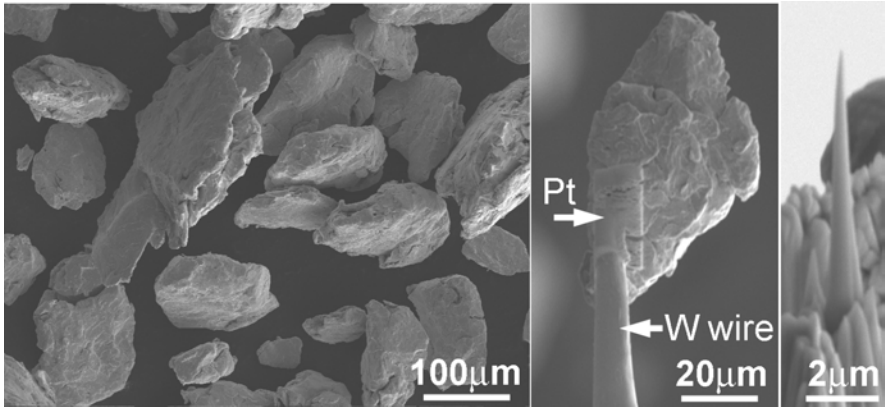


Uniform grain size (<500 nm)

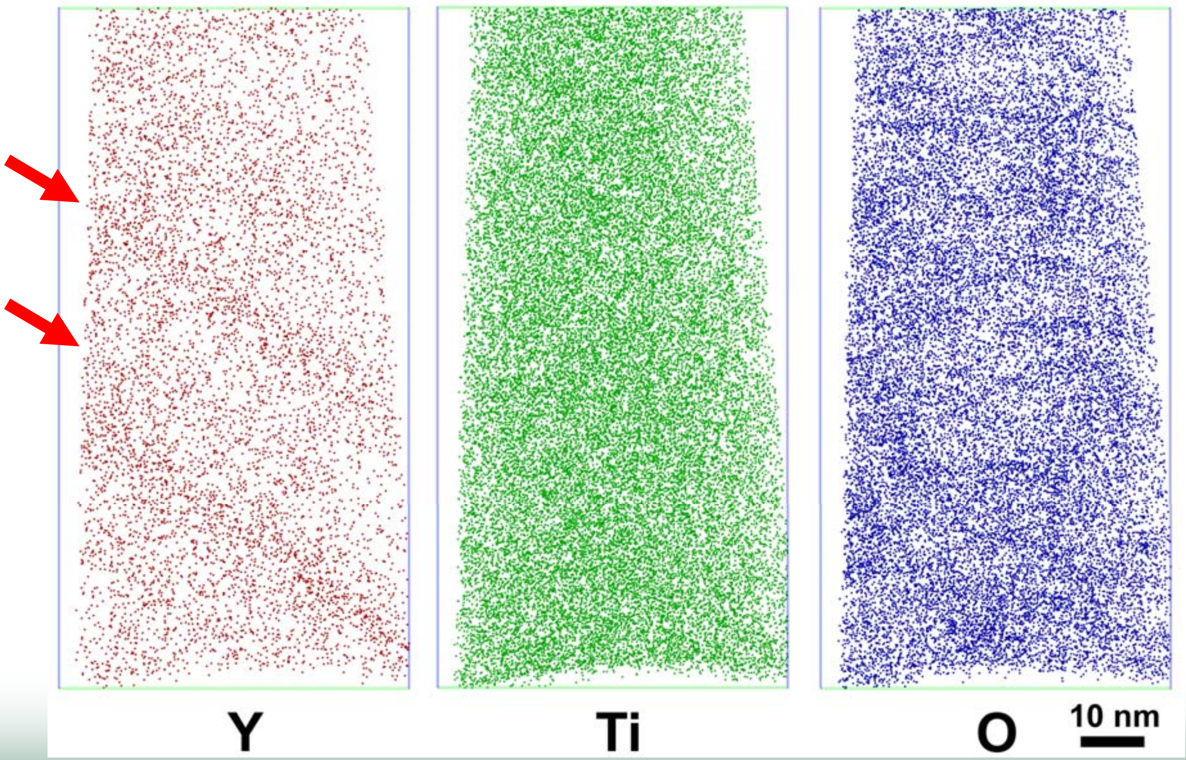
Homogeneous NC distribution

Other factors to consider: *Starting powder size and milling time*

Y_2O_3 can be forced into solution with bcc Fe by milling



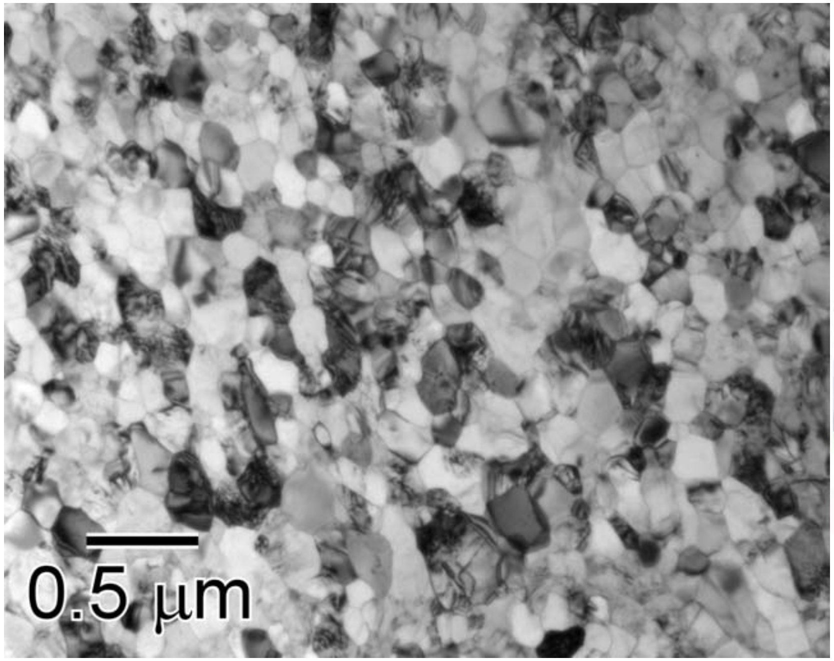
Local Electrode Atom Probe



- Atom maps revealed no evidence of nanoclusters or remnants of the Y_2O_3 particles in the 40 h ball milled powder of 14YWT
- Significantly higher O level in the bcc Fe matrix compared to equilibrium level
- ***The formation of NC occurs during annealing or consolidation of the ball milled powders at high temperatures***

