



U.S. DEPARTMENT OF  
**ENERGY**

**Nuclear Energy**

# Fuel Cycle Research and Development: **Core Materials Technologies Overview - Fast Reactor and LWR Fuel Cladding**

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**DOE NE Materials-Cross-Coordination  
Webinar**

**July 30, 2013**

***LA-UR-13-25972***



# Contributors

## Nuclear Energy

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# Advanced Fuels Campaign Mission & Objectives in the Fuel Cycle Research and Development Program

## Mission

Develop and demonstrate fabrication processes and in-pile (reactor) performance of advanced fuels/targets (including the cladding) to support the different fuel cycle options defined in the NE roadmap.

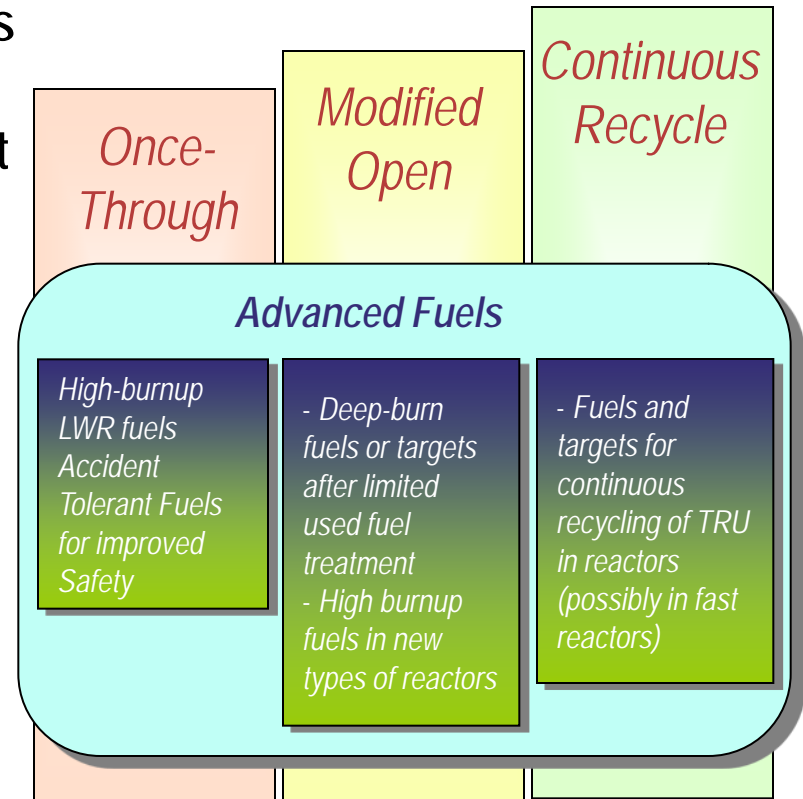
## Objectives

### Development of the fuels/targets that

- Increases the efficiency of nuclear energy production
- Maximize the utilization of natural resources (Uranium, Thorium)
- Minimizes generation of high-level nuclear waste (spent fuel)
- Minimize the risk of nuclear proliferation

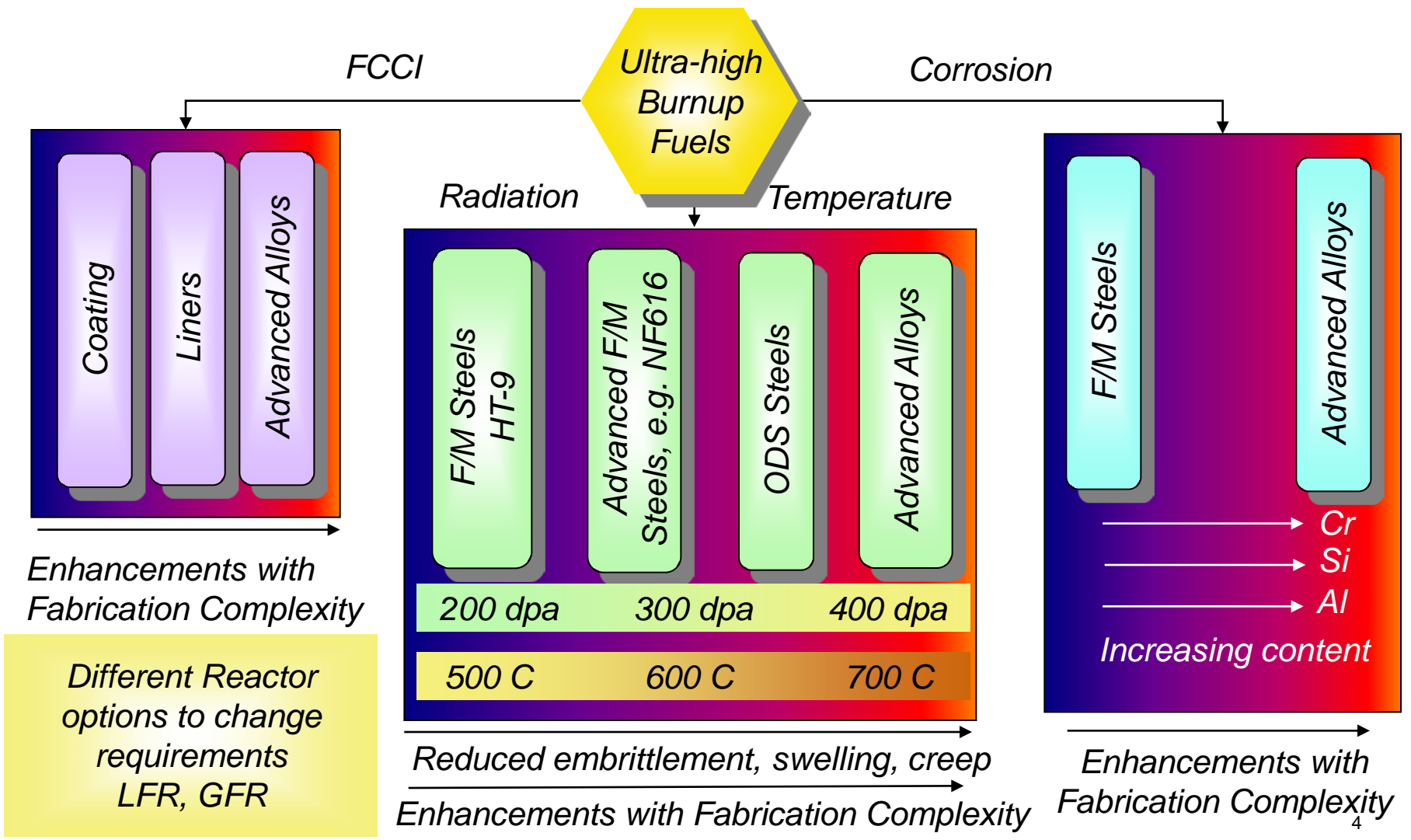
## Grand Challenges

- Multi-fold increase in fuel burnup over the currently known technologies
- Multi-fold decrease in fabrication losses with highly efficient predictable and repeatable processes



# Approach to Enabling a Multi-fold Increase in Fuel Burnup over the Currently Known Technologies

**Ultimate goal: Develop advanced materials immune to fuel, neutrons and coolant interactions under specific reactor environments**





### ■ **Qualify HT-9 to Radiation Doses >250 dpa**

- *Test previously irradiated materials (ACO3 duct and FFTF/MOTA specimens)*
- *Measure data for model development – rate jump testing*
- *Extend irradiation data to higher doses – Re-irradiation of specimens in BOR-60*

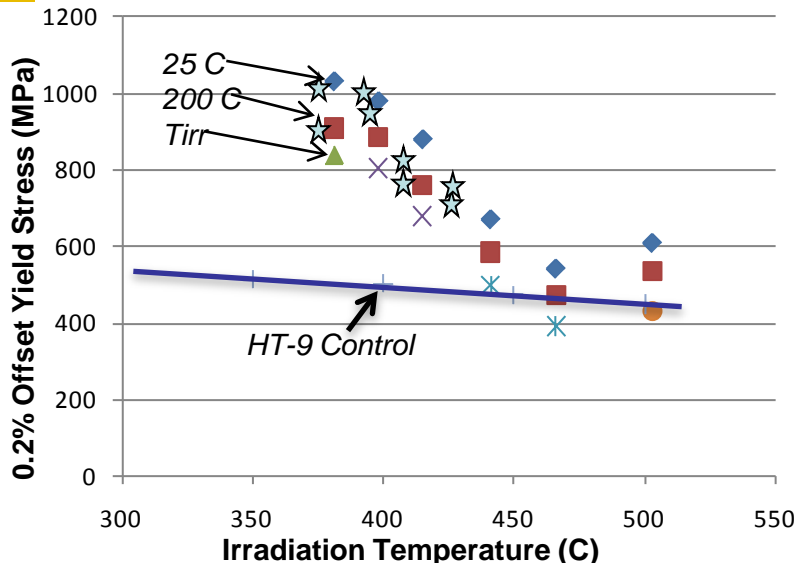
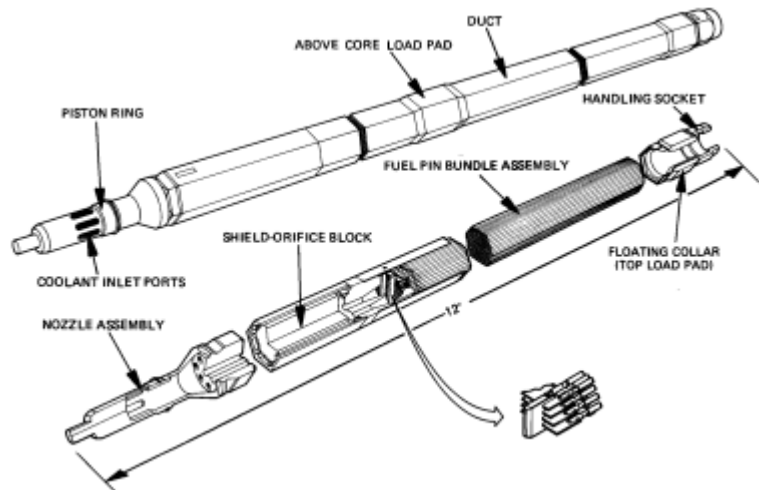
### ■ **Develop Advanced Radiation Tolerant Materials**

