INL/MIS-22-66110-Revision-0

# Alloy 709 Advanced Austenitic Stainless Steel

February 2022

Changing the World's Energy Future

Ting-Leung Sham

Idaho National Laboratory

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**February 2022**

**Idaho National Laboratory**
**Idaho Falls, Idaho 83415**

**http://www.inl.gov**

**Prepared for the**
**U.S. Department of Energy**
**Under DOE Idaho Operations Office**
**Contract DE-AC07-05ID14517**

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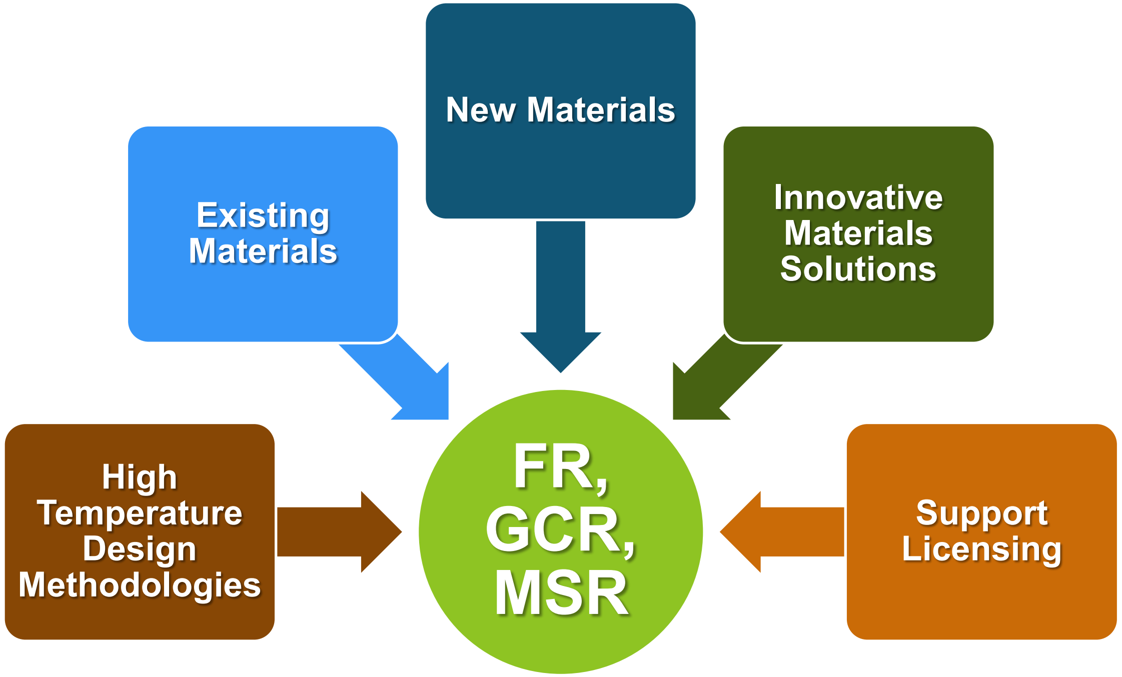
# Alloy 709 Advanced Austenitic Stainless Steel

GIF Very High Temperature Reactor System
Metals and Design Methods Working Group Virtual Meeting
February 21, 2022

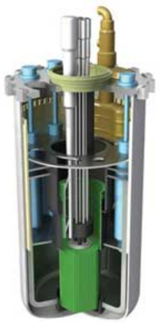
Idaho National Laboratory

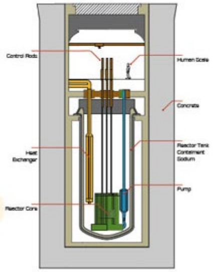
# DOE Office of Nuclear Energy, Advanced Reactor Technologies (ART) Program, Advanced Materials

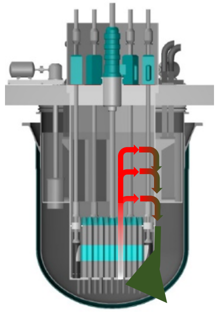
- Provide material solutions to enabling design, construction, licensing and operation of advanced reactors
  - Including Fast Reactors, Gas-cooled Reactors and Molten Salt Reactors (solid or liquid fuel)
    - Could be of modular or micro designs, and from hundreds of MWe to kWe
- Provide technical bases needed for design and licensing of advanced reactor components
  - Develop & validate improved high temperature design methodology
  - Provide qualification data (to NQA-1 or equivalent) on structural materials
    - Utilize consensus standards when appropriate (e.g., ASME, ASTM, etc.)
- Target resolution of issues needed for near to mid-term deployment of advanced reactors