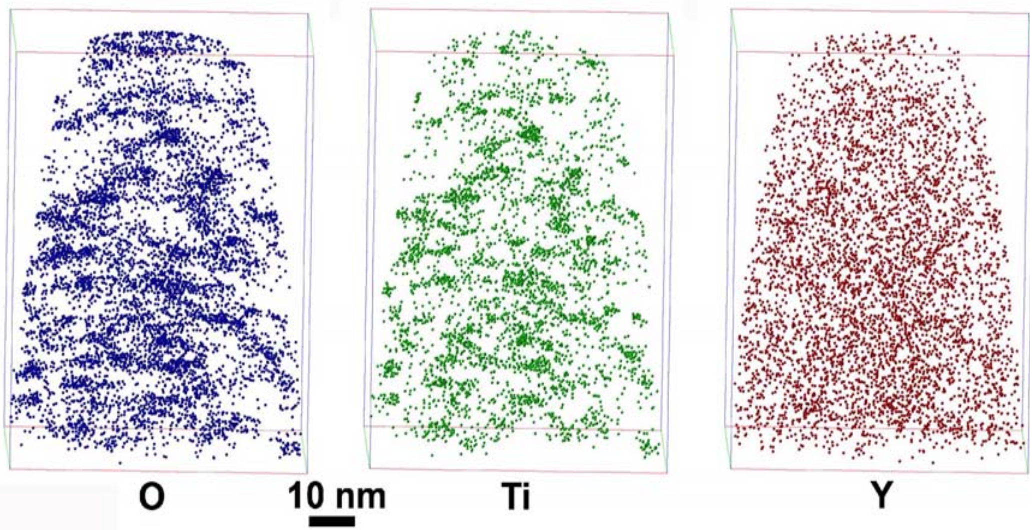
Optimum ball milling produces nano-size grains and high concentration of nanoclusters in 14YWT

BF TEM of SM10 Heat

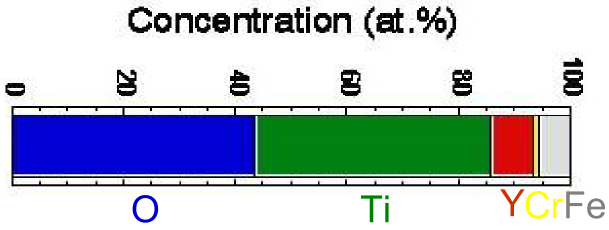


Grain size = 136 (+/- 14) nm
GAR = ~ 1.2

Local Electrode Atom Probe (LEAP)



N_v = 1-7 x 10^{23} m^{-3} **<r> = 1.8 $^{+}$/- 0.4 nm**



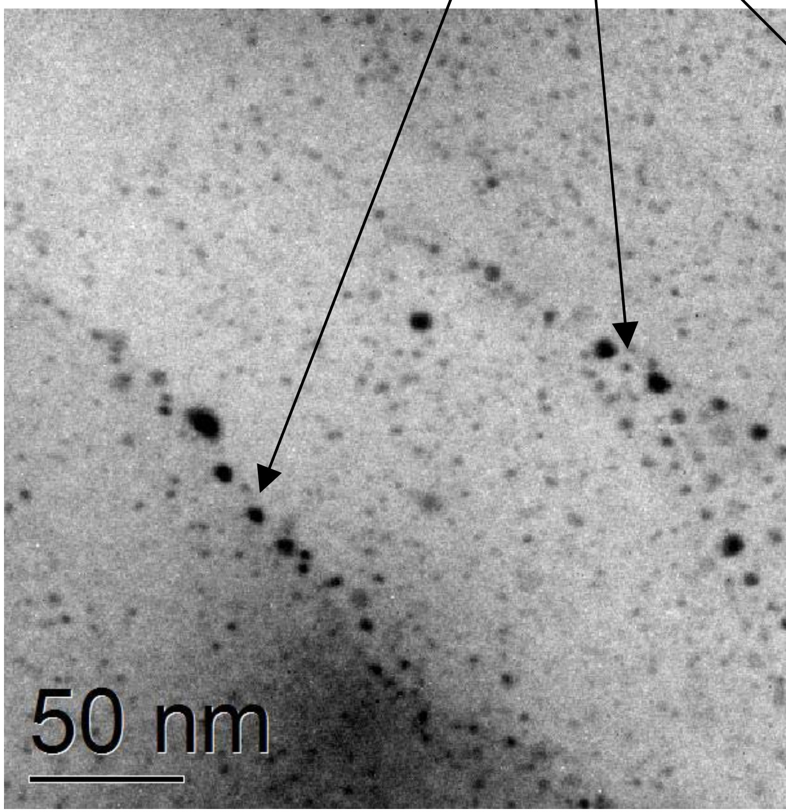
- *Very high interfacial surface area (NC and grain boundaries) may enhance trapping and recombination of point defects*

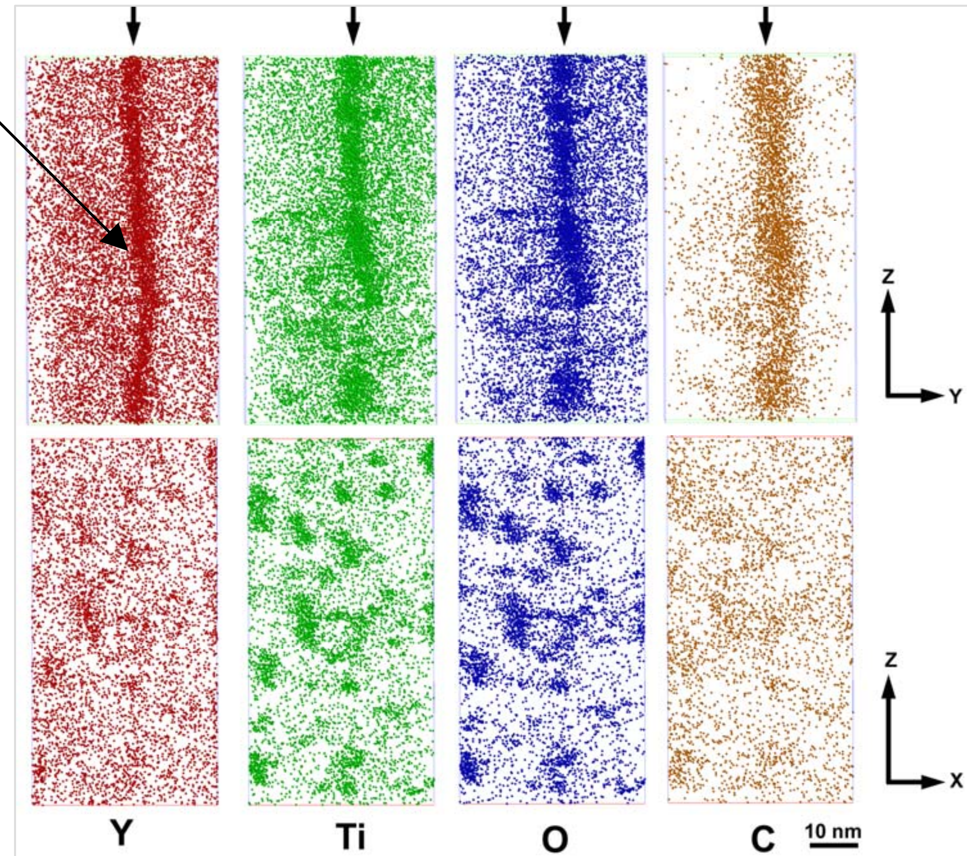
Nucleation of NC (and larger oxide particles) on grain boundaries stabilizes the nano-size grains