- High dose irradiation testing
- High dose ion irradiation testing
- Scale up ODS processing (15 kg milling runs complete)
- Tube production and weld development

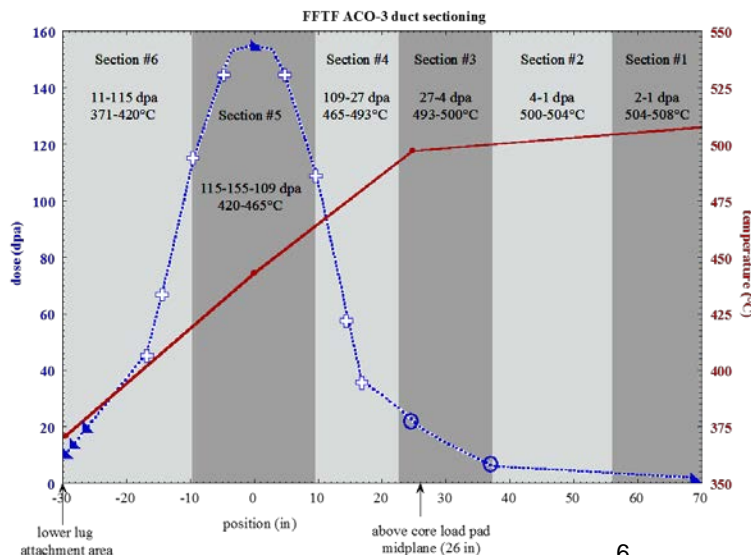
### ■ **Develop Coatings and liners to prevent FCCI**

- Diffusion couple test
- TiN coating on tube

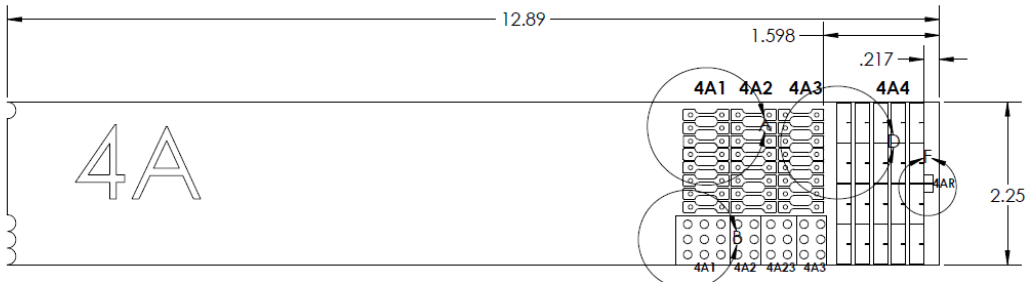
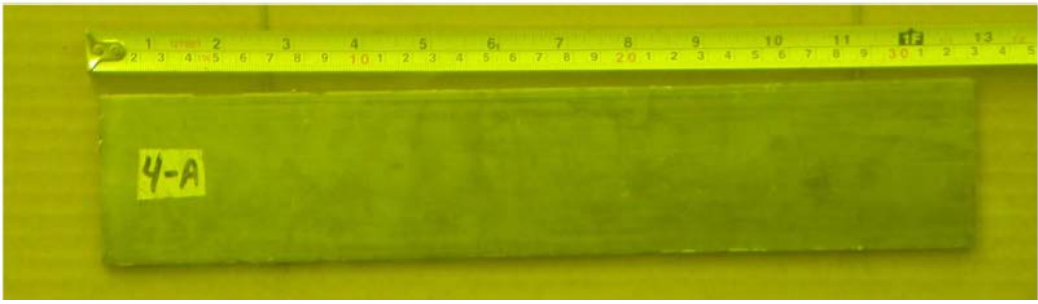
# Analysis of Specimens from ACO-3 Duct



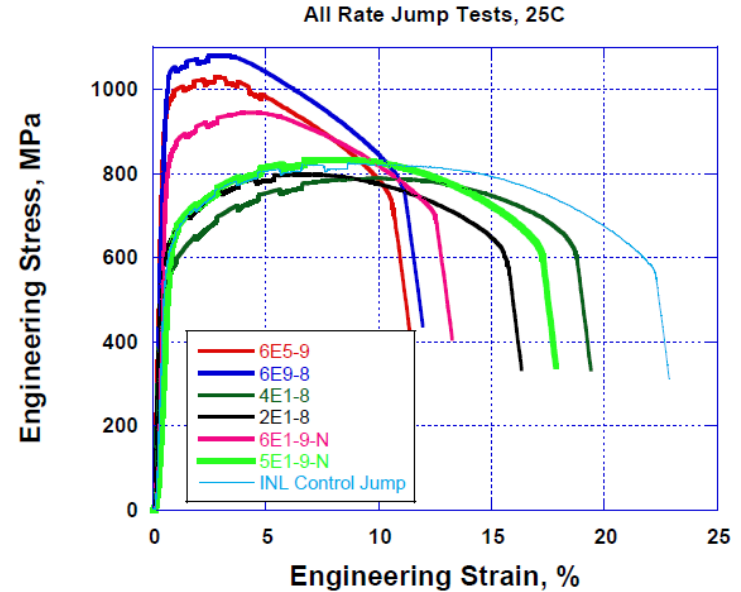
- Total specimens= 144 Charpy, 57 compact tension, 126 tensile specimens, 500 TEM
- Charpy and Compact Tension specimens completed testing at ORNL. Thermal annealing testing completed.
- Completed tensile testing from 6 different locations along the duct at 25, 200 and the irradiation temperature.
- Completed Rate Jump Testing at 25° C
- Detailed microstructural analysis performed.
- New specimens EDM machined for BOR-60 Irradiation



# Tensile Testing Completed on High Dose Irradiated F/M Steels



*Diagram showing specimen cut plan from ACO-3 duct for re-irradiation in BOR-60*



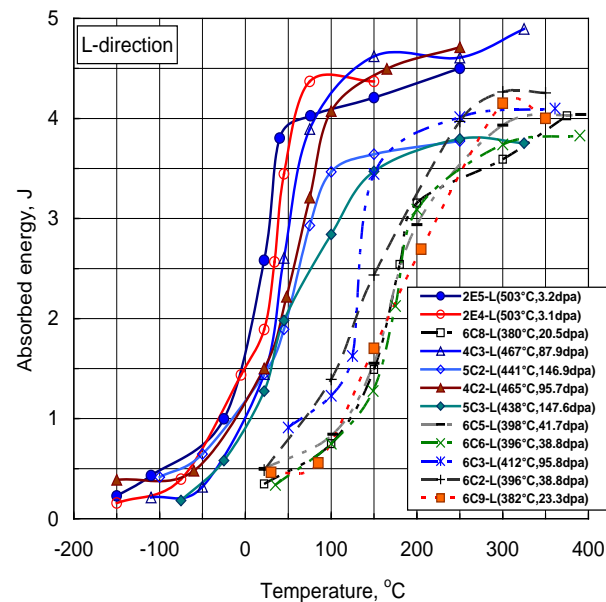
*Stress-strain curves measured on irradiated HT-9 while performing rate jump testing*

- LANL recently shipped samples to Russia for re-irradiation in BOR-60 through CRADA with Terrapower.
- LANL completed rate jump tests on specimens from the ACO-3 duct. Data is being coordinated with model development.