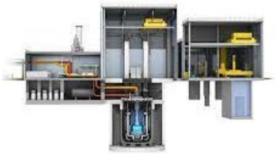


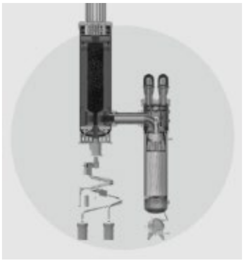
# Examples of Different Advanced Reactor Designs

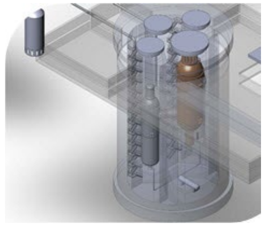


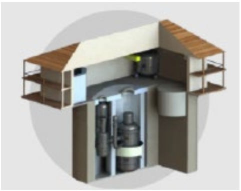


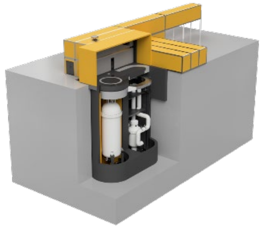


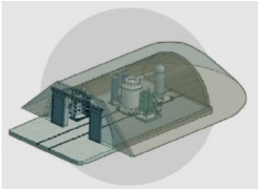




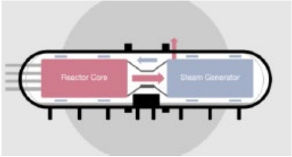




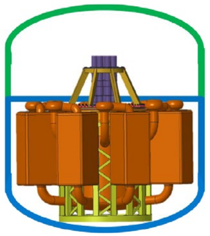




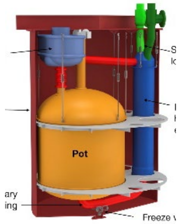
BWXT, BANR



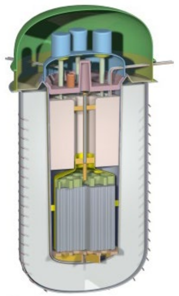

MIT, Horizontal Compact HTGR



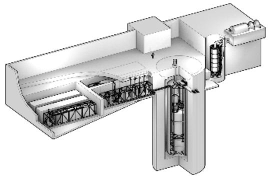
Elysium, MCSFR



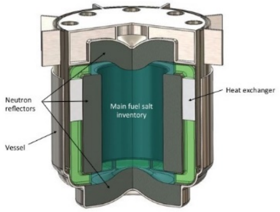

ThorCon



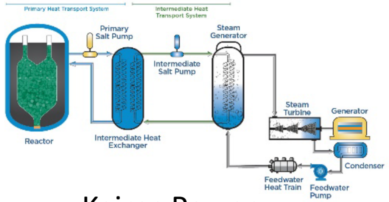
Terrestrial Energy IMSR



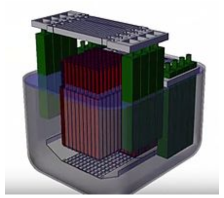
Flibe Energy LFTR (thorium)




