Refractory Metal Cladding and Mo-alloy Development for Accident Tolerant Fuel

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OECD/NEA Expert Group on Accident Tolerant Fuel for Light Water Reactors – Task Force 2

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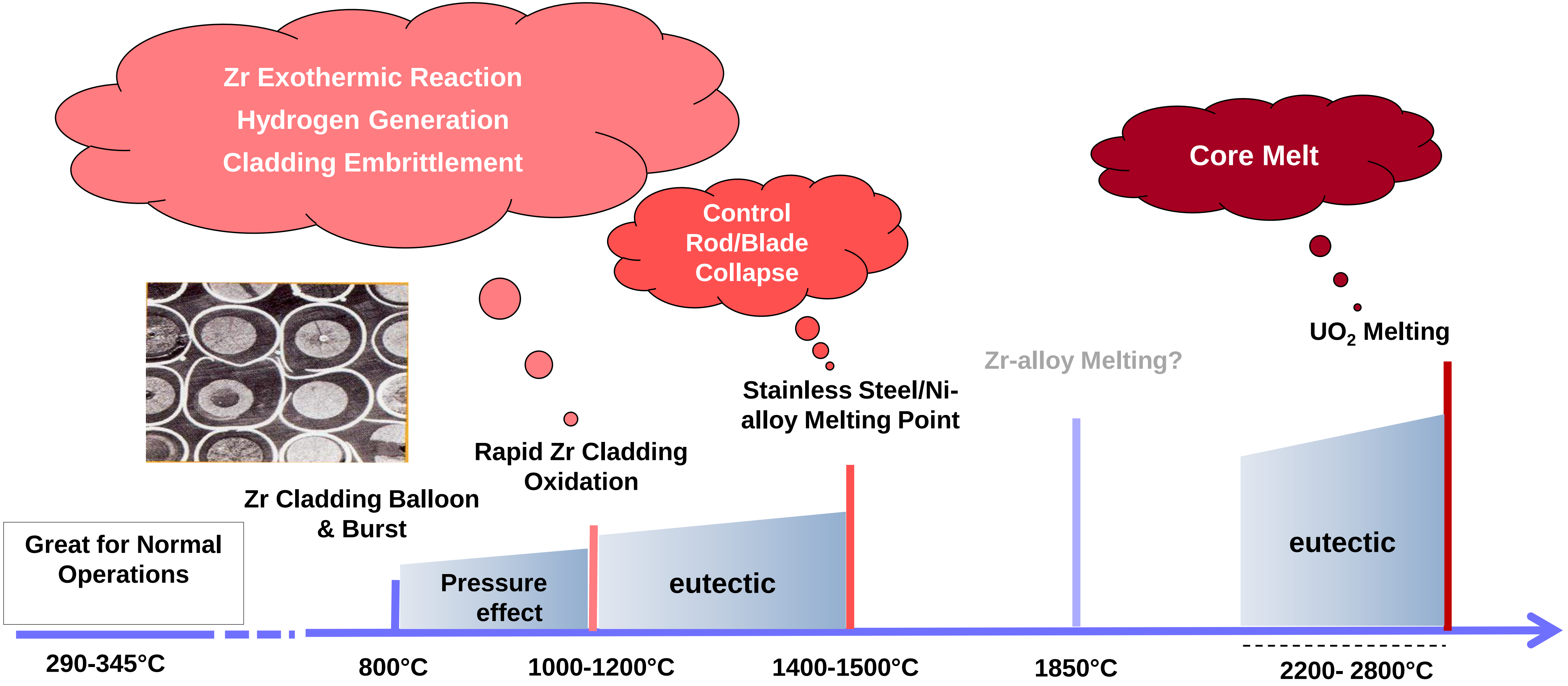
Refractory Metals as Cladding Materials for Enhanced Accident Tolerance

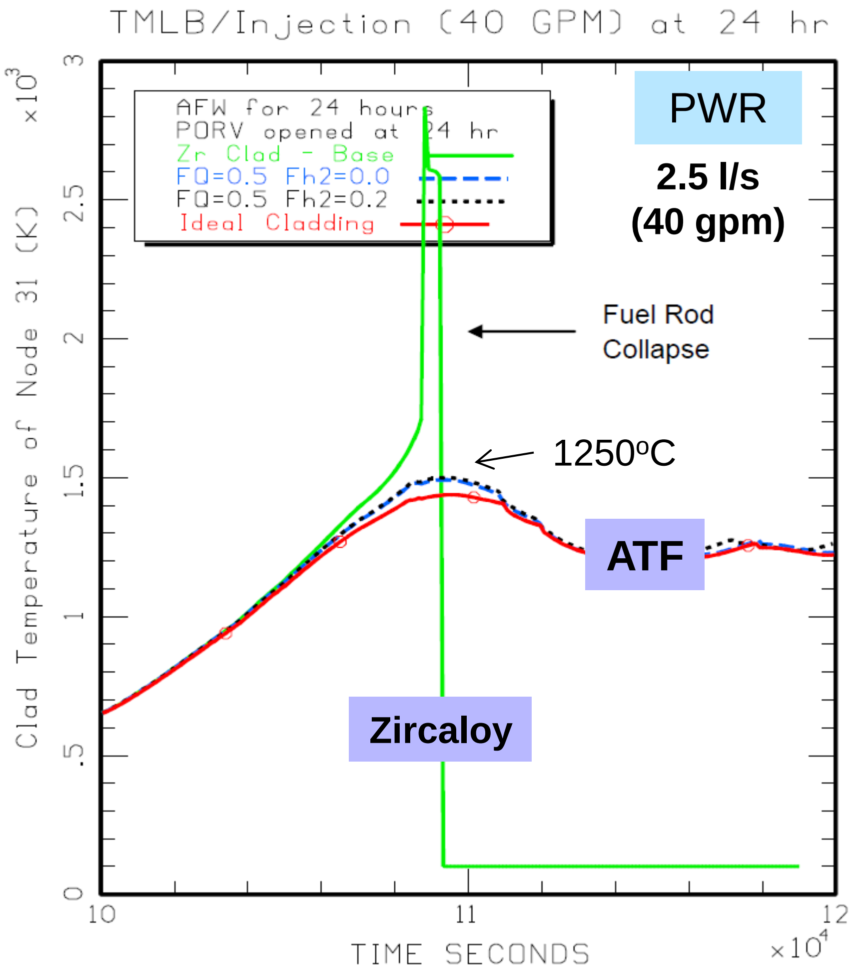
Behavior of Fuel/Core Materials in Severe Accidents

Zr-alloys, Fe-based and Ni-based Alloys and UO_2



What Can Enhanced Accident Tolerance Achieve?