# Study on Annealing Recovery of Fracture Toughness in ACO-3 Duct HT9 by Specimen Reusing Technique



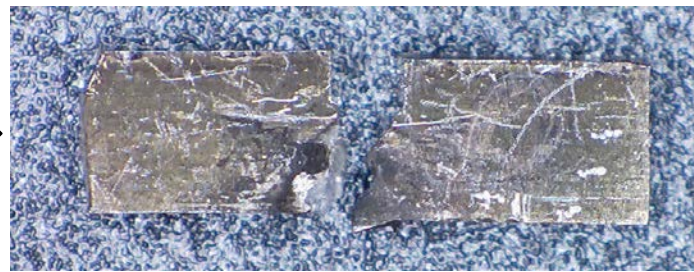
Charpy impact test data



*These Charpy specimen halves were reused for J-R tests: annealed, notched, precracked, and fracture (J-R)-tested.*



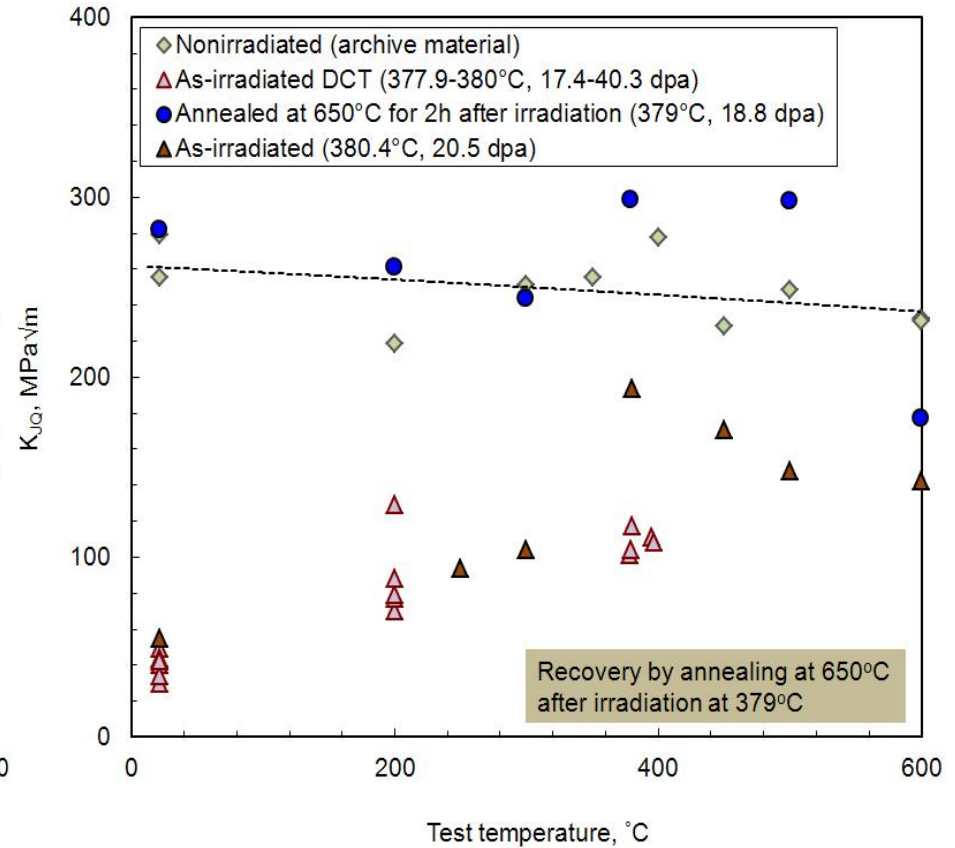
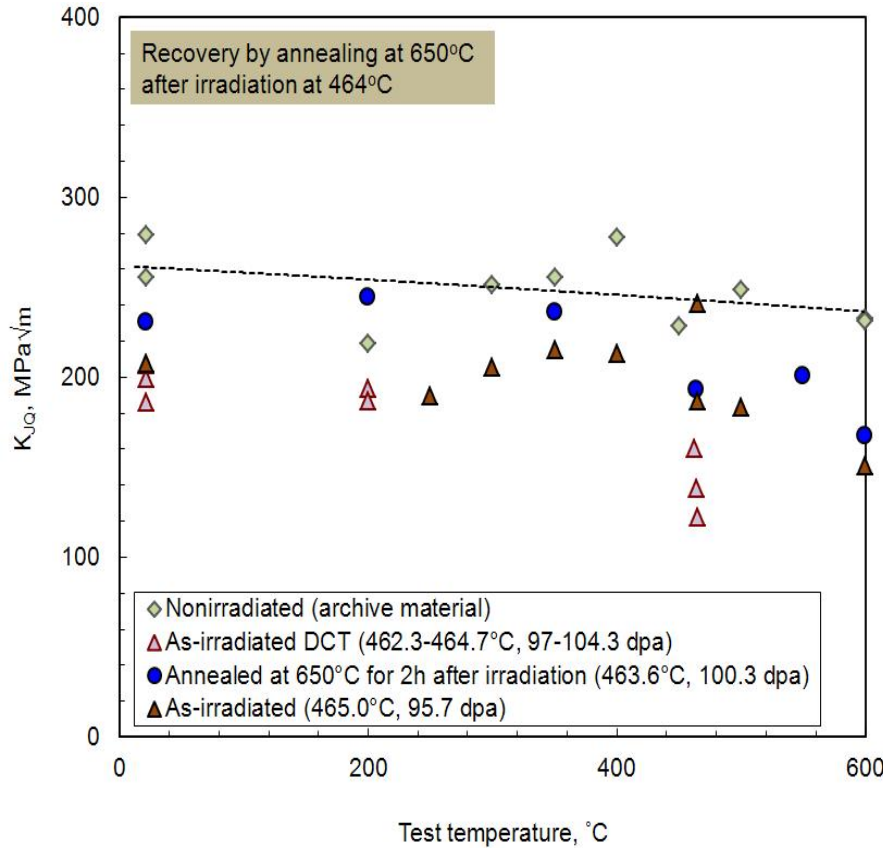
An annealed half



Pieces after fracture(J-R) test



# Recovery of $K_{JQ}$ by 650°C Annealing after High Dose Irradiation



- Complete or near-complete recovery of fracture toughness was observed after 650° C annealing. The toughness recovery was particularly strong after low temperature (~380° C) irradiation.
- After 650° C annealing a decrease of  $K_{JQ}$  occurred when the test temperature > 500° C although the lowest fracture toughness measured at 600° C was still higher than 170  $MPa\sqrt{m}$ .
- ❖ **Thermal annealing treatment can be a mitigation tool against the radiation-induced embrittlement in HT9 steel core.**



# Objectives

## ■ Qualify HT-9 to Radiation Doses >250 dpa

- Test previously irradiated materials (ACO3 duct and FFTF/MOTA specimens)
- Measure data for model development – rate jump testing
- Extend irradiation data to higher doses – Re-irradiation of specimens in BOR-60

## ■ *Develop Advanced Radiation Tolerant Materials*

- *High dose irradiation testing*
- *High dose ion irradiation testing*
- *Scale up ODS processing (15 kg milling runs complete)*
- *Tube production and weld development*

## ■ Develop Coatings and liners to prevent FCCI

- Diffusion couple test
- TiN coating on tube

# Analysis of High Dose Neutron Irradiated MA957 Tubing Underway at PNNL

## Irradiation conditions

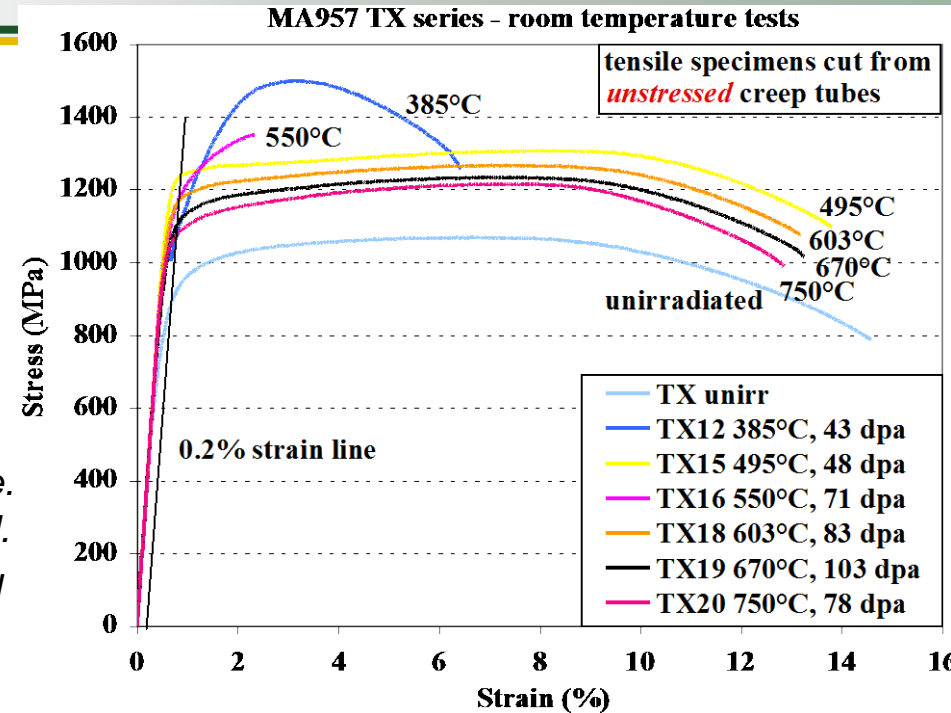
- (385° C, 18-43 dpa)
- (412° C, 110 dpa)
- (500-550° C, 18-113 dpa)
- (600-670° C, 34-110 dpa)
- (750° C, 33-120 dpa)

## Status

- First set of room temp tensile tests complete.
- Initial microstructural exams using APT complete.
- In-reactor creep and swelling response analyzed.
- 500 dpa ion irradiations complete with measured swelling.