TerraPower MCFR




Kairos Power KP-X

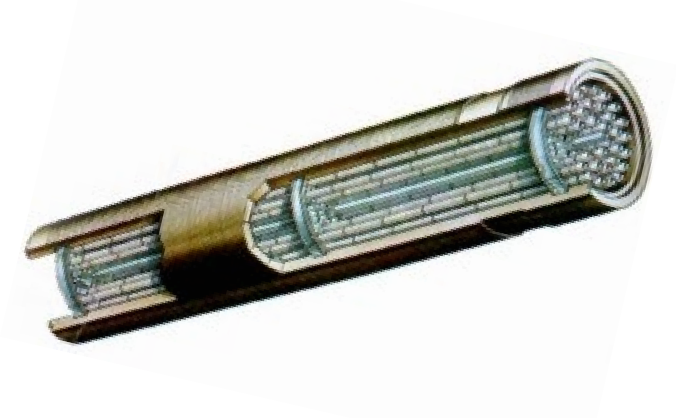


Moltex Energy, SSR

# DOE ART Program Effort on Alloy 709 Qualification

- Collaboration among staff from DOE Lab complex and subject matter experts
  - Idaho National Laboratory
    - Richard Wright, Ryann Rupp, Michael McMurtrey, Rongjie Song, Sam Sham, Laura Carroll (former)
  - Oak Ridge National Laboratory
    - Yanli Wang, Zhili Feng, Hong Wang, Yukinori Yamamoto
  - Argonne National Laboratory
    - Meimei Li, Xuan Zhang, Yiren Chen, Ken Natesan (retired)
  - Subject Matter Expert
    - George Young

# History of 20Cr-25Ni Austenitic Alloys



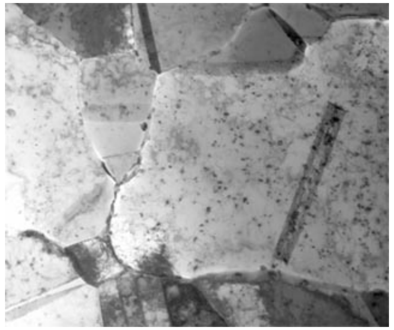
- 20Cr25Ni/Nb stainless steel (1950s)
- Used as fuel cladding in UK AGR fleet (since 1962)
- Temperature 550ºC to 850ºC
- Neutron exposure ~ 6 yrs
- 0.38 mm wall thickness, 14.5 mm diameter, 1 m long
- Approximately 90,000 fuel pins per AGR
- 14 AGRs built

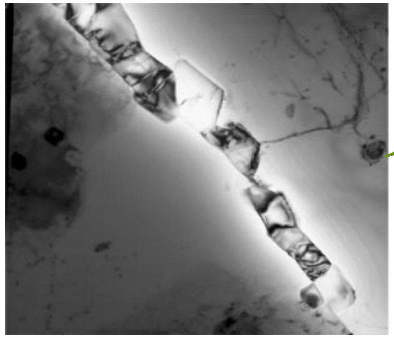
- Nippon Steel NF709 seamless tubing (1980s)
- Superheater and reheater applications in power boilers ('95 to '05, ~500 metric tons used in Japan power plants)
- Based on modified 20Cr25Ni composition
- UNS No. S31025
- ASTM A213 TP310MoCbN (for seamless tubes)
- ASME SA-213 Code Case 2581 for Section I power boilers

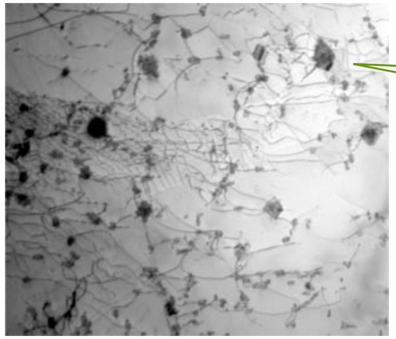
| | C | Mn | Si | P | S | Cr | Ni | Nb | B | Mo | Ti | N |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 20Cr25Ni/Nb | 0.015 | 0.5 | 0.6 | 0.01 | 0.02 | 20 | 25 | 0.6 | 0.0001 | | | <0.004 |
| NF 709 Spec | 0.10 max | 1.50 max | 1.00 max | 0.03 max | 0.01 max | 19.0-23.0 | 22.0-28.0 | 0.10-0.40 | 0.002-0.010 | 1.0-2.0 | 0.02-0.20 | 0.10-0.25 |
| Typical NF 709 | 0.07 | 0.97 | 0.4 | 0.001 | 0.007 | 20.68 | 24.7 | 0.24 | 0.005 | 1.45 | 0.04 | 0.17 |

# Alloy 709 Is Nitrogen-stabilized, Niobium-Strengthened Austenitic Alloy

- Based on the Fe-20Cr-25Ni composition for power boiler applications
- Excellent oxidation resistance at high temperatures
- Niobium and nitrogen additions increase the tensile and creep strength