- Add coping time for plant to recover
- Reduce hydrogen generation rate
- Eliminate design base LOCA concerns
- *Enhance passive LWR designs?*
- Reduce post-SBO heat removal requirement to low flow rate water injection (few liters/sec)



Assumes PWR with 24 hr passive cooling post-shutdown, then SBO with water injection at 2.5 l/s

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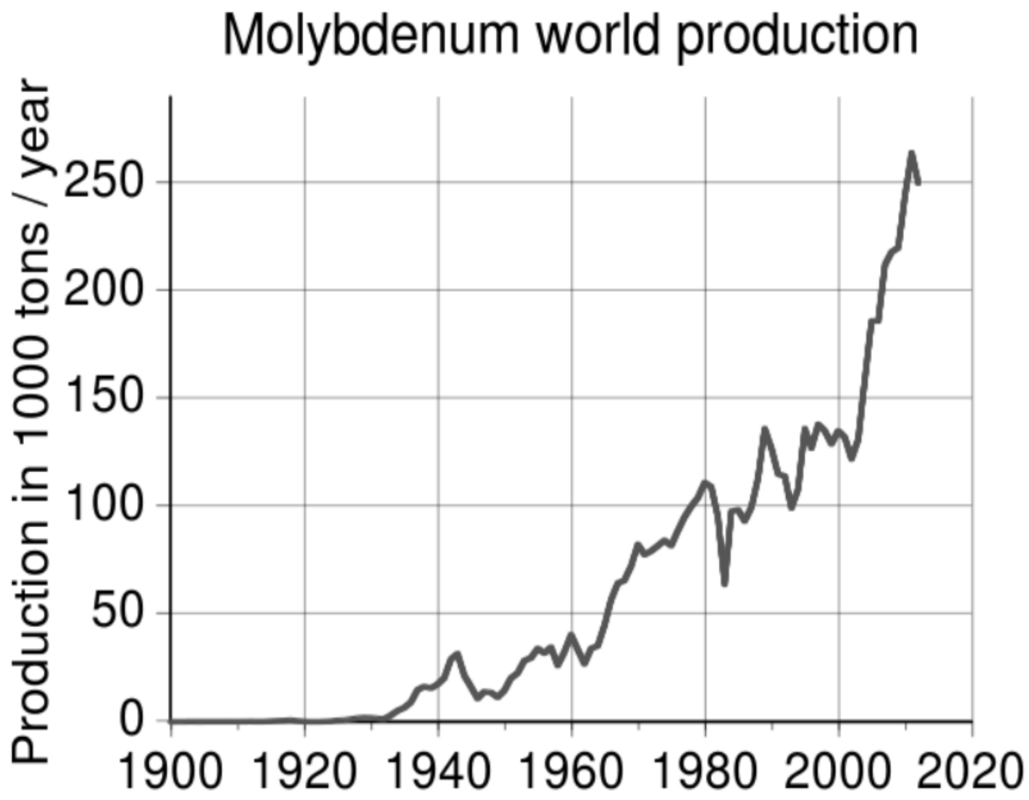
Refractory Metals

- W, Ta, Re, Mo, Os, and Nb have the highest melting temperatures among metals in the periodic table
- Availability and neutronic absorption properties limit the viable candidates to Mo and Nb for use as bulk cladding
- Industrial use of Mo is widespread
  – Annual production of Mo is ~ 250,000 t
  – Tool steel alloys to improve strength, hardness, and corrosion resistance
- Nb availability is more limited geographically and quantitatively (63,000 metric t/yr)



Source: USGS

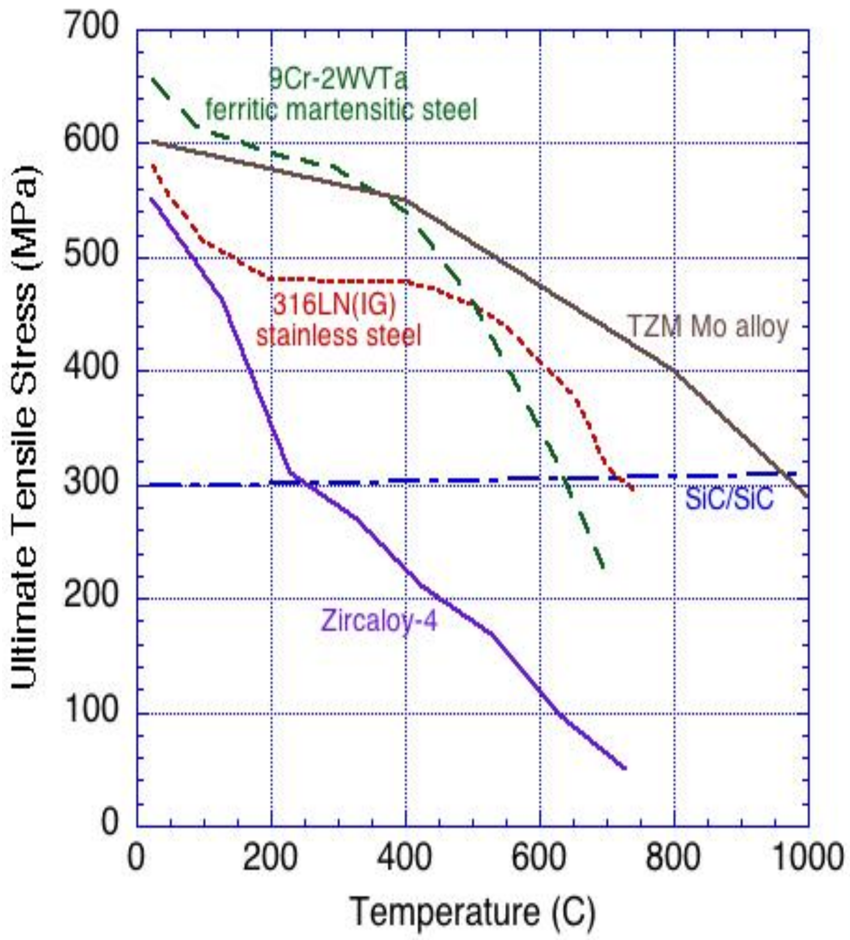
Candidate Advanced Cladding Materials:
Ceramics, Refractory Metals, Fe-based Alloys

Material	Melting Temp (^oC)	Thermal Neutron Absorption, barns	Thermal Conductivity, W/m-K	Comments
Zr alloys	~1800	~0.19	22	Weakens at ~750-800^oC
Stainless Steels	~1400-1500	~2.6-2.8	16	Fe-B eutectic melting at 1161^oC; with Al addition resists steam to 1350^oC due to formation of Al_2O_3
Inconel/Ni alloy	~1400	~4.0-4.2		Yields activation Co-58 product
SiC	(2600)*	0.09	20 (composite)	Ceramic, brittle
Mo	2623	2.6	138	Vaporizes as MoO_3 under oxidizing conditions; stable in reducing conditions to 2000^oC
Nb	2477	1.15	53	Limited supply; susceptible to hydriding
ZrO_2	2715		2	Stable in steam to 1900^oC

*sublimation

Viable candidate materials are limited: SiC, Mo, stainless steels, and materials that form protective surface coatings, *i.e.*, Al_2O_3 ZrO_2, SiO_2 and Cr_2O_3

High Temperature Mechanical Properties of ATF Cladding Material Candidates



Tensile properties of ATF cladding candidate materials (after S. Zinkel)

Ultimate Tensile Strength, MPa

Material	300°C	1000°C
Zircaloy-4	270	nil
Stainless Steel 304	475	<10
Ferritic Martensitic Steel	480	<10
SiC/SiC Composite	300	300
Molybdenum alloys	400-570	200-300