## Current post-irradiation results:

- Tensile: No loss in ductility at all but lowest irradiation temperature exhibits higher strength.
- In-Reactor Creep: Comparable to HT-9 in creep resistance to up to 550° C, much better resistance at 600° C and higher.
- Swelling: No swelling after 110 dpa neutrons. Slight swelling after 100 dpa ions, 4.5% max swelling after 500 dpa ions:
- Microstructure from APT: See next slide.

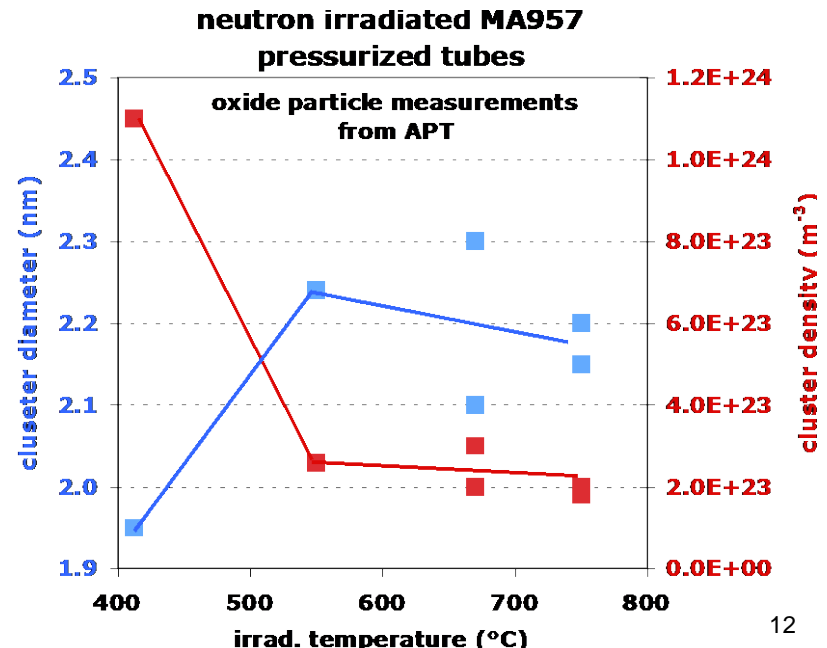
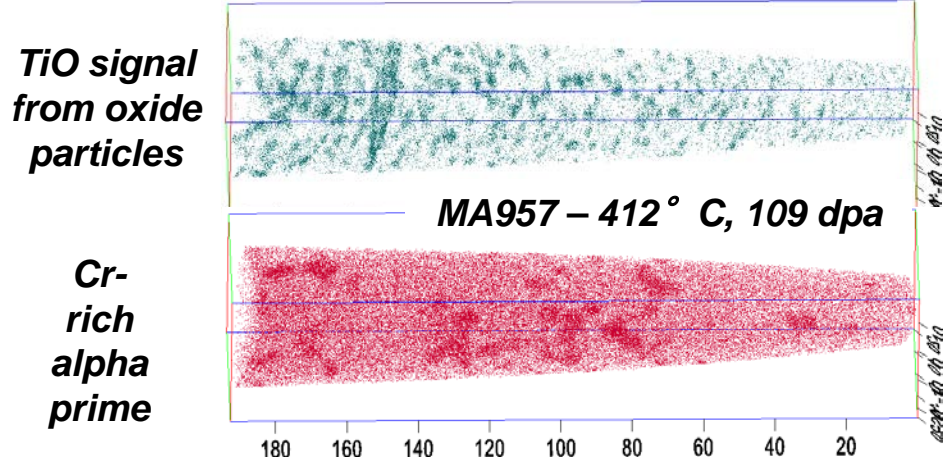


# High Dose MA957 ODS Ferritic Alloy APT Exams at UC Berkeley

- Objective – Study microstructure of neutron irradiated ODS ferritic steel, with emphasis on oxide particle morphology.
- Material - MA957 from in-reactor pressurized tube creep specimens.
- Preliminary APT examinations completed on specimens irradiated at 412, 550, 670, and 750° C to 109-121 dpa.

## Initial Results

- MA957 pressurized tubes have a small oxide particle size of ~2 nm similar to newer ODS steels such as 14YWT.
- No obvious ballistic dissolution at these irradiation temperatures, but small difference in oxide particle population at 412° C.
- Cr-rich alpha-prime clusters observed at 412° C irradiation temperature consistent with 14Cr composition.
- Some grain boundary segregation.



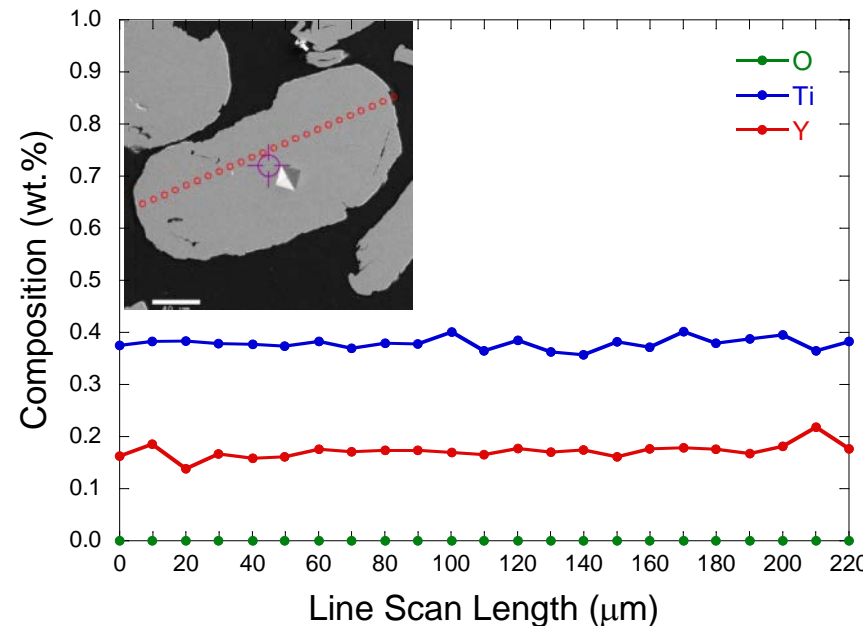


# Scale Up Production of 14YWT Ferritic Alloy (Heat FCRD-NFA1)

- 4 of 4 ball milling runs completed by Zoz
  - V540-01: 15 kg of coarse ( $>150\ \mu\text{m}$ ) powder
  - V540-02: 15 kg of medium (45-150  $\mu\text{m}$ ) and fine ( $<45\ \mu\text{m}$ ) powder
  - V540-03: 15 kg medium, fine and small amount of V540-01 coarse powder
  - V540-04: 15kg medium, fine powder mixed with yttria for the oxide dispersion.

V540-02 Ball Milled 40 h	
MET. SPECIMEN NO: 12-0581	
LOAD in grams: 200	
Indent no.	HV
1	723.57
2	744.47
3	726.78
4	713.14
5	700.18
6	768.03
AVERAGE = 729.36	
STD = 23.99	

- EPMA showed 40 h ball milling distributed Y uniformly in fine and medium powders
- 40 h ball milling did not distribute Y uniformly in coarse powders
- Mechanical testing underway.



# High Toughness ODS Ferritic Alloy Development in FC R&D (I-NERI)

- ***Development and Characterization of Nanoparticle Strengthened Dual Phase Alloys for High Temperature Nuclear Reactor Applications***
- **To develop high toughness NFAs\* for high temperature (700°C) high dose (>300 dpa) applications: 100 MPa√m over the range of RT - 700°C.**
- **Use grain boundary strengthening/modification techniques.**
- ***ORNL (TS Byun & D.T. Hoelzer) – KAERI (JH Yoon)***
- ***Dec. 1, 2010 – Nov. 30, 2013***

\* *Nanostructured Ferritic Alloys (NFAs) vs. Oxide Dispersion Strengthened (ODS) Alloys*



# Production of Base Materials (9YWTV)

## Nuclear Energy



Two alloy power heats (8 kg each) have been produced by gas atomization process at ATI Powder Metals:

**Fe-9Cr-2W-0.4Ti-0.2V-0.12C+0.3Y<sub>2</sub>O<sub>3</sub>** &  
**Fe-9Cr-2W-0.4Ti-0.2V-0.05C+0.3Y<sub>2</sub>O<sub>3</sub>**



Ball milling for 40 hours in Zoz CM08 machine (6 loads)/ Canned & degassed (6 cans, 920g each)