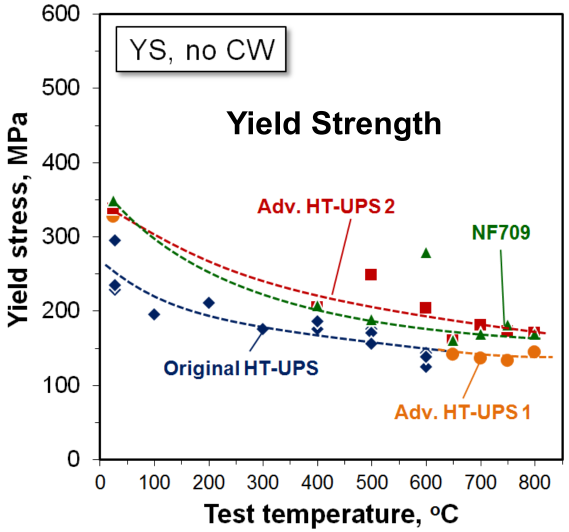



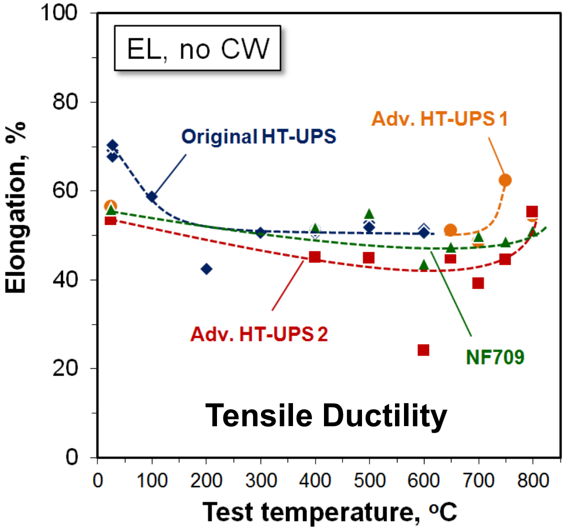



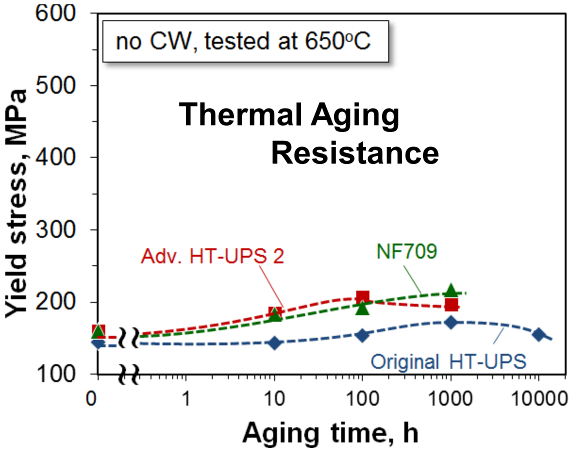

Microstructure after creep test for 5015h @ 750C, 100MPa (TEM-BF images)

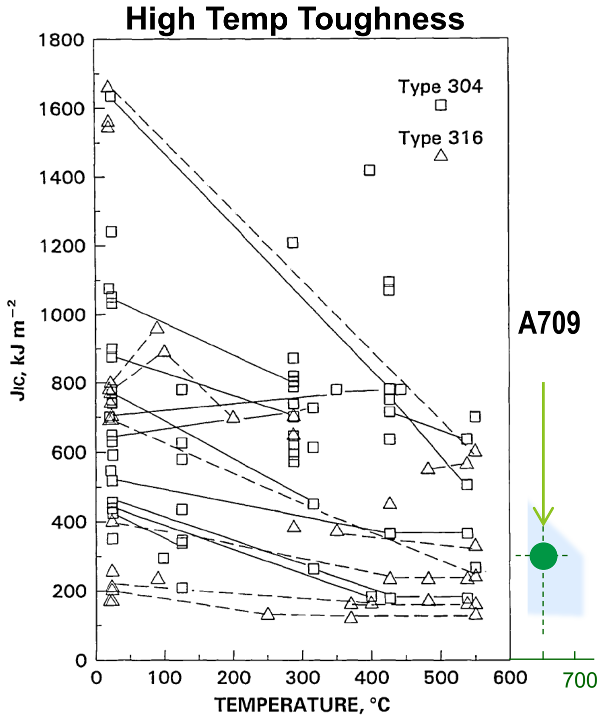
- Most of the grain boundary (GB) is fully covered by precipitates
- Two different sizes of precipitates in the grain interior (GI)