EFTEM Fe M Jump Ratio Image

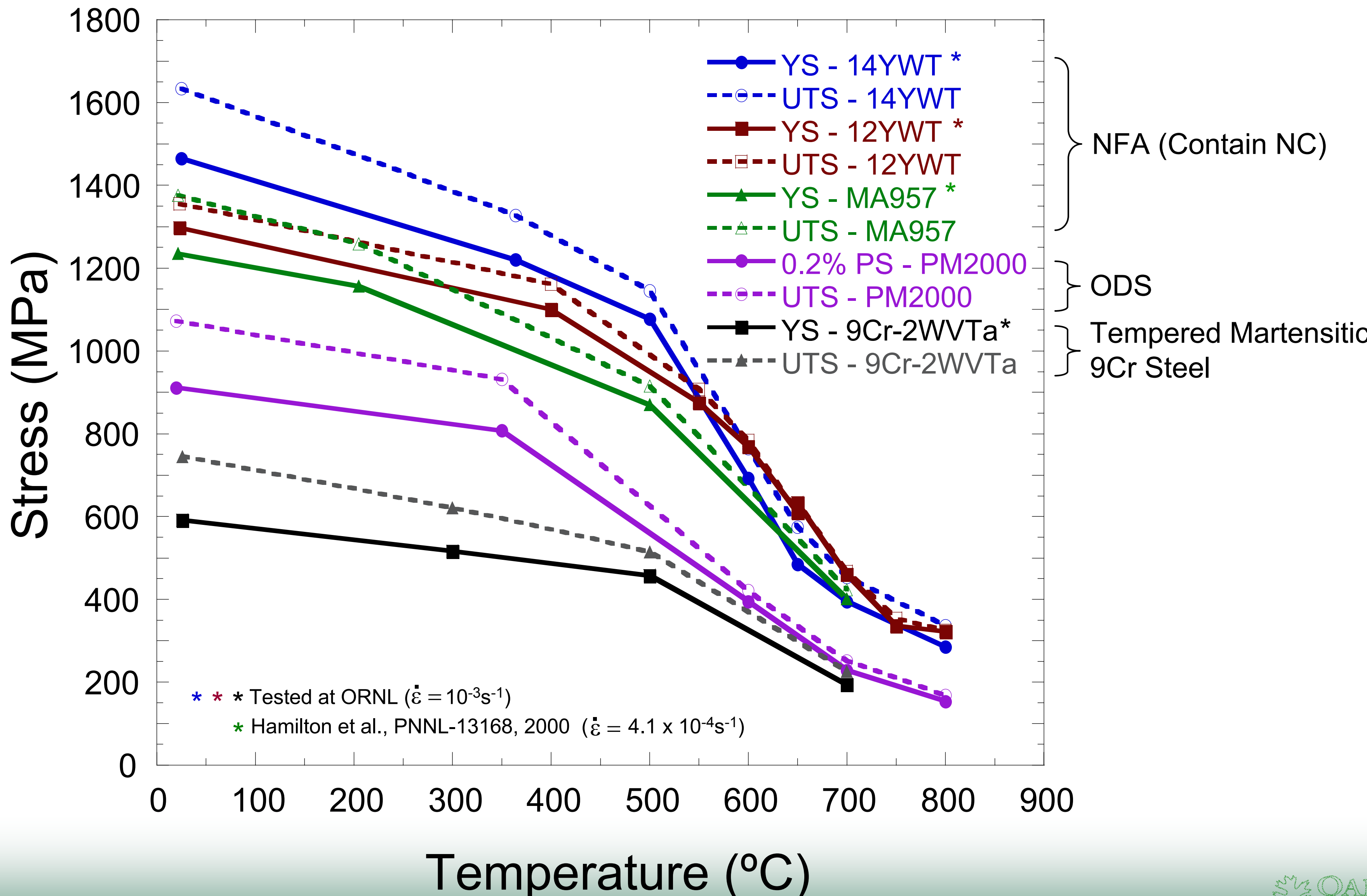
Local Electrode Atom Probe (LEAP)