Extruded below 850°C  
Cut into 4 inch long blocks



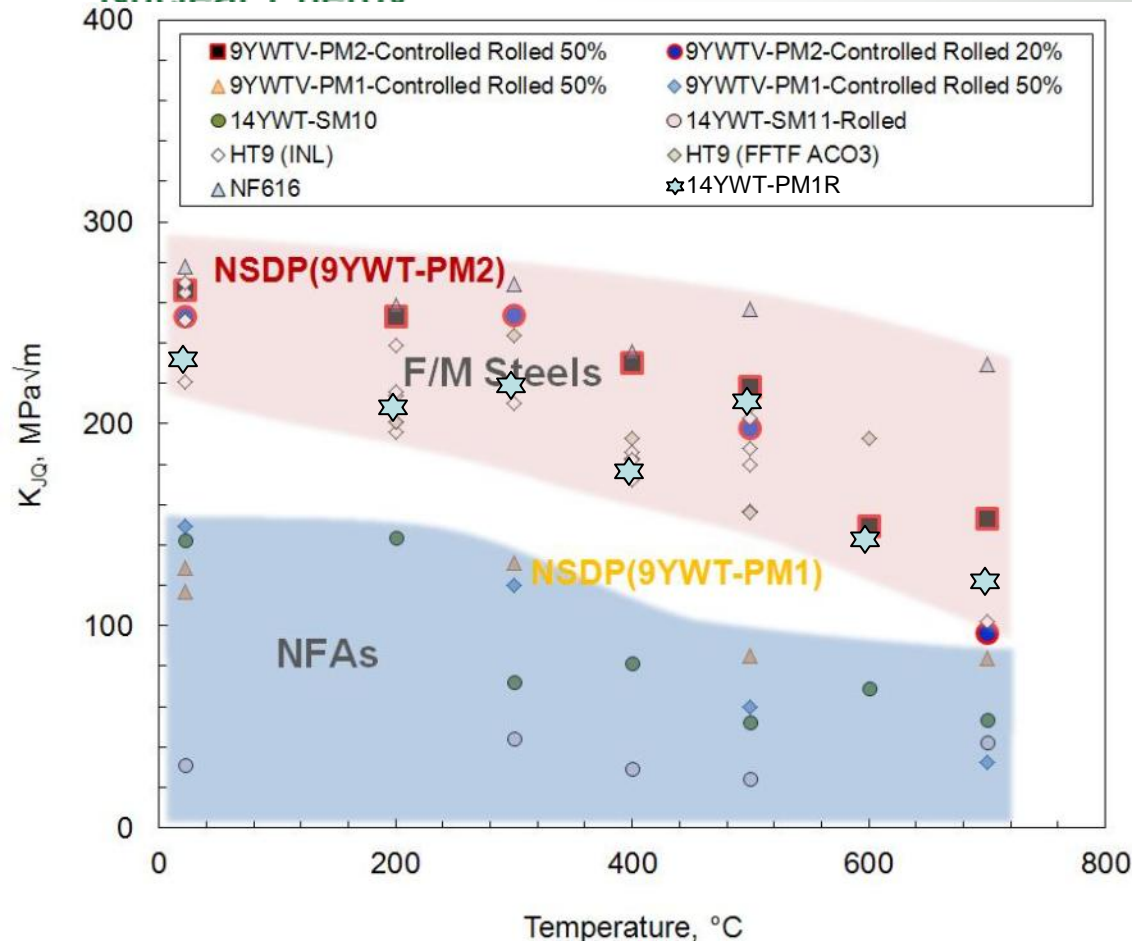
Characterization

- Goals of Yrs 2 & 3:**
- Post-Extrusion TMT Optimization
  - Micro & High Temp. Characterization
  - Feedbacks for new processing



# Preliminary Results for Fracture Toughness

## Nuclear Energy



- 9YWTV-PM2-850C-200m: Annealed at 850°C for 200 minutes.
- 9YWTV-PM2-850C-20H: Annealed at 850°C for 20 hours.
- 9YWTV-PM2-900C-50%R: Hot-rolled for multi-step 50% reduction after annealing at 900°C.

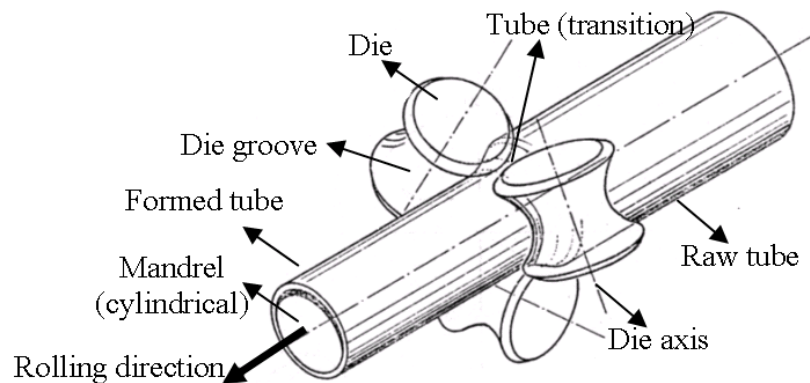
- **Fracture toughness can be significantly improved by some controlled rolling, and the  $K_{JQ}$  values are as high as those of FM steels.**
- Further development/optimization of processing is underway.



# Fabrication of Cladding Tubes from ODS alloys

- 3 cans were designed and fabricated for producing thick wall tubes from the ODS 14YWT and 9Cr-ODS alloys
- Powder has been ball milled, canned and hot extruded.
- Potential collaboration with Y. de Carlan, CEA, Saclay to produce cladding tubes

*High-Precision Tube Roller  
Pilger equipment at CEA*





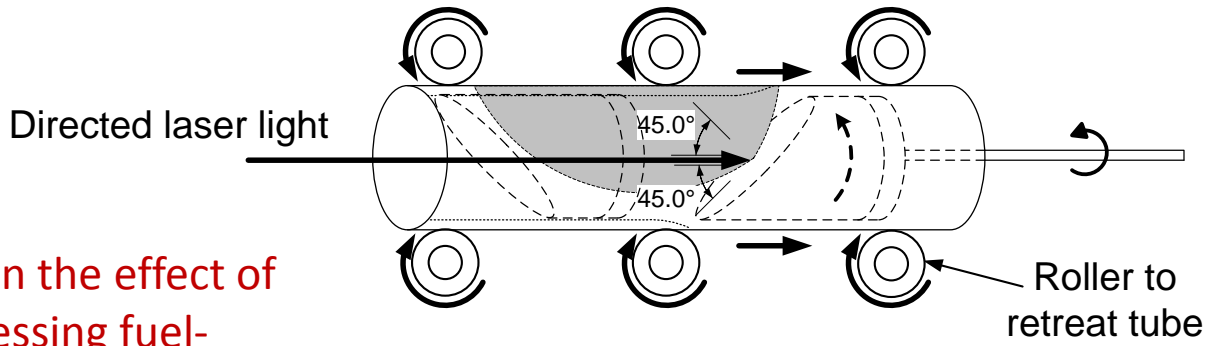
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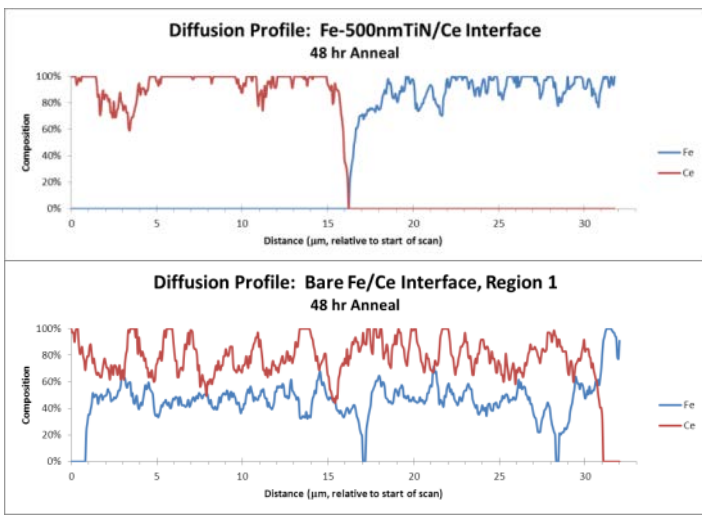
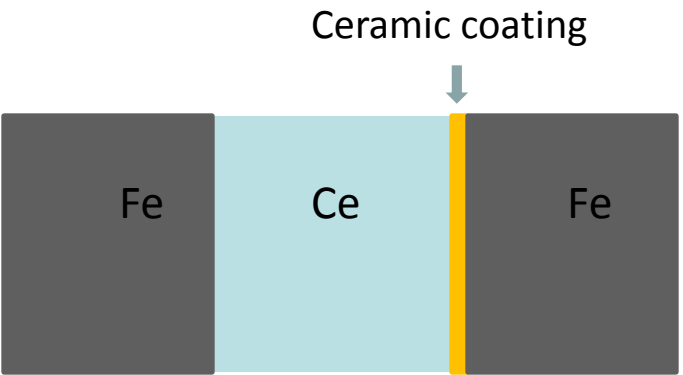
# Coating and Diffusion Couple Study for FCCI Mitigation

A customer-designed laser deposition system for inner wall coating of long tube is being used at Texas A&M University for the FY2012 coating work

Retreating tube with rotating target pellet holder



Diffusion couple studies on the effect of ceramic coating on suppressing fuel-cladding-chemical-interaction (550 – 600 °C for 12-24 hours)



The effect of a 500 nm thin TiN coating on Fe-Ce interaction (550°C/48 hrs)