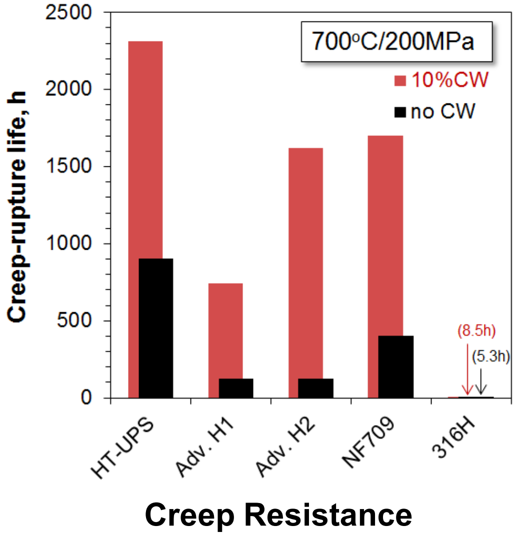
# Austenitic Alloys Down-Selection – Balanced Properties

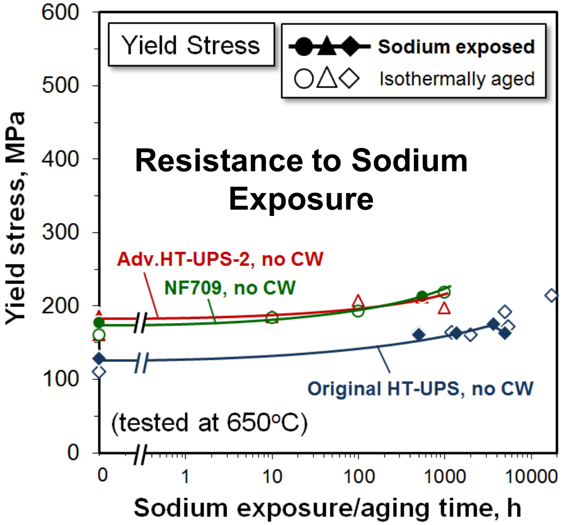


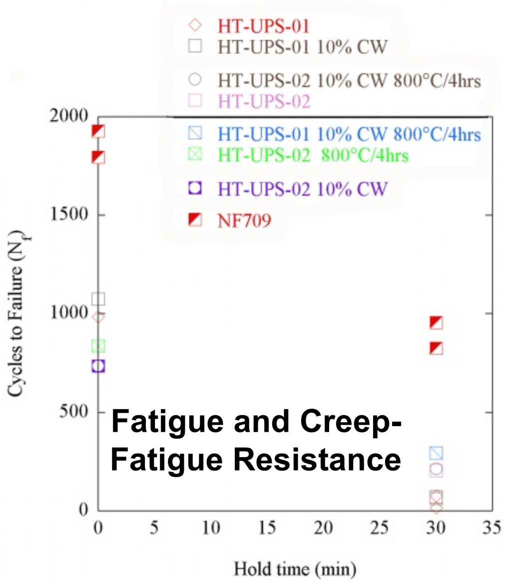



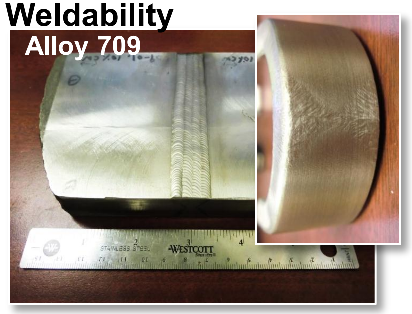



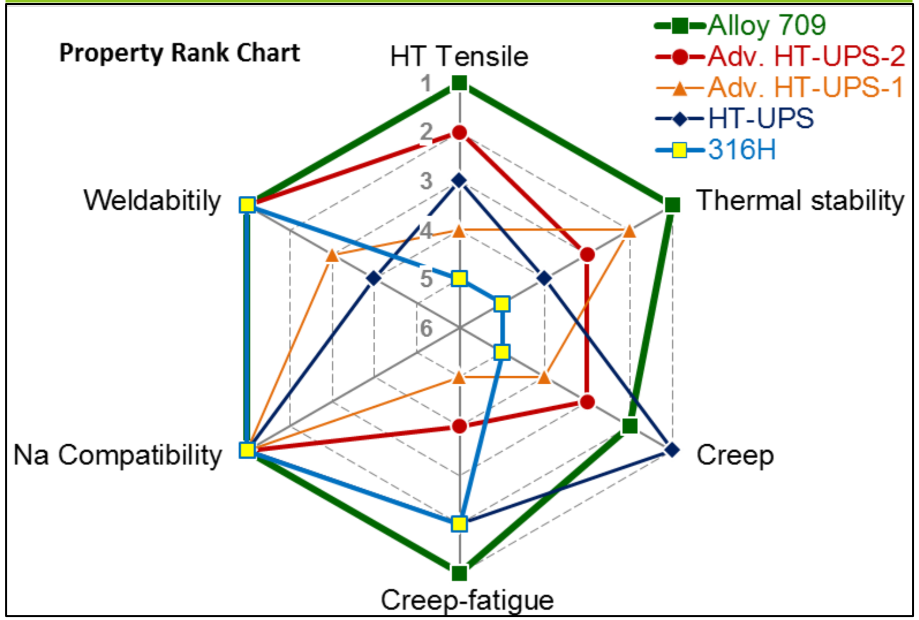

Weldability



# Down-Selected Alloy 709 for ASME Code Qualification

- Alloy 709 offers improved safety margins and design flexibility as well as reduced commodity requirements compared to the austenitic stainless steels qualified for high-temperature nuclear construction
- Alloy 709 ranked as #1 in 5 different properties comparing to other austenitic alloys under consideration in previous analysis
- Alloy 709 has the following improved properties compared to 316H
  - Higher creep strength
  - Better performance in sodium and supercritical $CO_2$ according to short-term test data
  - Higher swelling resistance based on ion irradiation