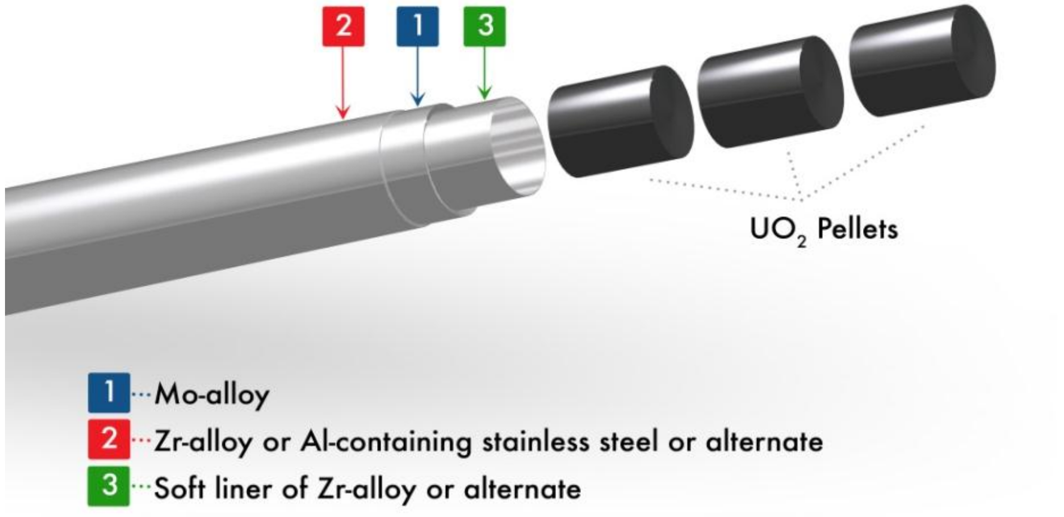
Mo as Principal Refractory Metal Option for Cladding

- Beneficial properties:
  - Tensile and creep strength at 1000 - 1800 °C
  - High stability in reducing and inert environments to ~2000 °C
  - Fabricability into long, thin wall tubes
  - Suitable for welding (i.e., end caps)
- Challenges for LWR fuel applications:
  - Higher neutron absorption cross sections than Zr (cladding wall thickness needs to be reduced, *i.e.*, <0.25 mm)
  - Reacts with high temperature steam (needs improvement/protection)
  - Susceptible to radiation embrittlement (needs further evaluation)
  - Industry infrastructure for Mo cladding not established
  - R&D needed to support industrial applications

Progress on Mo-alloy Cladding Feasbility Studies

EPRI Coated Mo-alloy Cladding Designs

- All metal cladding concept
  - High strength Mo-alloy as core material
  - Coating on outer surface
    - Zr-alloy, or
    - Al, Cr-containing stainless steel
  - Optional inner coating: Zr or Nb



- Anticipated properties
  - Under normal operations
    - Zr-alloy or (Cr, Al)-containing stainless steel is compatible with LWR coolants
  - In accidents at >1000ºC
    - Maintain rod integrity
    - Zr completely forms “protective” ZrO_2 at >1000ºC
    - FeCrAl forms thin protective Al_2O_3 /Cr_2O_3

Scope of Feasibility Study

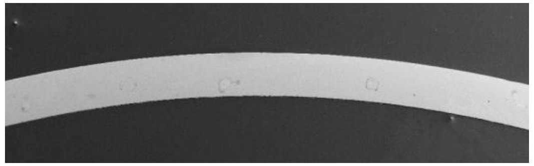
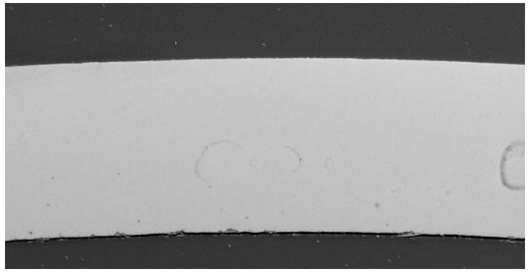
- Fabrication of thin-wall Mo tubes: 0.2-0.25 mm (8-10 mil)
  - Process and mechanical property optimization
- Reliable coating of Zr-alloy or FeCrAl
- Characterizations of key properties
  - Corrosion resistance in LWR coolants
  - Oxidation resistance at 1000-1500^{o}C
  - Welding
  - Chemical/mechanical stability of coating (inter-diffusion)
  - Mechanical and burst/creep properties
- Irradiation effects
  - Coolant compatibility and embrittlement resistance
- Analysis:
  - Neutronic property (MCNC/Lattice Codes)
  - Thermal-mechanical behavior (FALCON) – PCMI, RIA
  - Accident tolerance (MAAP/MELCOR)

Fabrication of Thin-Wall Mo-alloy Cladding (1)

Mo and Mo+(0.3-1.0%)La_2O_3 ODS

- Tubes dimensions
  - PWR and BWR OD dimensions, 0.2-0.25 mm wall
  - ~1.5 meter (5 ft) long tubes
  - Good straightness, uniform wall thickness
- 7 batches fabricated so far
  - Generation 1 tube (stress relief annealed)
    - For coating, corrosion/oxidation testing, and welding
  - Generation 2 tube (recrystallized)
    - UTS ~450 mpa (65 ksi), 8 - 10% elongation at 320°C
    - 8 - 12% axial tube elongation



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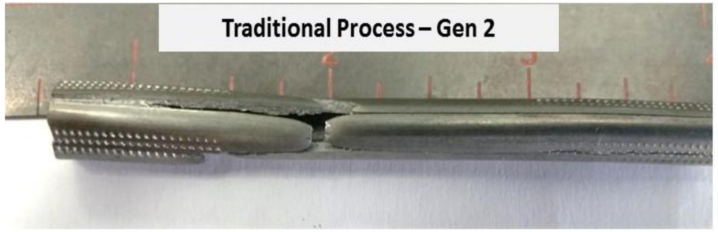
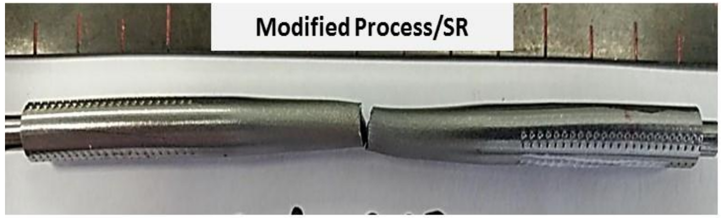
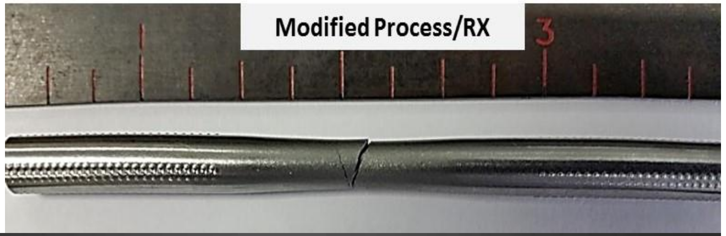
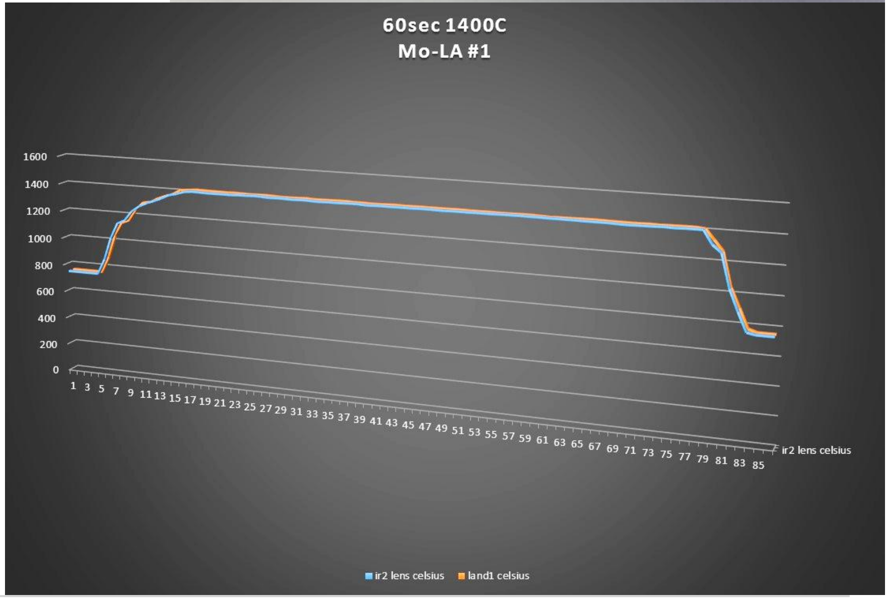
Fabrication of Thin-Wall Mo-alloy Cladding (2)