# Met Level 2 Milestone to Fabricate Coated Cladding Tube for Fuels Irradiation in ATR



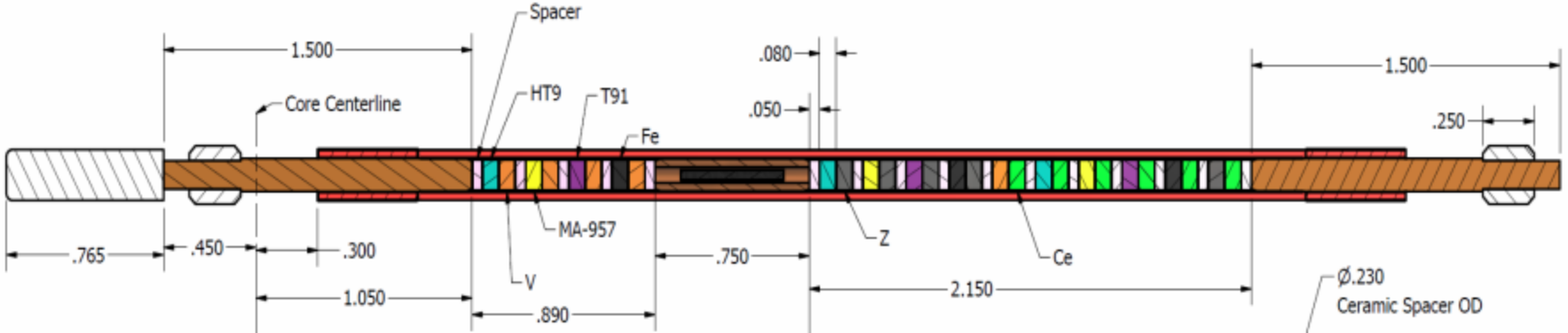
**TiN Inner coating formed on glass tube to test TiN coating process**



**Successful run performed on HT-9 tube for ATR irradiation.**

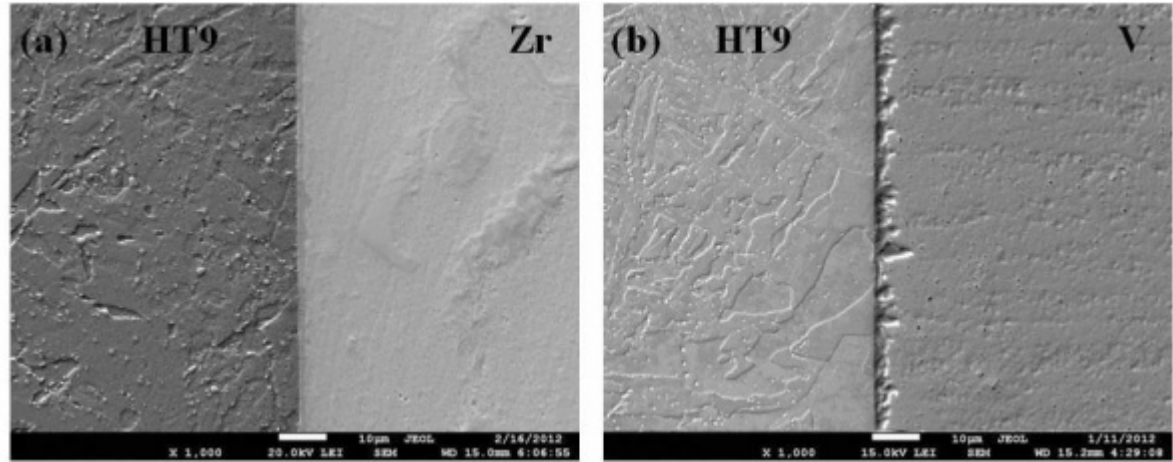
# Diffusion Couple Studies on FCCI Mitigation

Designed a diffusion couple irradiation experiment in ATR (550 °C for 50 days) to meet the temperature and post-irradiation-examination requirements.



Interaction zone thickness: 0.5  $\mu\text{m}$     Interaction zone thickness: 8  $\mu\text{m}$   
 Interdiffusion zone thickness: 18  $\mu\text{m}$     Interdiffusion zone thickness: 28  $\mu\text{m}$

Diffusion couple thermal annealing studies on chemical compatibility at the cladding – liner interface (HT-9 vs. V or Zr). (704 – 815 °C for 50-200 hours)



704 °C for 200 hrs

# Core Materials Research and Development – 5 Year Plan

**Qualify HT-9 for high dose clad/duct applications (determine design limitations)**

FFTF (ACO-3 and MOTA) Specimen Analysis

Rev. 6 of AFCI (FCRD) Materials Handbook

Re-irradiation of FFTF specimens in BOR-60

Data to 250-300 dpa on F/M and 100-150 on Inn. Material

**Advanced Material Development (improved radiation resistance to >400 dpa)**

STIP- IV (PSI) Specimen PIE

MATRIX-SMI and 2 (Phenix) Specimen PIE

Data on Advanced Materials to 80-100 dpa

ODS Ferritic Steel Material Development

Develop ODS Tubing and Weld specifications

Produce ODS Tubing

Advanced Materials Irradiation in BOR-60 and CEFR

**Advanced Material Development (improved FCCI resistance to >40 % burnup)**

Development of Coated and Lined Tubes

PIE on Lined Irradiated Tube

FY'11      FY'12      FY'13      FY'14      FY'15      FY'16

Provides data for NEAMS model development of Cladding

# Grand Challenge for Core Materials for Next Generation LWR Fuels

## Develop and test advanced alloys for Next Generation LWR Fuels with Enhanced Performance and Safety and Reduced Waste Generation

- Low Thermal Neutron Crosssection
  - *Element selection (e.g. Zr, Mg)*
  - *Reduce cladding wall thickness*
- Irradiation tolerant to at least 15 dpa
  - *Resists swelling and irradiation creep*
  - *Does not accumulate damage*
  - *Stable microstructure (resists RIS)*
- Mechanically robust under loading and transportation conditions
- Compatibility with Fuel and Coolant
  - *Resists stress corrosion cracking*
  - *Resists accident conditions (e.g. high temperature steam)*
  - *Resists abnormal coolant changes (e.g. salt water)*
- Weldable and Processed into tube form
  - *Maintain hermetic seal under normal/off-normal conditions*

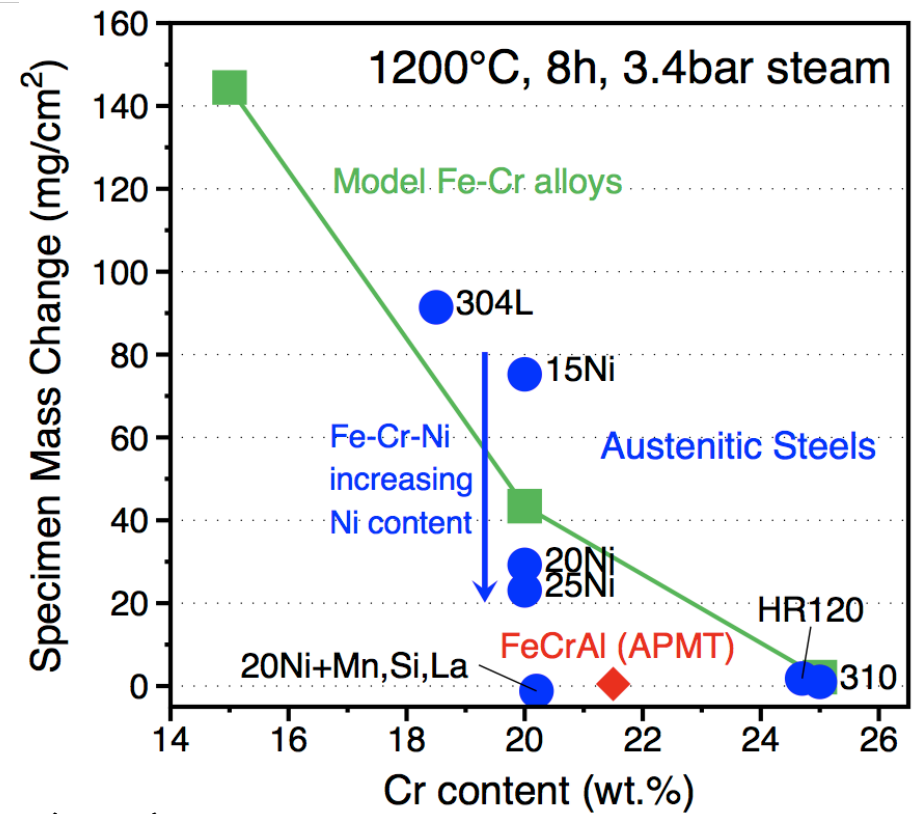
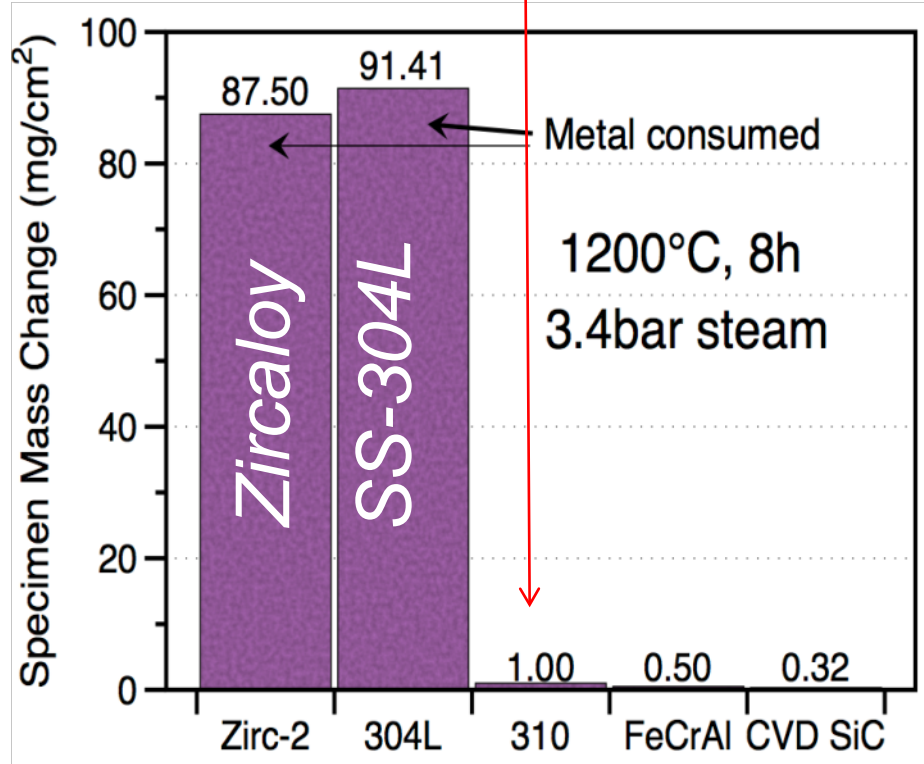
# Objectives