Grain boundaries

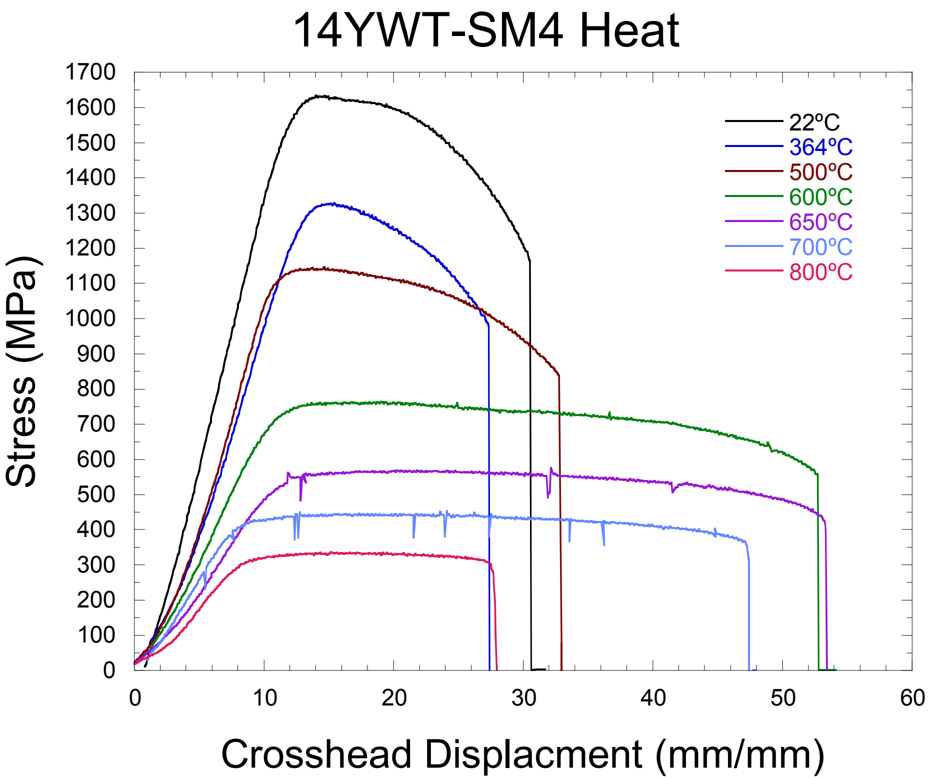


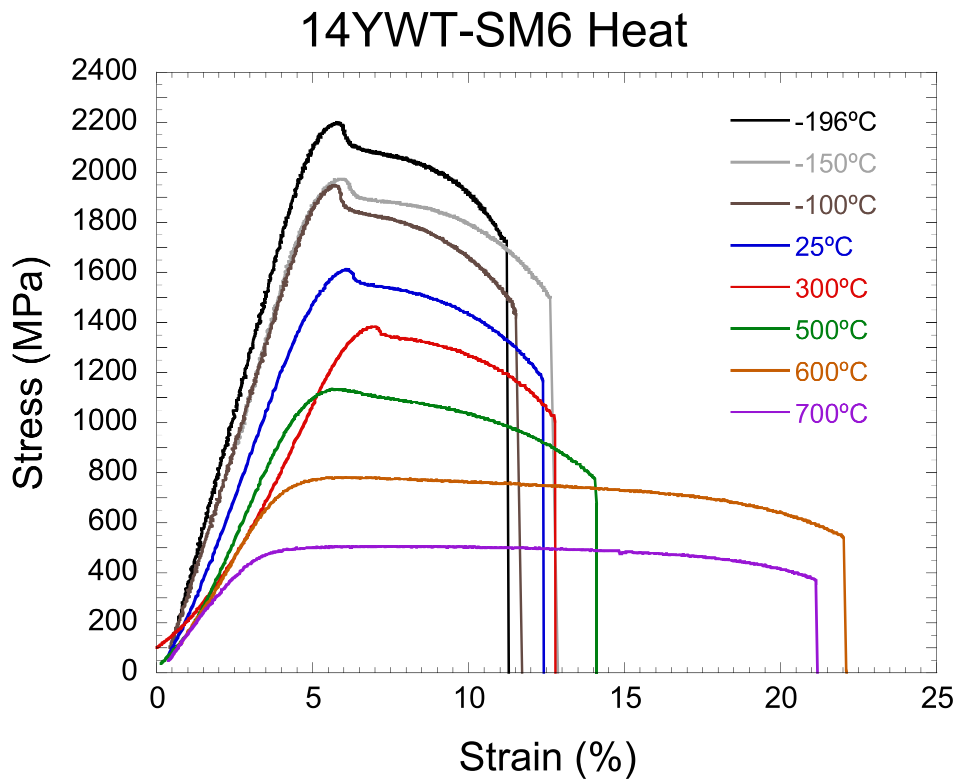


High temperature strength of 14YWT (SM4 heat) is similar to 12YWT and MA957



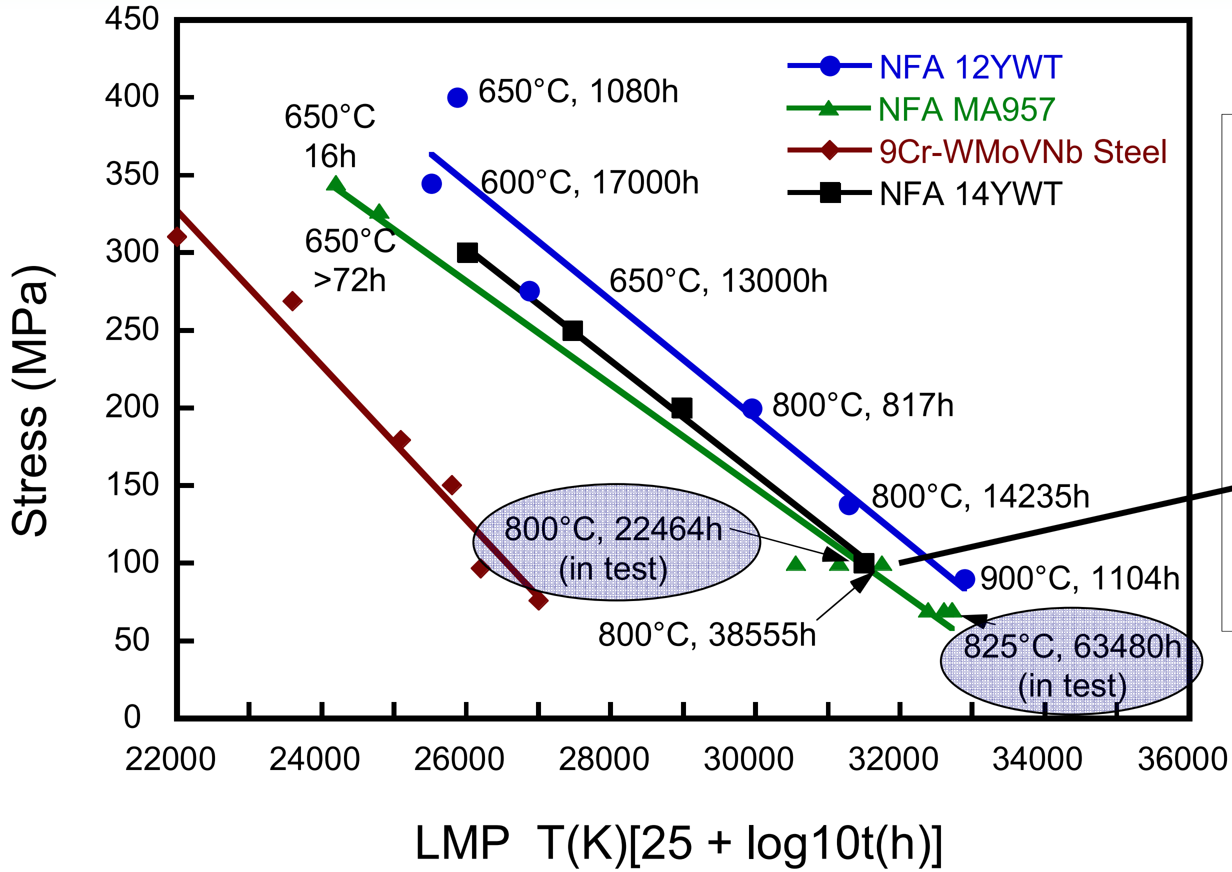
High-strength properties of 14YWT heats is offset with low ductility properties