**Property rank chart for austenitic alloys**



# Comparison Between Alloy 709 and 316H Stainless Steel

| | **316H Stainless Steel** | **Alloy 709** |
|---|---|---|
| Composition | **18Cr-12Ni-**2Mn-**2.5Mo-**0.07C | **22Cr-25Ni-**2Mn-**1.5Mo-**V-Nb-C-B-N |
| Strengthening mechanism | Solution hardening (Mo) + Precipitate hardening ($M_{23}C_6$) | Precipitate hardening {M(C,N), $M_{23}C_{6,}$ CrNbN} |
| YS/UTS/EL (RT) | 205MPa/ 515MPa/ 35% | 270MPa/ 640MPa/ 30% |
| at 650$^{o}$C | 156MPa/ 349MPa/ 24% | 200MPa/ 450MPa/ 45% |
| Advantage | • Lower material cost<br>• Good oxidation resistance<br>• Good weldability<br>• Good sodium compatibility<br>• Widely used, large experience base | • Excellent creep properties<br>• Better oxidation resistance<br>• Good sodium compatibility<br>• Better compatibility with sCO2<br>• Higher creep strength expands design envelope |
| Disadvantage | • Lower creep strength restricts design envelope | • Higher commodity cost due to high Ni<br>• Need improvement on welding |