- Generation 3 tube under development
  - Goal: Fine equiaxed grain structure
  - Modification of texture during processing
  - Induction heat treatment
  - Looking for improved mechanical properties
- Areva FOA scope in 2015
  - Includes generation 3 Mo-alloy tubes
  - Scheduled fabrication in Q2 or Q3



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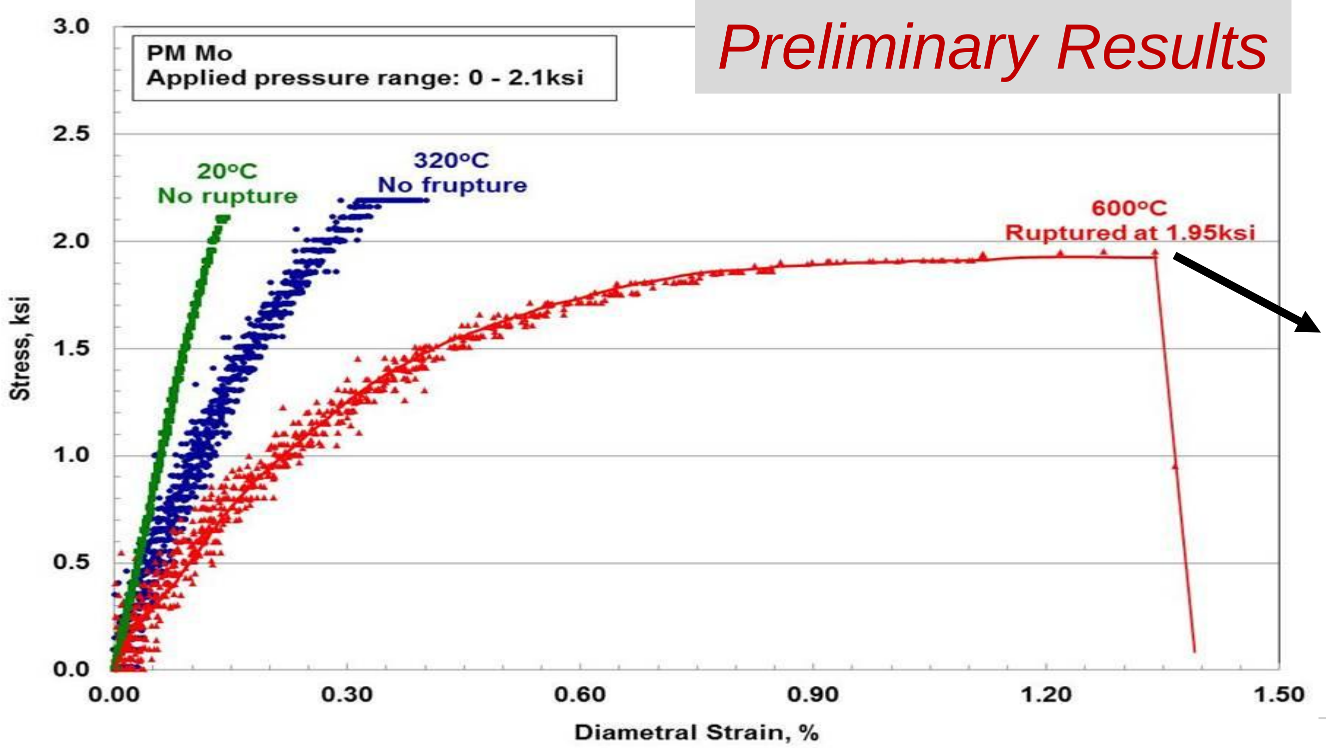
Mechanical Property Tests

- Tube tensile properties (Rhenium Alloy Co., PMT, AREVA)
  - Room temperature, 320 °C
- Diametral tensile and creep properties (GE-GRC, AREVA)
  - Temperatures up to 1000 °C

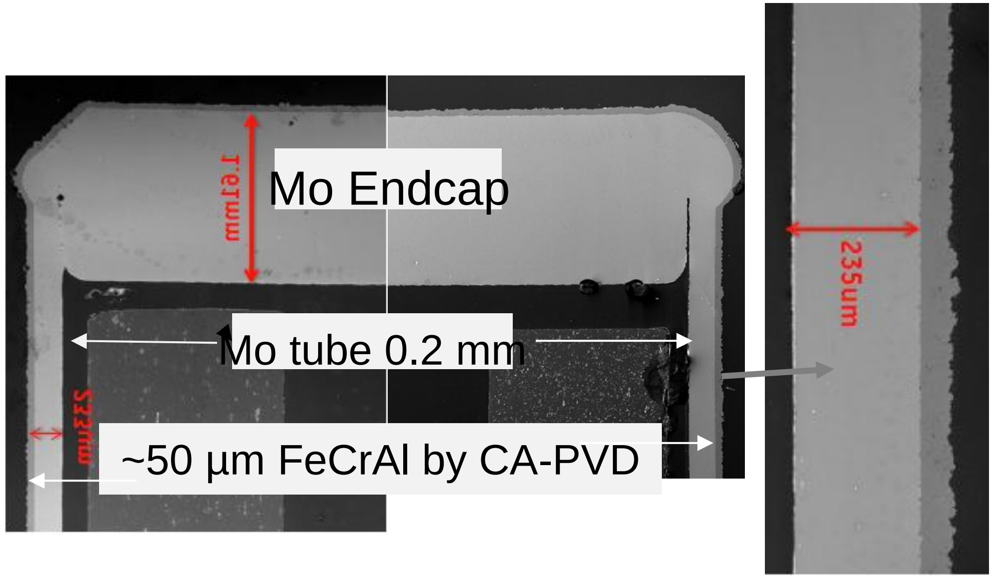


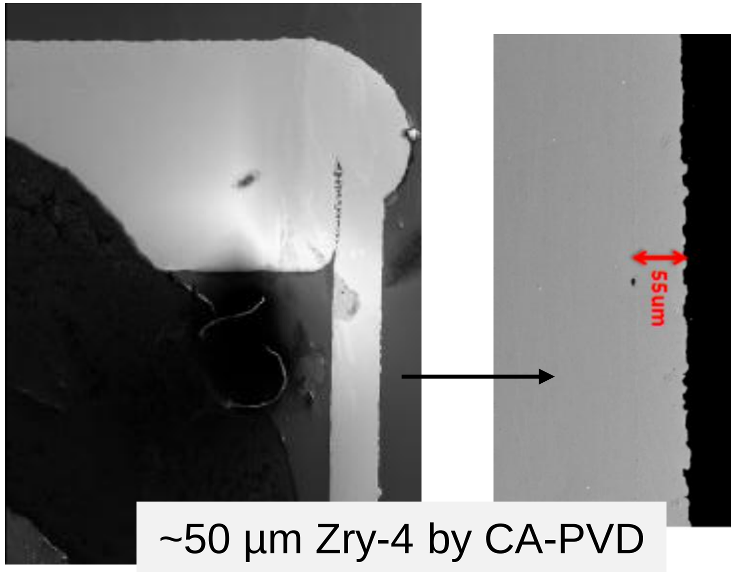
Rod internal pressure at 600°C
- PWR ~727 psi
- BWR ~428 psi