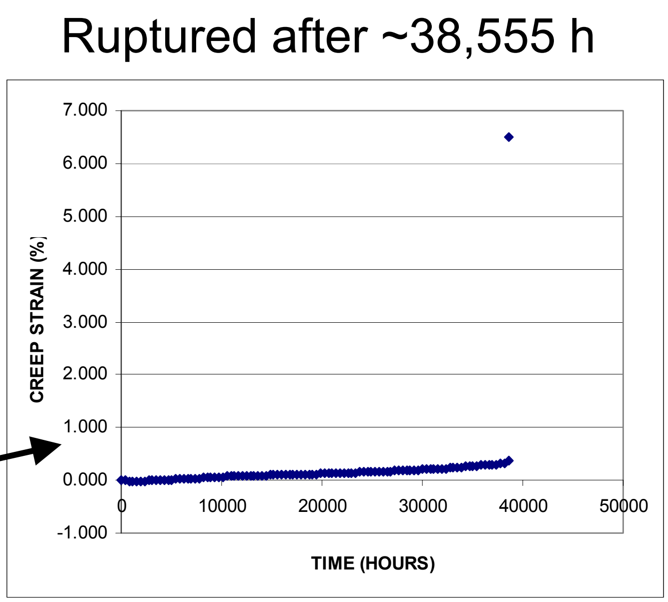




- Low uniform elongation, but extensive plastic deformation occurs after plastic instability until failure
- Total elongation initially increases with higher temperatures, but then starts to decrease up to 800ºC

Creep performance of NFA 12YWT, MA957 and 14YWT





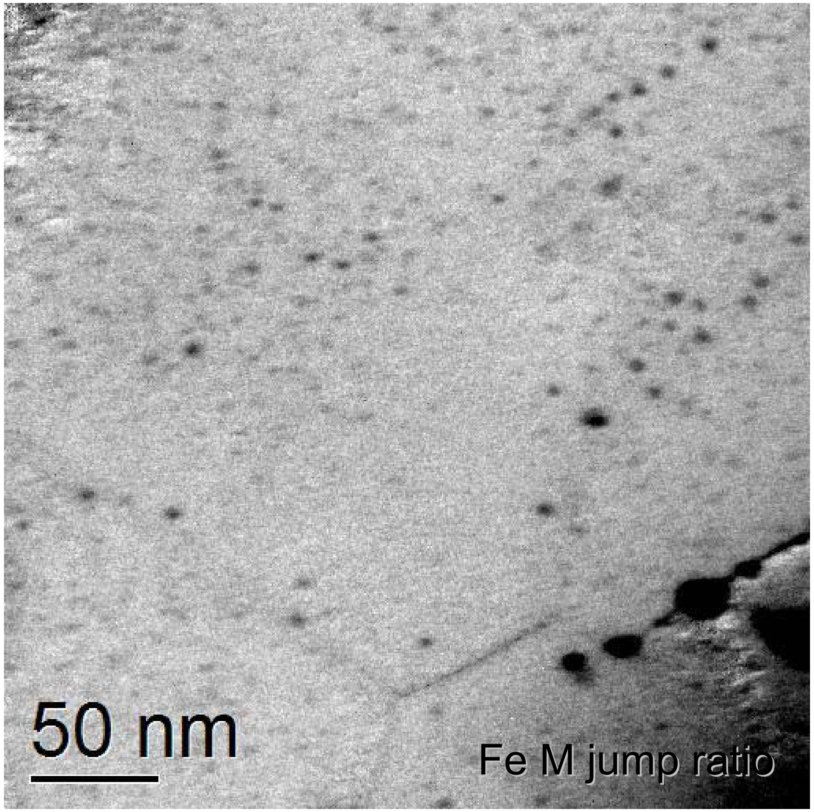
- *Klueh et al, J. Nucl. Mat., (2005)*
- *I-NERI FY01-04*

- Creep test on ruptured MA957 started in Oct., 2003 (INERI)
  - Extensometer creep strain prior to rupture was 0.361% (0.003 in. displacement)
  - The minimum creep rate was ~1.2 x 10^{-11} s^{-1} ($d\varepsilon/dt$)
- Creep test on 14YWT-SM10 started in April, 2008

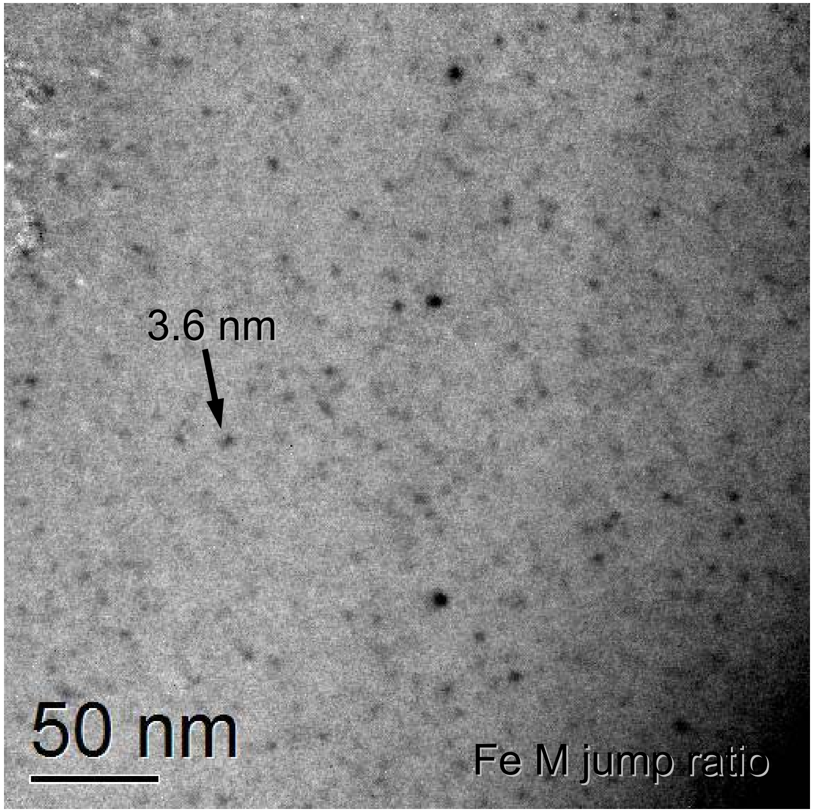
NC are very stable at elevated temperatures