# Alloy 709 Fabrication Scale-up

400-lb heats

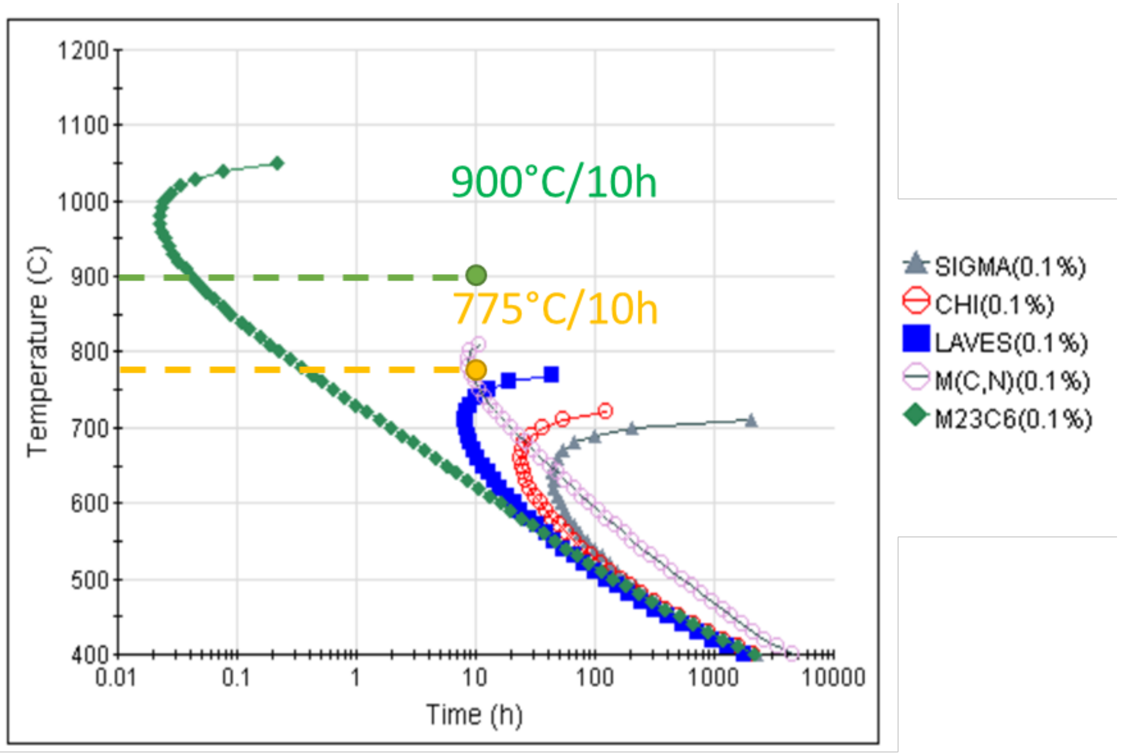
1st 45,000-lb commercial heat, from Carlson

2nd 40,000-lb commercial heat, from ATI

3rd 40,000-lb commercial heat, from ATI, to be delivered in June 2022

# Precipitation Treatment (PT) of Alloy 709

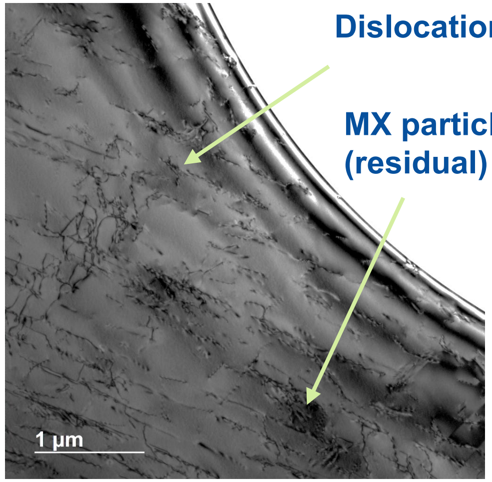
- **Objective**
  - Develop heat treatment plan to age Alloy 709
  - To bring out the desired nano-sized precipitates, such as MX (Nb, Ti, V:C, N) or Z-phase (CrNbN) on dislocations
  - To result in optimized and balanced mechanical properties (creep versus creep-fatigue)
- **Modeling**
  - Conducted thermodynamic and kinetics modeling
  - Selected precipitation treatment (PT) of 775C for 10 hours (775C/10hrs) to:
    - Avoid the formation of the intermetallic laves phase ($Fe_2Mo$, $Fe_2Nb$), and
    - Promote the formation of $M_{23}C_6$ (Cr, Fe, Mo, Ni:C)




Quench temperature: 1150 °C

# Characterization of Precipitation Treated Alloy 709

### ESR Solution Anneal @ 1100C



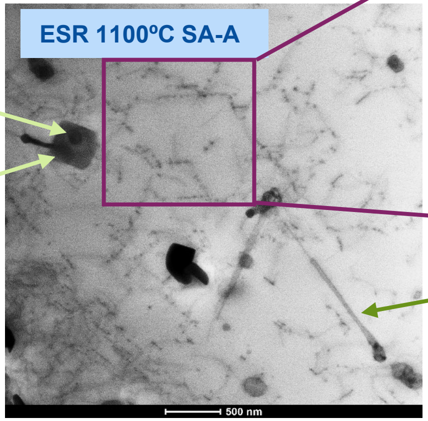

Dislocations

MX particles (residual)

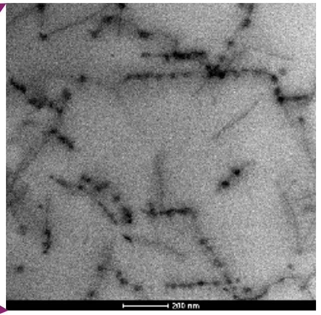
### After Precipitation Treatment (PT) of 775C for 10 hrs