Failure Strength 48 Ksi vs 17 Ksi for Zircaloy
(331 Mpa vs 120 Mpa)

Coating of Mo-alloy Tubes (via Deposition)

- Successful coating of Mo tubes and sheets
  - Physical vapor deposition (PVD) (CA-, EB-, DVD)
  - HVOF, HVAF spray
  - Vacuum plasma spray (VPS)
- Process parameters optimized
  - Good bonding
  - Good coating density
  - Good interface structure
  - Good uniformity
  - Good stability in autoclave at ~300 °C and in steam at 1000 °C
- Length of coated samples
  - 8-10” tubes
  - 36” tube
- **Expensive, not conducive to scale up**





Coating of Mo-alloy Tubes (by Mechanical Co-reduction)

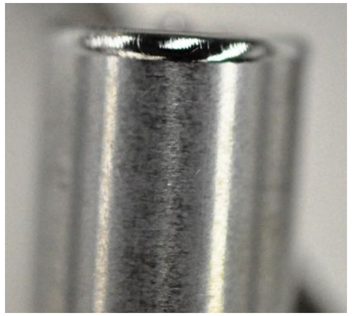
- Goal: Demonstrate a more feasible process for commercial production
  - Economics
  - Quality control
- Based on prior work
  - Zircaloy tubes with Zr-liner (3 mil) on ID for BWR fuel cladding
  - Low Sn-Fe Zr alloy coating (3 mil) on Zircaloy-4 for PWR fuel cladding
  - Stainless steel coated Nb and Ta tubes in 1960s
- Mechanical co-reduction for Mo will be much more challenging
  - Hipping (bonding metal layers at high temperature under high gas pressure) will be used to form either mechanical or metallurgical bonds
  - Warm mechanical co-reduction (>300 °C)
  - Work planned for 2015

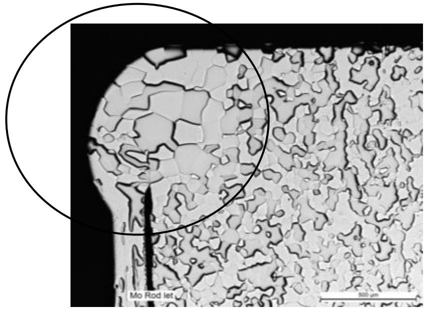
Tube to Plug Welding

- Successful with:
  - Plasma Welding
  - TIG (GTAW)
  - Electron Beam (EB) welding (ORNL, EBTec)
- EB welding employed for ATR rodlets
- Resistance projection welding feasible but needs development

Electron Beam Welding (ORNL/EBtec)

ATR Rodlets (Richard Howard, ORNL)

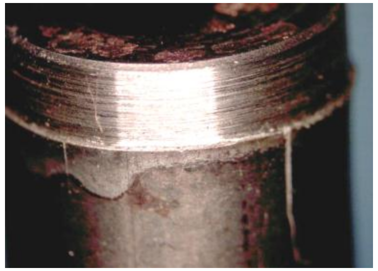


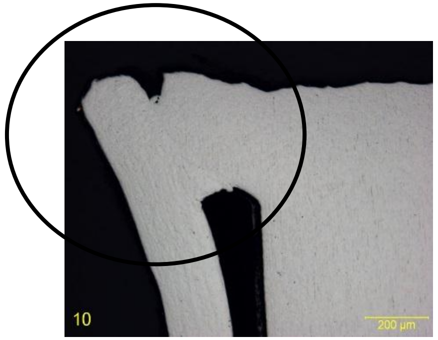


Pass pressure test: ~2800psi (19 Mpa)

Reproducible

Resistance Projection Welding (Solid State) - EWI





Appears feasible

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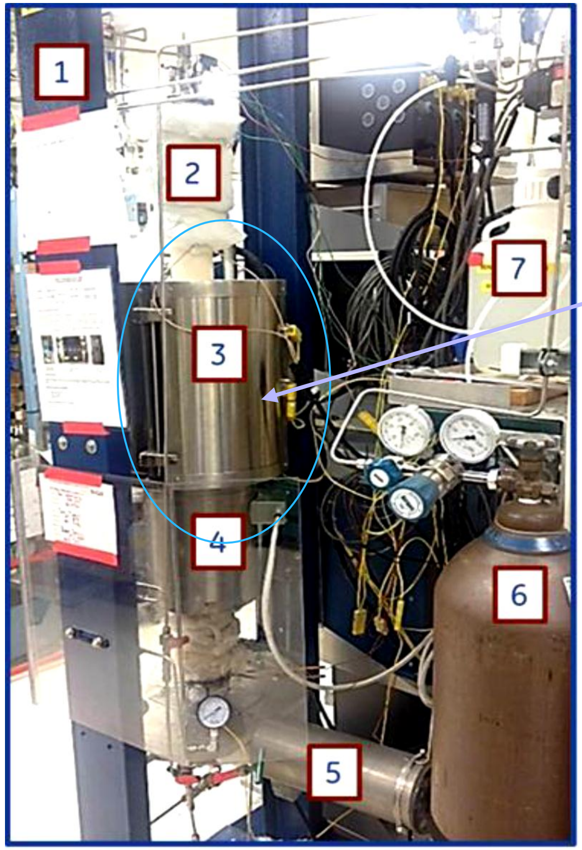
Oxidation Resistance in 1000 °C Steam (Bare and Coated Mo Tubes)

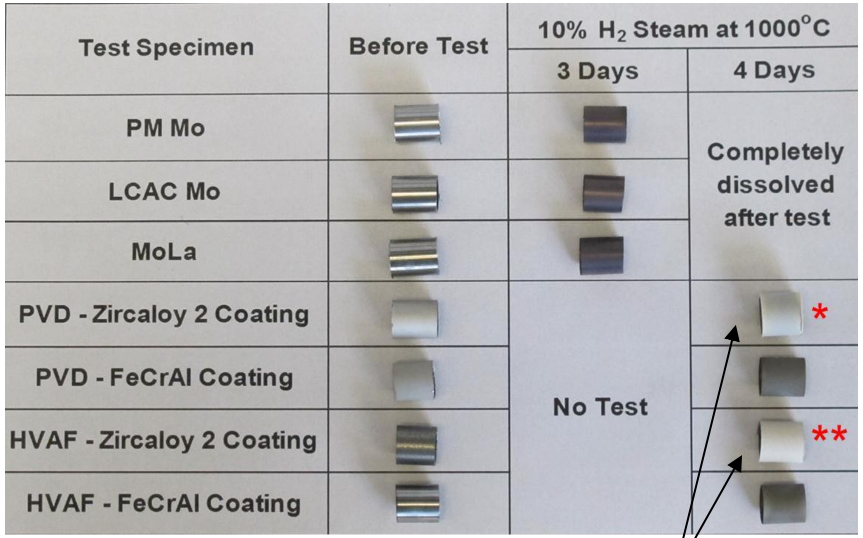
- Large test chamber
- Feedwater de-aerated by purging with Ar gas
- Flowrate: 2.5 cc/min
- Test for 1 - 7 days
- ~10 tests performed