MA957 Creep Specimen

As-received



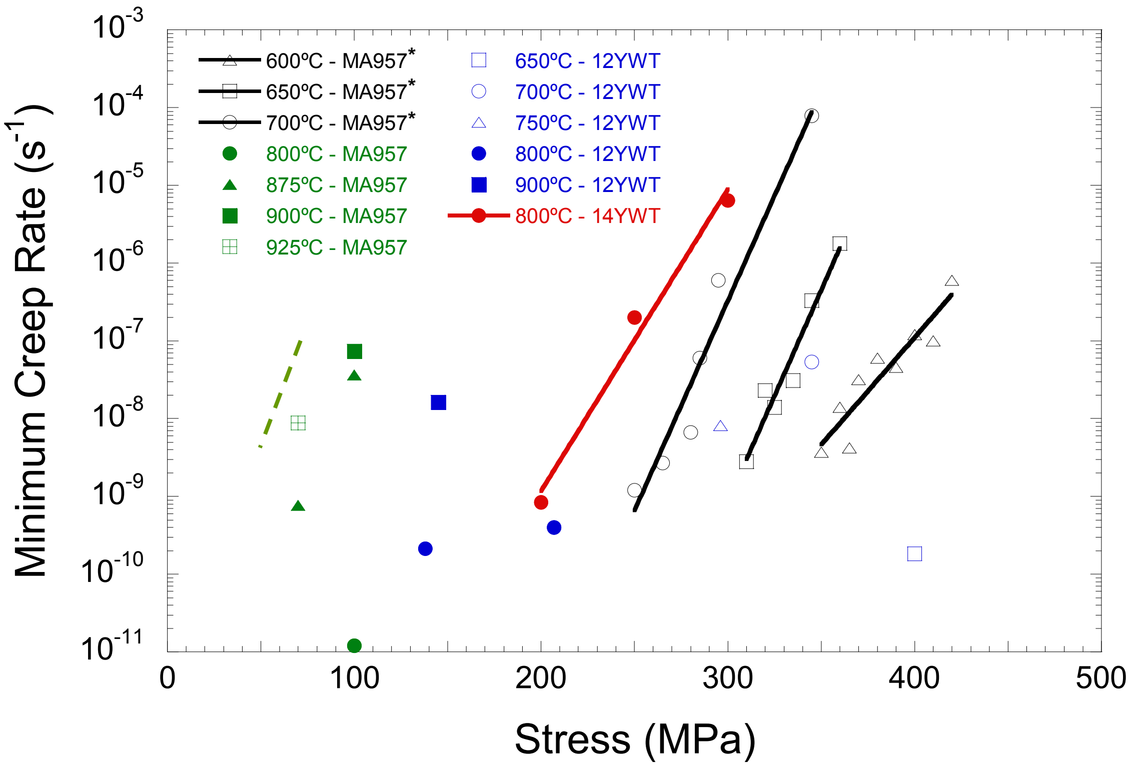
After 38,555 h at 800ºC



- EFTEM revealed no significant change in the size of the NC after 38,555 h (~4.4 years) at 800ºC and 100 MPa
- LEAP analysis has confirmed these results

Creep tests initiated on 14YWT (SM10 heat) in 2009 to study creep deformation mechanisms

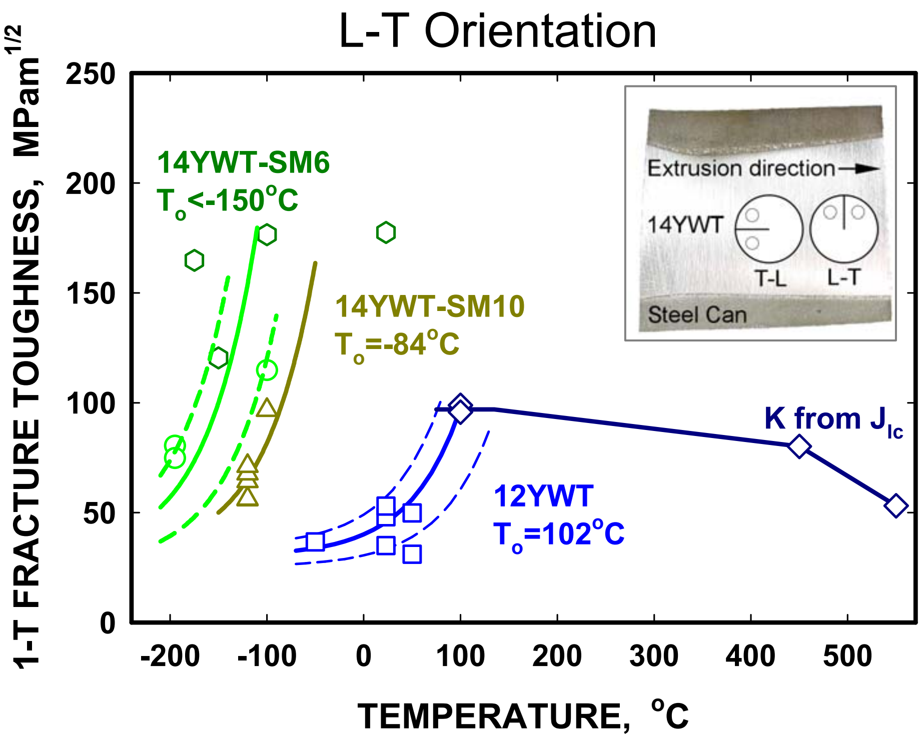
- Tests conducted using MTS with load control and extensometer
- Stress exponent = 24 for 14YWT at 800ºC
- Results are consistent with those for MA957 tested at 600 to 700ºC[1] that showed a high stress exponent (n ~ 35) and activation energy (815 kJ/mol) for creep
- High stress exponents are consistent with threshold stress mechanism