- Measure Kinetics of Oxidation in Steam
  - Steam oxidation testing up to 1300C (ORNL)
  - Fundamental oxidation studies in steam (LANL)
- Develop Processing Techniques to produce thin-walled tubing
  - Producing tubing of MA-956 with 250 micron thick walls (LANL)
  - Measuring mechanical properties of thin walled tubes (ORNL)
  - Weld development on thin-walled tubing (INL and ORNL)
- Measure Radiation Tolerance of ATF ferritic alloys
  - Ion irradiated materials (LANL)
  - ATR irradiated materials
    - Tensile testing (LANL)
    - Fracture toughness testing (ORNL)
- Developing Improved ATF alloy (ORNL)
  - Weld development for improved ATF alloy (INL)
  - Mechanical testing and ion irradiations (LANL)
- Develop Advanced ATF alloy (LANL)
  - Production of Mo tubing using FB-CVD processing



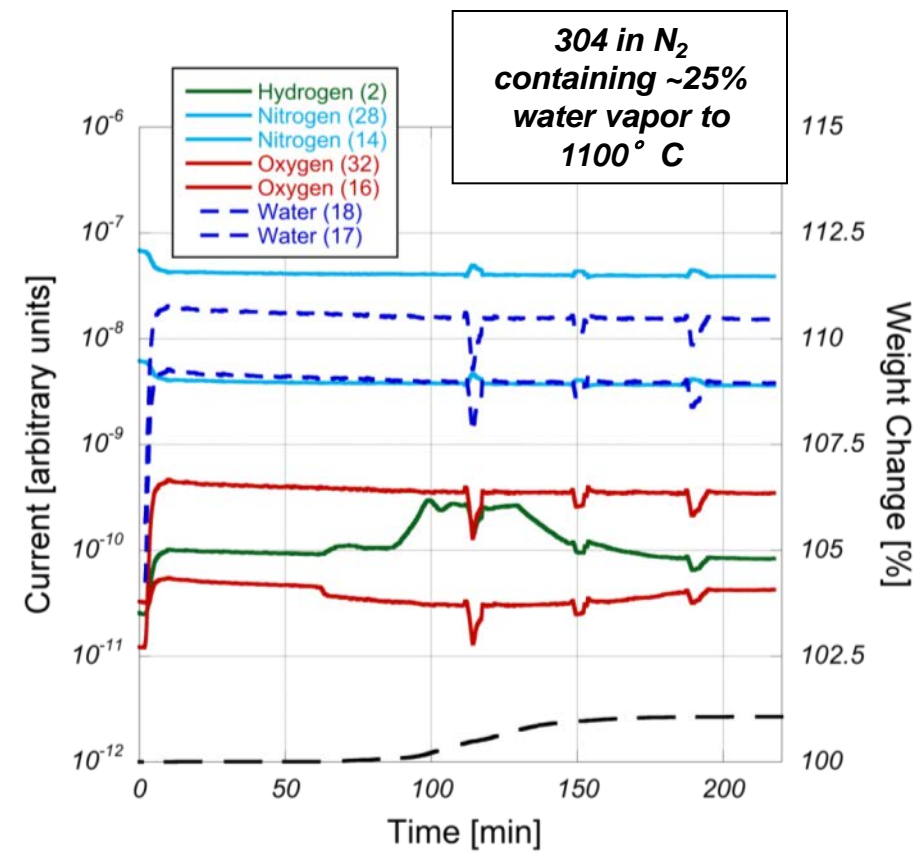
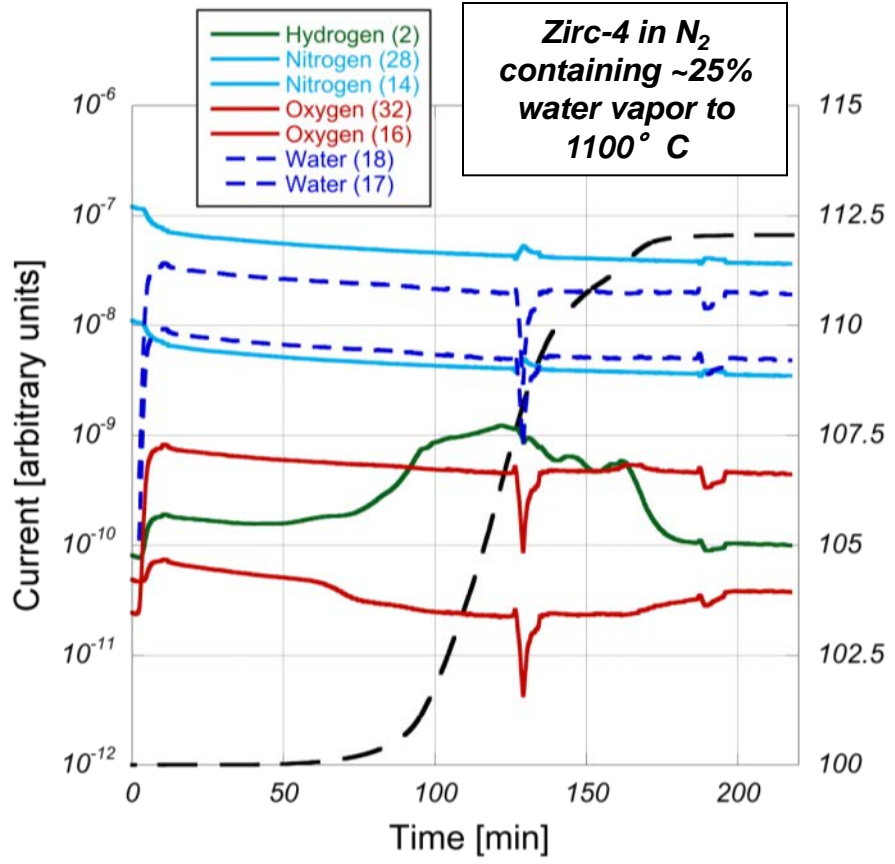
# Properly alloyed metals as protective as Si-based ceramics at 1200° C

- Example from FCRD experiments at 1200° C in steam at 3.4 bar (50 psia) for 8 h
- All low mass gain: 310SS (Cr<sub>2</sub>O<sub>3</sub>), FeCrAl, Kanthal APMT (Al<sub>2</sub>O<sub>3</sub>), CVD SiC (SiO<sub>2</sub>)



- Mass change is net value: oxide growth, spallation (minor) and volatilization
- Commercial and model alloys included to fundamentally understand role of composition and minimum amount of Cr (and Al) needed for protective behavior

# Measurements on hydrogen evolution performed in steam



- Hydrogen Production begins in Zircaloy-4 at ~700C and in 304L at ~1000C
- Similar testing will be performed on all advanced alloys in FY13