1. Operational instructions
2. Alumina retort
3. 3-heating zones furnace
4. Preheater
5. Steam generator
6. Testing gas
7. Water reservoirs
8. Specimens holder

Oxidation of Sealed Tubes at 1000 °C for 3 and 7 Days

Steam, Steam + 10% Oxygen, Steam +10% Hydrogen

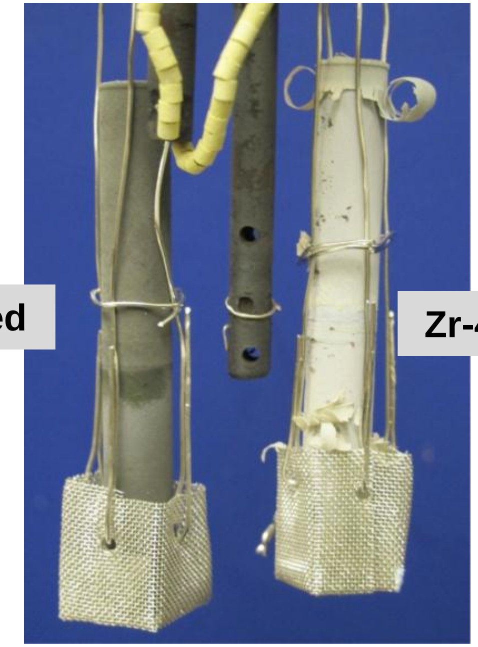


Test Specimen	Before Test	10% H_2 Steam at 1000°C	
		3 Days	4 Days
PM Mo			Completely dissolved after test
LCAC Mo			
MoLa			
PVD - Zircaloy 2 Coating		No Test	*
PVD - FeCrAl Coating			
HVAF - Zircaloy 2 Coating			**
HVAF - FeCrAl Coating			

Zr-2 coated

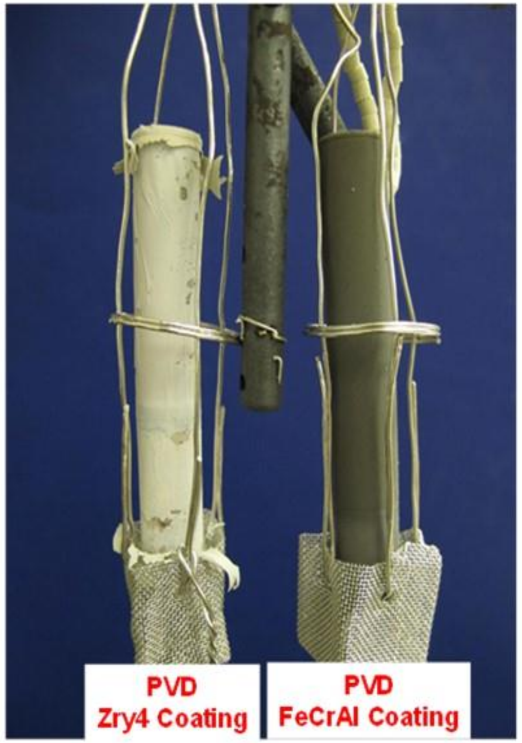
3 Day Test

FeCrAl Coated



Zr-4 coated

7 Day Test



~8 cm long sealed tubes

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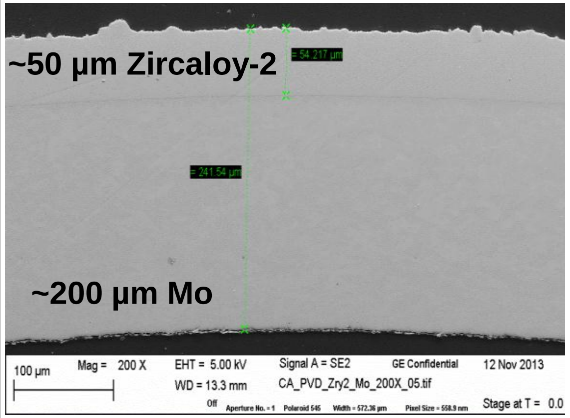
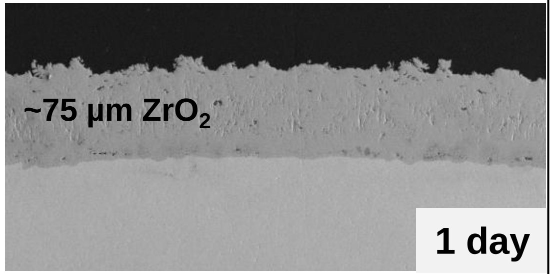
Oxidation of Coated Mo Tubes at 1000 °C

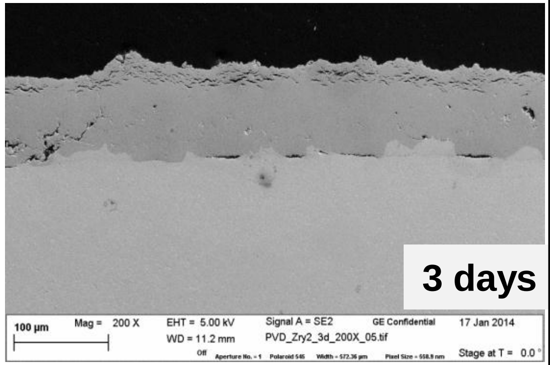
Mo tube with ~50 µm coating of Zircaloy-2