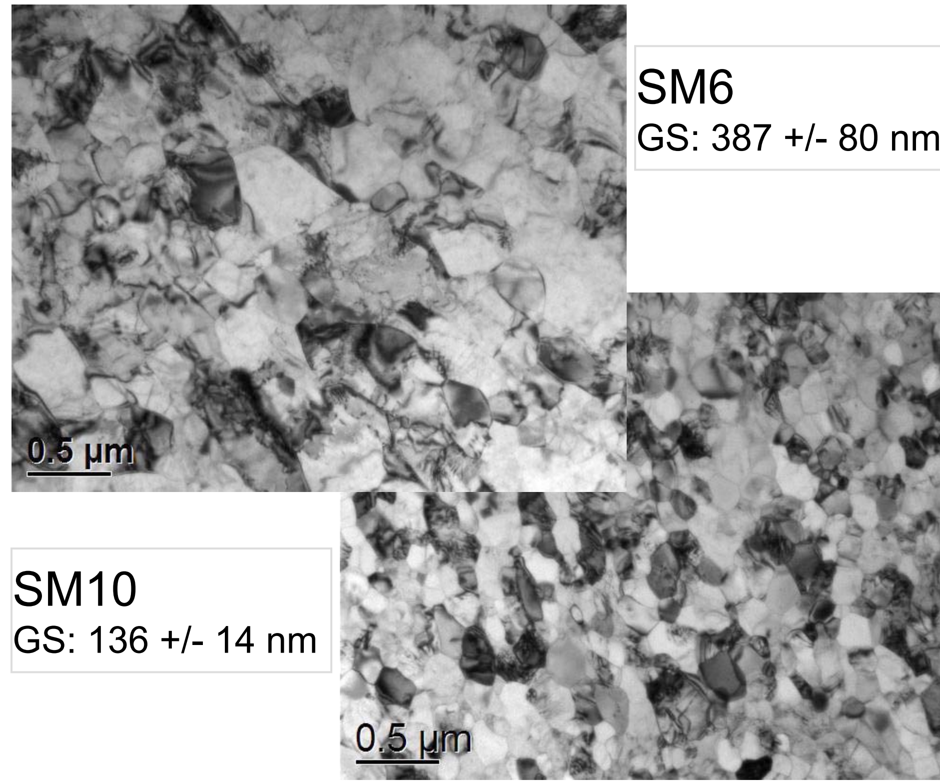
- *Initial results suggest that the nano-size grain structure of 14YWT-SM10 does not significantly degrade the creep properties*

[1] B. Wilshire and T.D. Lieu, Mat. Sci, Engin. A, 386, (2004), 81.