# Mechanical Property Testing

## Nuclear Energy

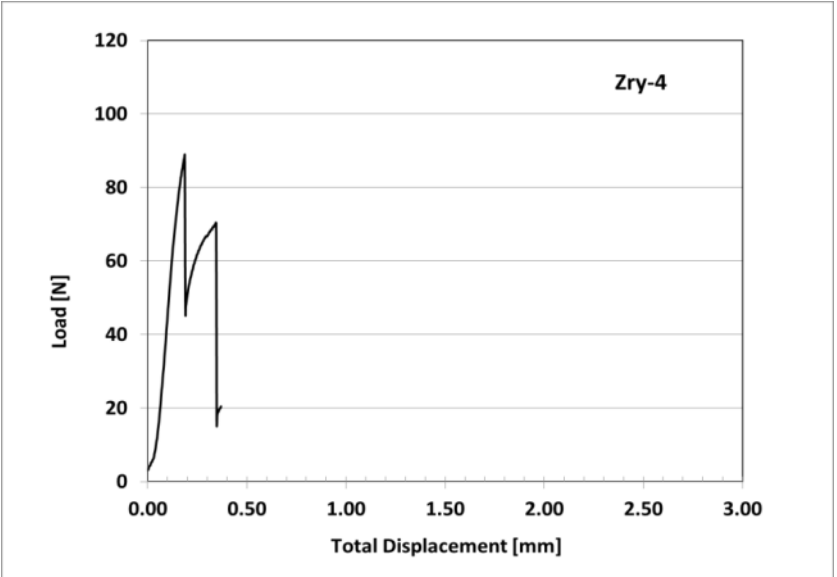


*Brittle*

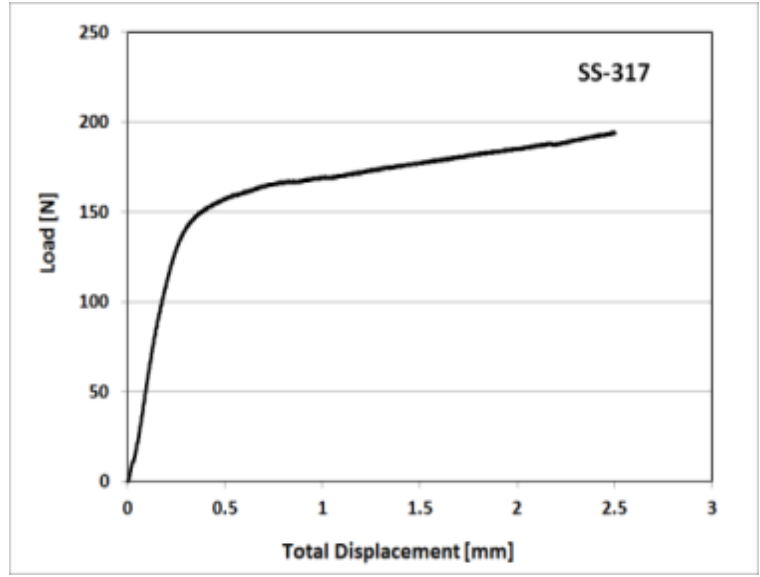
**Both samples have the same OD and wall thickness, and were oxidized at 1200°C for ~900s**



*Ductile*



*Ring-compression Load-Displacement curves with Zry-4 oxidized at 1200°C for CP-ECR=30%*



*Ring-compression Load-Displacement curves with SS-317 oxidized at 1200°C for CP-ECR=30%*

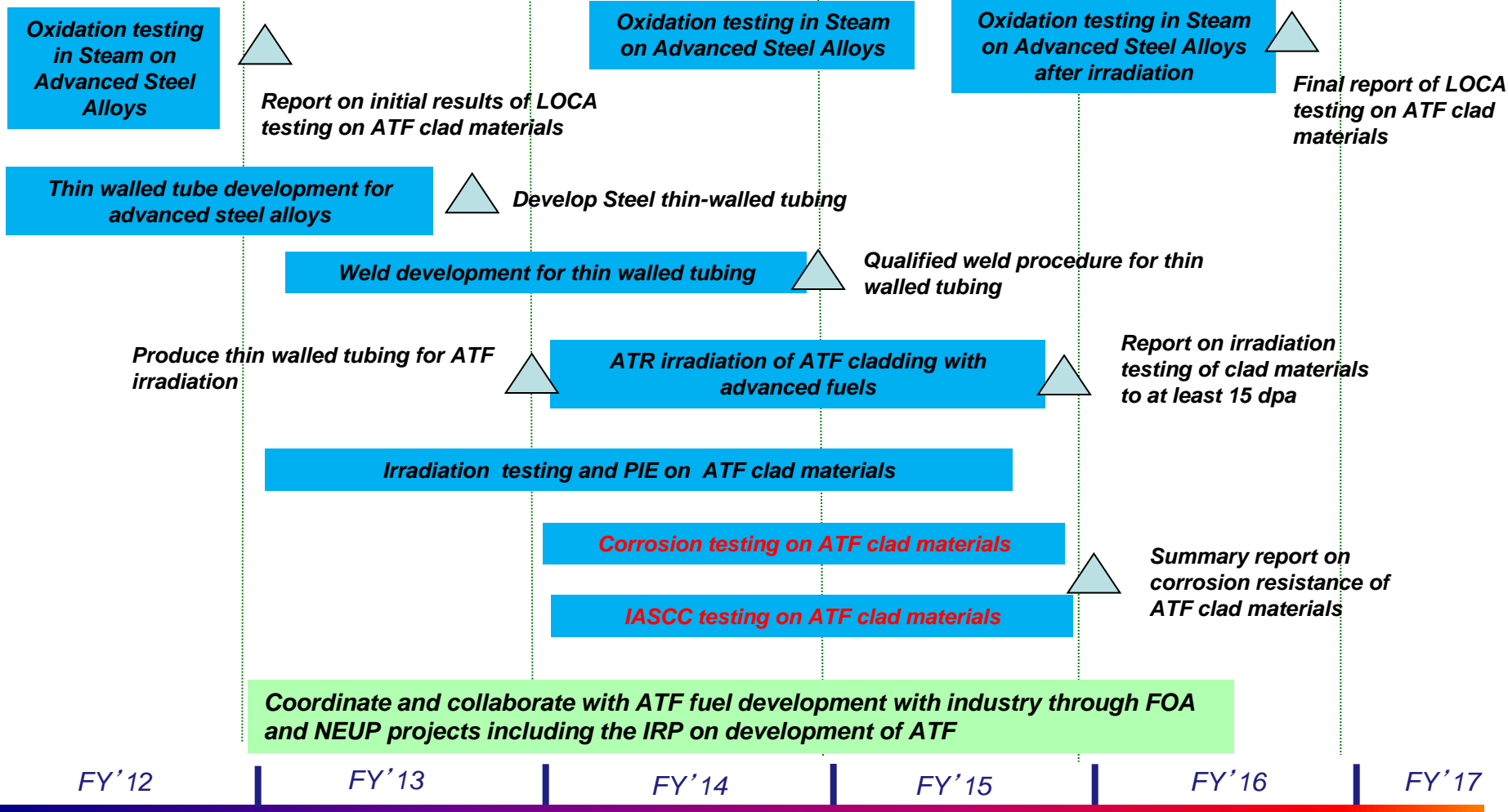
# Summary of Oxidation Kinetics Screening Tests

- A series of ~35 conditions has been carried out on silica formers (i.e. SiC) chromia formers (i.e. stainless steels) and alumina former (i.e. alumina forming alloys “AFA’ s”).
- Results are dependent on temperature, time, pressure, and velocity and therefore the specific beyond LOCA scenario may be critical. However, a subset of attractive materials (CVD and NITE SiC, 310 stainless, and AFA’ s) have been identified.
- A series of papers have been submitted:
  - T. Cheng : “Oxidation of Fuel Cladding Materials in Steam Environments at High Temperature and Pressure.” submitted Journal of Nuclear Materials.
  - K. Terrani et. Al. “Protection of Zirconium by Alumina- and Chromia-Forming Steels under High-Temperature Steam Exposure” to be submitted Journal of Nuclear Materials.
  - J. Keiser High Temperature Oxidation of Candidate Advanced Iron-Based Alloy Cladding Materials in Steam-Hydrogen Environments,” *Proceedings of Nuclear Fuels and Structural Materials for the Next Generation Nuclear Reactors*, Chicago, Illinois, June 2012.
  - B. A. Pint, et. al. “High Temperature Oxidation of Fuel Cladding Candidate Materials in Steam-Hydrogen Environments” 8th International Symposium on High-Temperature Corrosion and Protection of Materials



# Core Materials Research and Development ATF Clad Development - 5 Year Plan

## Advanced Material Development (improved accident tolerance for LWR's)



FY'12

FY'13

FY'14

FY'15

FY'16

FY'17

# Materials Integration and University and International Collaborations

## ■ Integrate FCRD Core Materials Activities

- Fuels Core Materials Work- (INL, PNNL, LANL, ORNL, LLNL)
  - *Materials teleconferences monthly*
- University Materials Research (attend university review, review quarterly progress reports)
  - *UCSB- Optimized Compositional Design and Processing-Fabrication Paths for Larger Heats of Nanostructured Ferritic Alloys*
  - *TAMU-Bulk nanostructured austenitic stainless steels with enhanced radiation tolerance*
  - *U. Ill Urb/Champaign-Development of Austenitic ODS Strengthened Alloys for Very High Temperature Applications*
- ATR Reactor Irradiations (provide materials and preparing to collaborate in testing)

## ■ Working group meetings and Workshops

- NE Materials Cross-cut Webinars in August 2012 and July-August 2013

## ■ International Collaborations

- INERI-GETMAT- 14Cr ODS material development
- INERI-KAERI- 9Cr ODS material development
- Participant in IAEA Coordinated Research Project on “Benchmarking of Structural Materials Pre-selected for Advanced Nuclear Reactors” – met in Vienna, May 2-6, 2011.
- DOE-CIAE Collaboration – Proposed irradiation in CEFR
- DOE-Russia – Proposed irradiation in BOR-60
- LANL-Terrapower CRADA – proposed irradiation of ACO-3 specimens in BOR-60