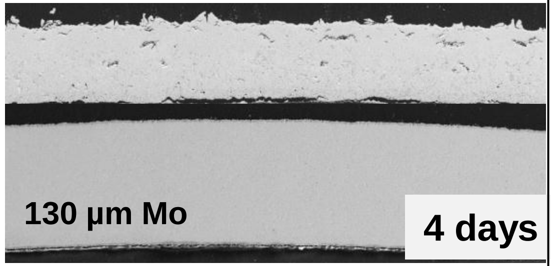
Before test



After test

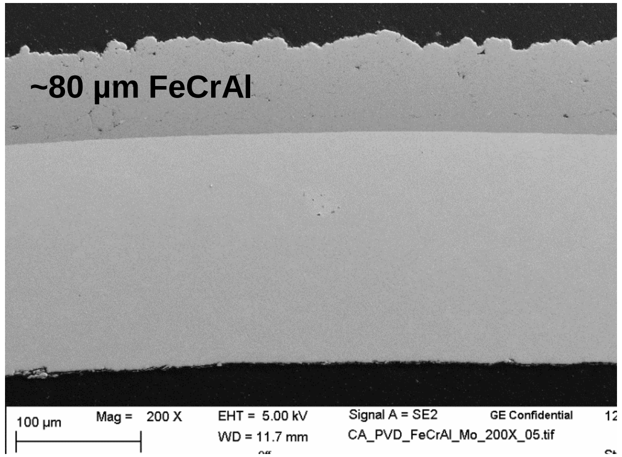




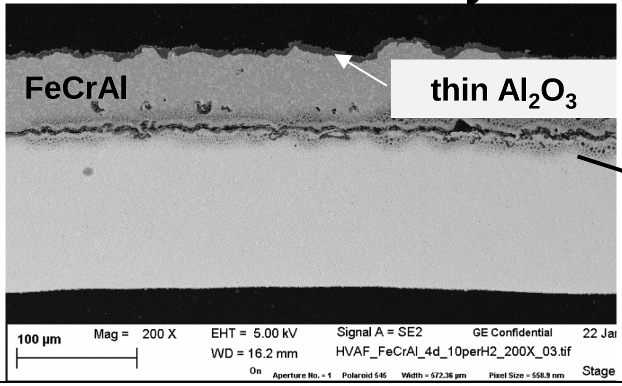


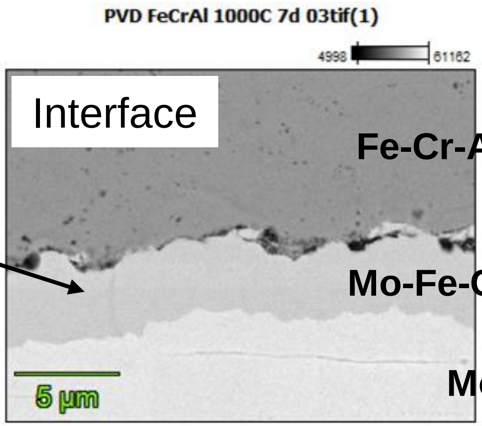
Mo tube with ~80 µm coating of FeCrAl

Before test



After test – 4 days





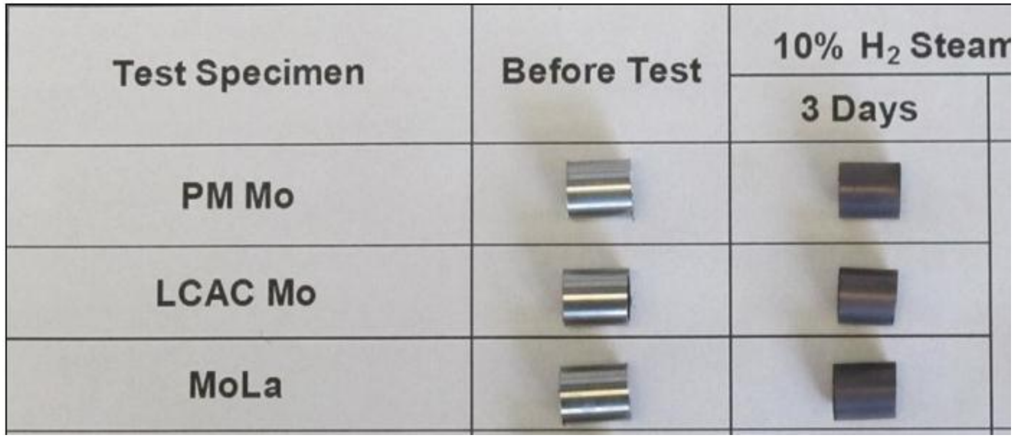
Inter-diffusion layer thickness

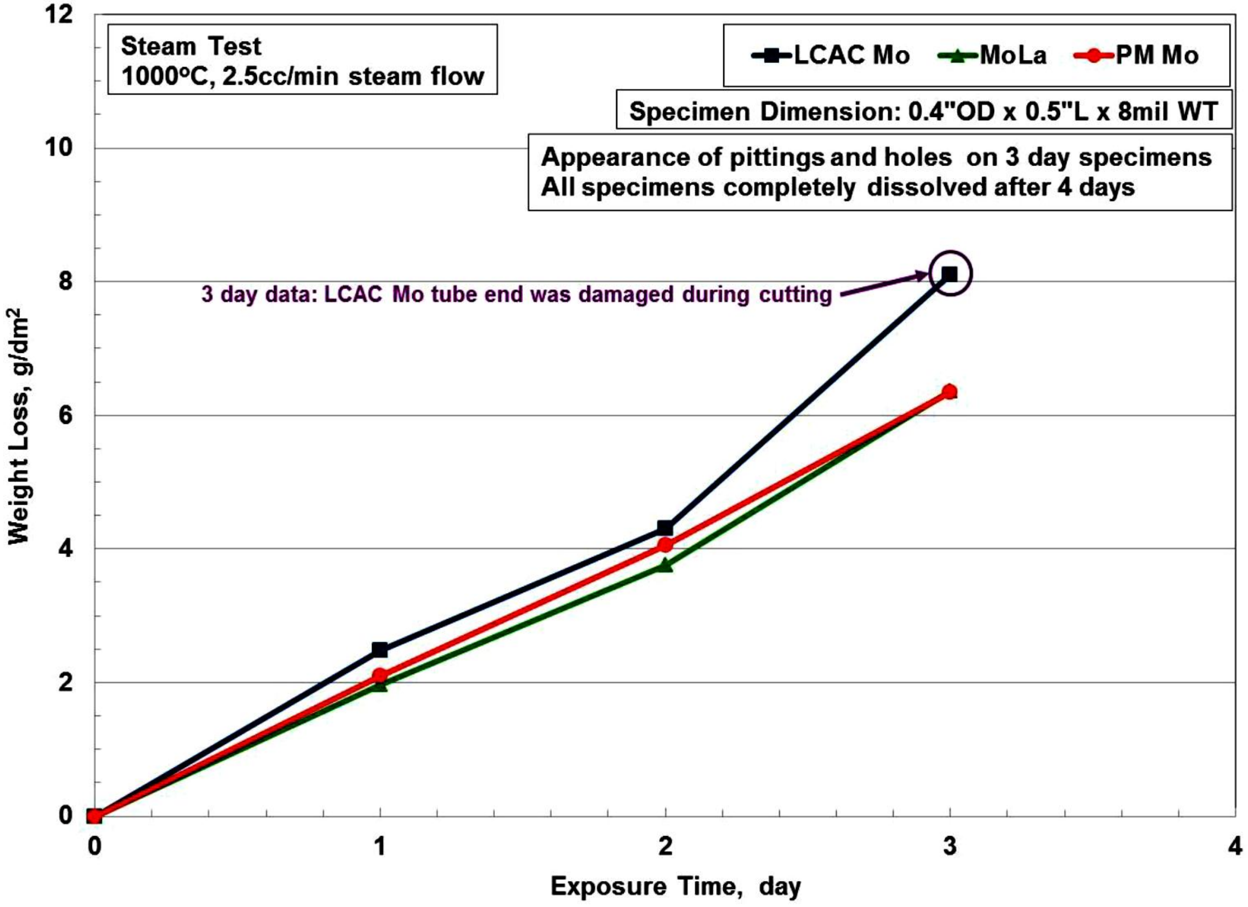
- **1000ºC**
  - **1 day: 2 µm**
  - **3 day: 4 µm**
  - **7 day: 5 µm**
- **1200ºC**
  - **1 day: 20 µm**

Bare Mo Oxidation Rate in De-aerated Steam at 1000 °C

- **Bare Mo oxidation rate at 1000 °C ~20 µm/day**
  - <1% of Zr oxidation rate

Bare Mo Open Tubes
Oxidation in 1000ºC steam 3 days:





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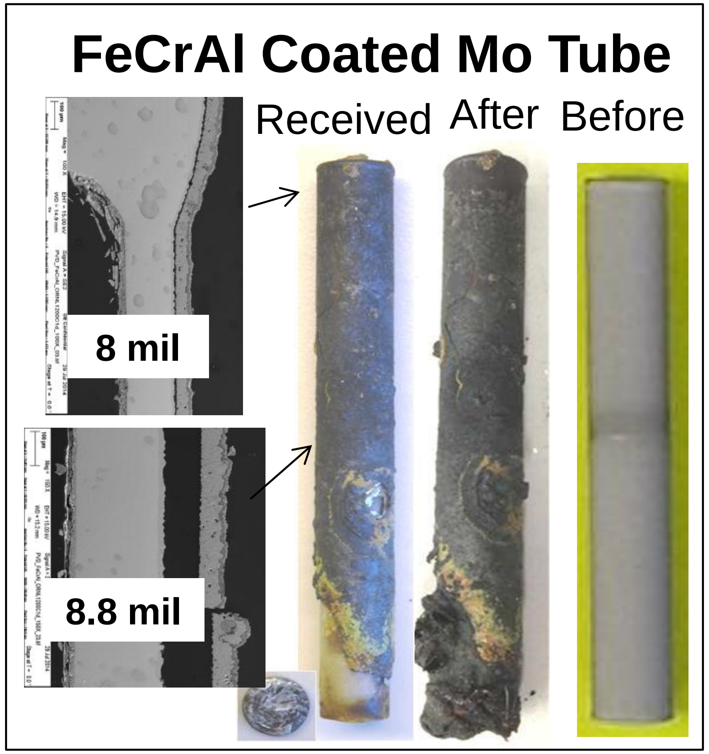
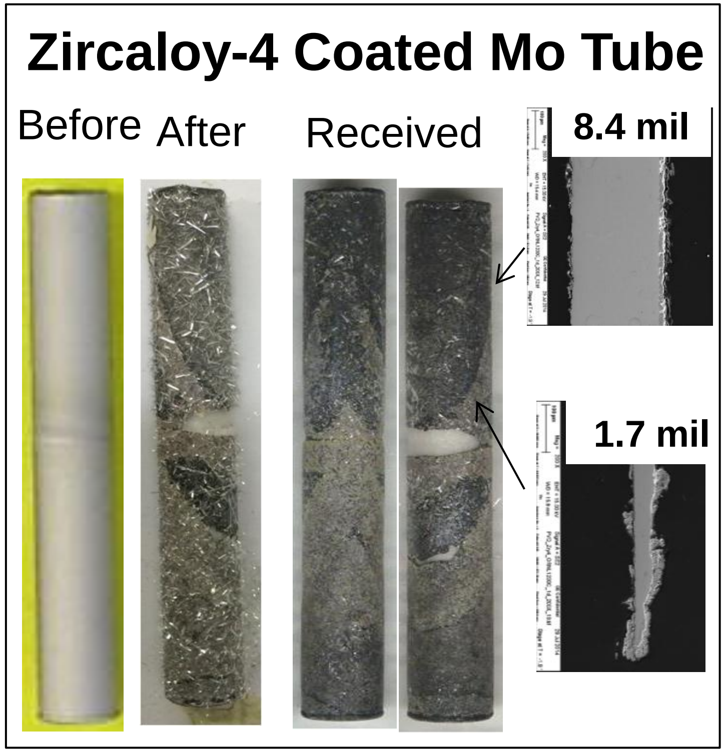
Steam Oxidation Tests >1000 °C





1200 °C - 24 Hour Test at ORNL
(Courtesy Kurt Terrani - Funded by DOE-FCRD)

- Cause of localized oxidation under evaluation
- Majority of tubes intact with little metal loss
- Addtional testing at 1200 – 1500 °C (GE-GRC and AREVA – France) to be completed in 2/3Q 2015

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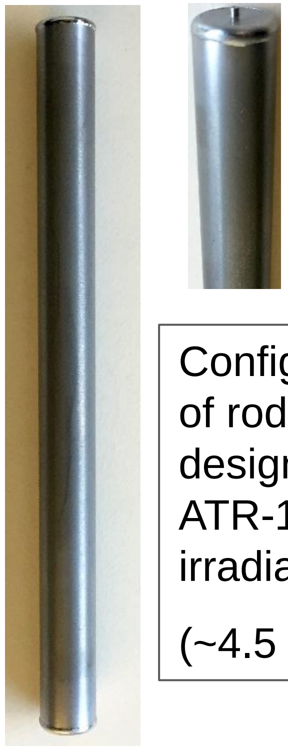
Irradiation of Mo-alloy Cladding

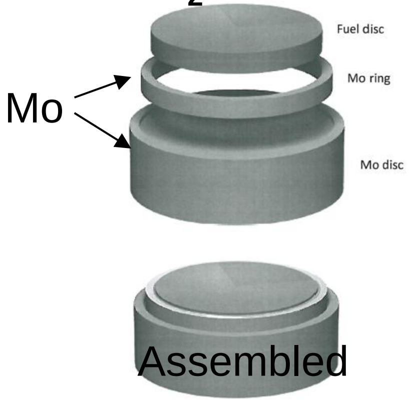
- Participation in DOE funded ATR-1 irradiation
  - 4 rodlets (~10 cm long with 4% enriched UO_2) in inert He gas
  - UO_2 purchased from AREVA
  - Rodlet assembly at ORNL
  - Irradiation to start in May 2015
- Possible future irradiations
  - INL ATR-2 in PWR water loop in 2016
  - Halden Reactor Program irradiation to start in 2016
  - Compatibility of Mo with UO_2 Pellets
  - PIE of coupled Mo-UO_2 discs irradiated at 500-400 °C in Halden Reactor to 112 GWd/MTU (samples courtesy of Halden Project)
  - Data needed to determine need for inner protective layer



Configuration of rodlet design for ATR-1 irradiation

(~4.5 in long)

UO_2 waffle



Challenges for Resolution in Next 1 - 2 Years

- Optimize processes for GEN3 tube fabrication of Mo and Mo-ODS (Gen-3 tubes)
  - Fine equiaxed grain structure with uniform properties
- Mechanical co-reduction of outer layers
- Steam oxidation tests at ≥1200 °C (to ~1500 °C)
- Mechanical property characterization
  - Diametral tensile, creep and burst tests
- Solid state welding via resistance projection process (including coated tubes)
- Irradiation tests for embrittlement resistance
- New Mo alloys or surface chemistry modifications to improve corrosion resistance

Path Forward

- **EPRI is collaborating with AREVA on Mo-alloy cladding development under DOE ATF FOA Phase 1B funding with a scope on Mo-alloy cladding**
- Los Alamos National Laboratory is preparing (with EPRI input) a Technology Implementation Plan on Mo Cladding Development for U.S. DOE
- EPRI is also supporting two university groups on DOE – NEUP funding calls related to “resistance welding of coated Mo cladding” and “Modelling of ATF cladding”

Research Team

Major technical contributors (outside of EPRI)

- **Young Kim** + +, GE-GRC: coating, testing, evaluation…
- Todd Leonhardt, Rhenium Alloy Co.: tube fabrication
- Peter Ring: Heat treatment, hipping
- Sam Armijo, Consultant

AREVA: Forward research collaboration (through DOE FOA Phase 1B funding)

Analysis:

- RT Chiang: Neutronics
- Frank Rahn, MAAP accident analysis (+Fauske)
- Joe Rashid: Fuel rod thermal-mechanical behavior analysis

Collaborators

- Stuard Maloy, Los Alamos National Laboratory: nano-grain size Mo alloy, oxidation,….
- Kristine Barratt, INL – ATR test manager
- Richard Howard/Kurt Terrani, Oak Ridge National Laboratory: ATR rodlet welding, 1200^{o}C steam test,
- EWI: Welding
- Ross Luther, PMT (now Thermocore Materials Technology), new Mo alloys
- Wah Chang: Zr-alloy supply
- Peter Hosemann, U.C. Berkeley
- AREVA: fuel pellets for ATR irradiation rodlets, research teaming
- Brian Cockeram, Bettis Laboratory

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