Fracture toughness transition temperature of 14YWT

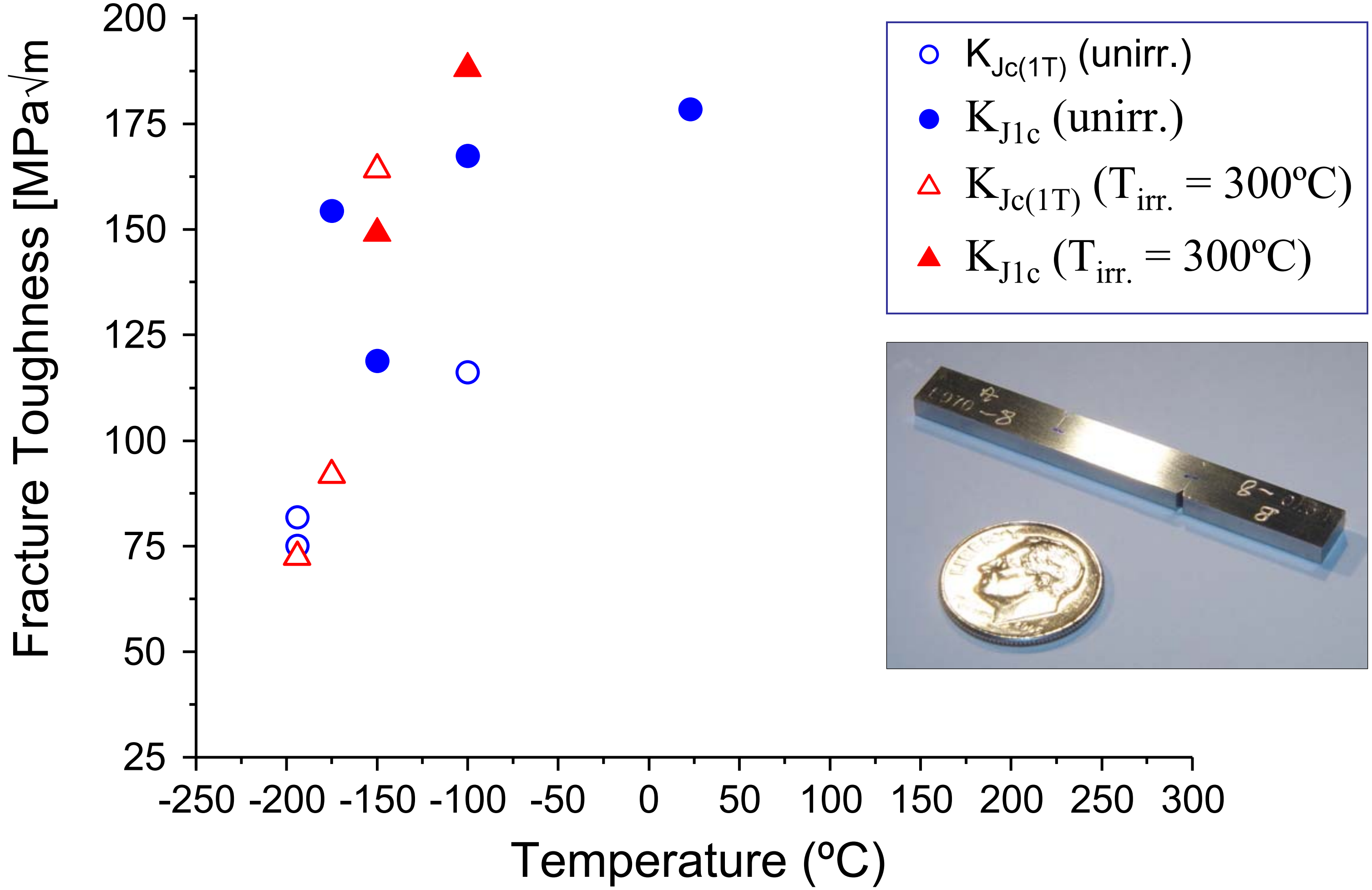


Two heats of 14YWT alloys



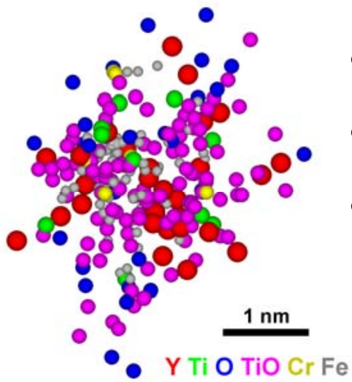
- FTTT in the L-T orientation is very low, but depends on the 14YWT heat
  - *grain size difference is not a major factor*
- FTTT for 14YWT heats were still significantly lower than that of 12YWT
- New results for SM10 showed T_0 of -84ºC in L-T compared to 18ºC in T-L
  - *anisotropy still had a significant effect on the FTTT*

Fracture toughness of 14YWT (SM6) after low dose and temperature HFIR neutron irradiation experiment



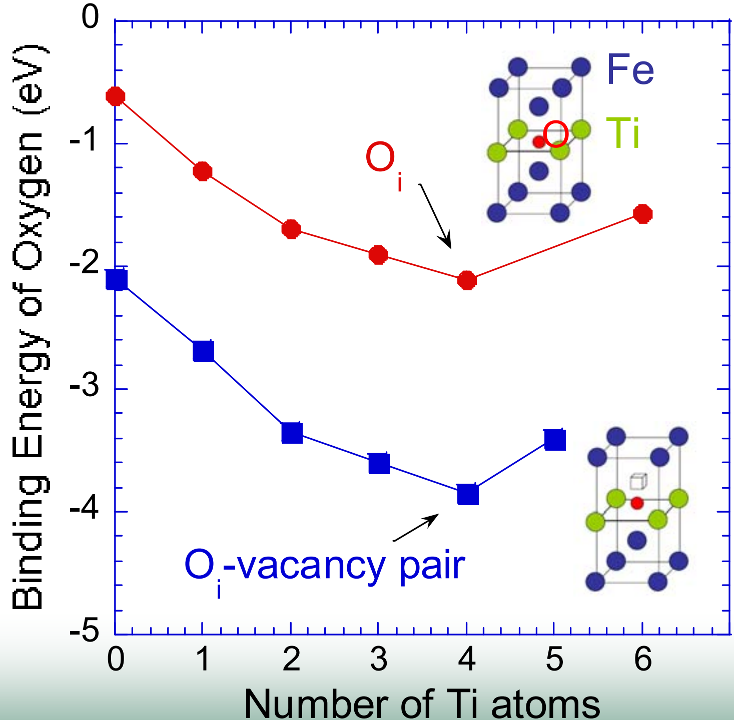
No shift in FTTT observed after irradiation at 300ºC to ~ 1.5 dpa

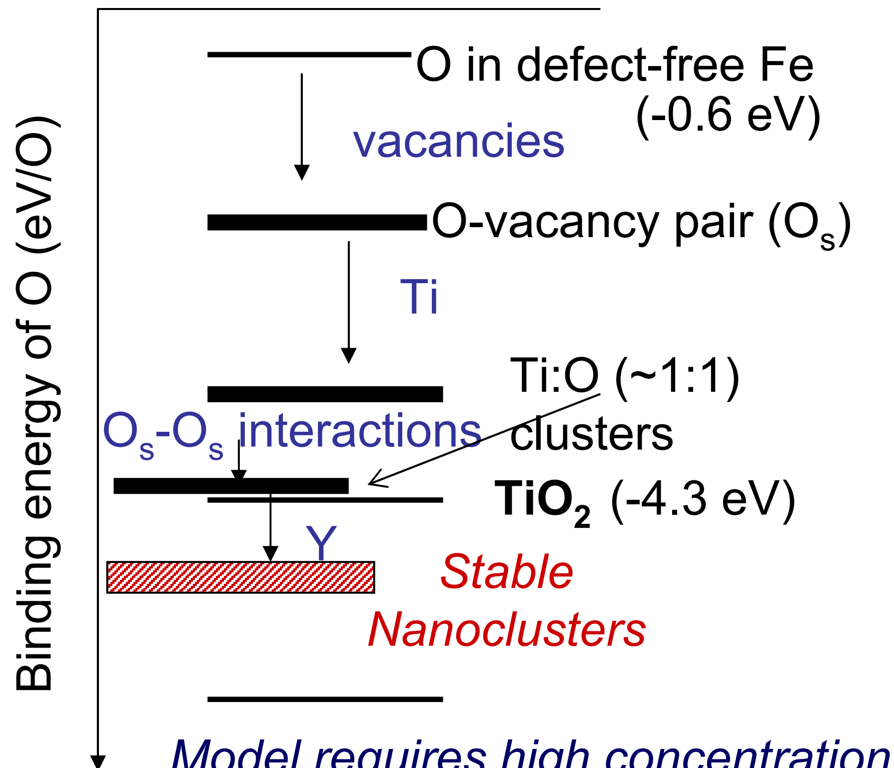
Theoretical model indicates vacancies may play a vital role in the formation and stability of nanoclusters



- Y+Ti (M):O ratio ≅ 1.2 (not consistent with known oxides)
- Unusually strong vacancy-oxygen binding in bcc Fe
- But, very high vacancy formation energy

Ti (and Y) strengthen O-V binding energy





Model requires high concentration of vacancies that only ball milling can produce at low temperatures

Fu and Krcmar; First Principles Theory (BES: C.T. Liu, P.I.)

Summary of R&D of advanced ODS ferritic alloys over the past 9 years

- Advanced ODS ferritic alloys strengthened by nanoclusters possess attractive high-temperature strength and creep properties
  - But ductility and failure mechanisms suffer
- Nanoclusters show remarkable stability during long-term creep; low (neutron) and high (ion) dose irradiations; and short-term high-temperature exposures
  - NC appear to trap He and possibly point defects, causing their recombination
  - But information about their structure and chemistry is still lacking
- Development of 14YWT has approached “maturity”
  - Numerous small heats have been produced for a variety of studies
- But:
  - *heat-to-heat variations still influence mechanical properties*
  - *Plus, anisotropy still affects the mechanical properties, even though the GAR is reduced with nano-size grains*

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