Core: MX particles (residual)

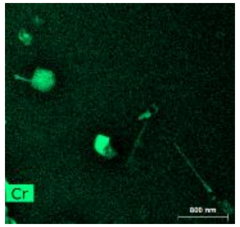
Shell: $M_{23}C_6$

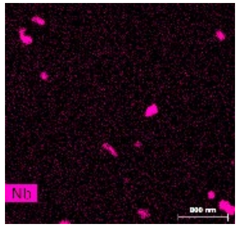


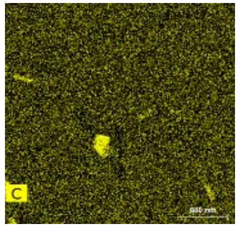

Nb-rich particles on dislocations

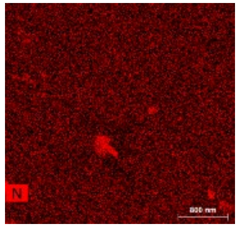


Tail: Cr-rich phase



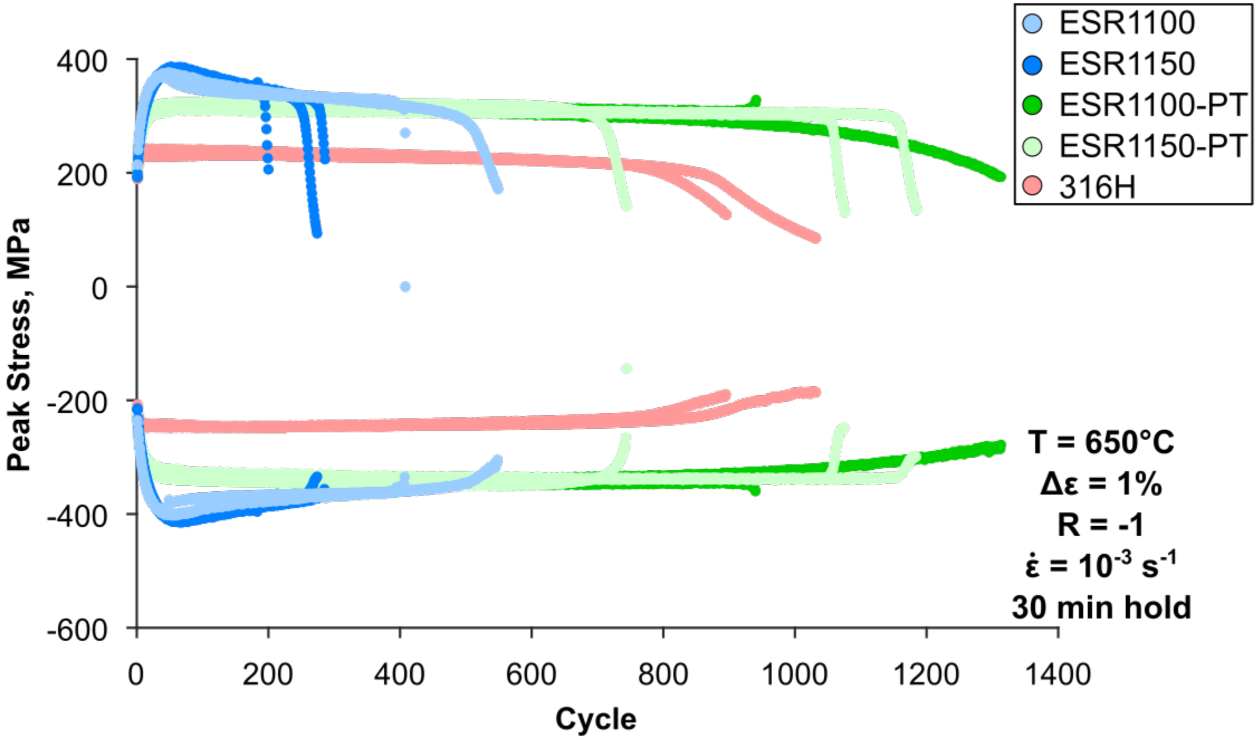




Chemical composition of melt of A709 heat # 58776 (in wt%)

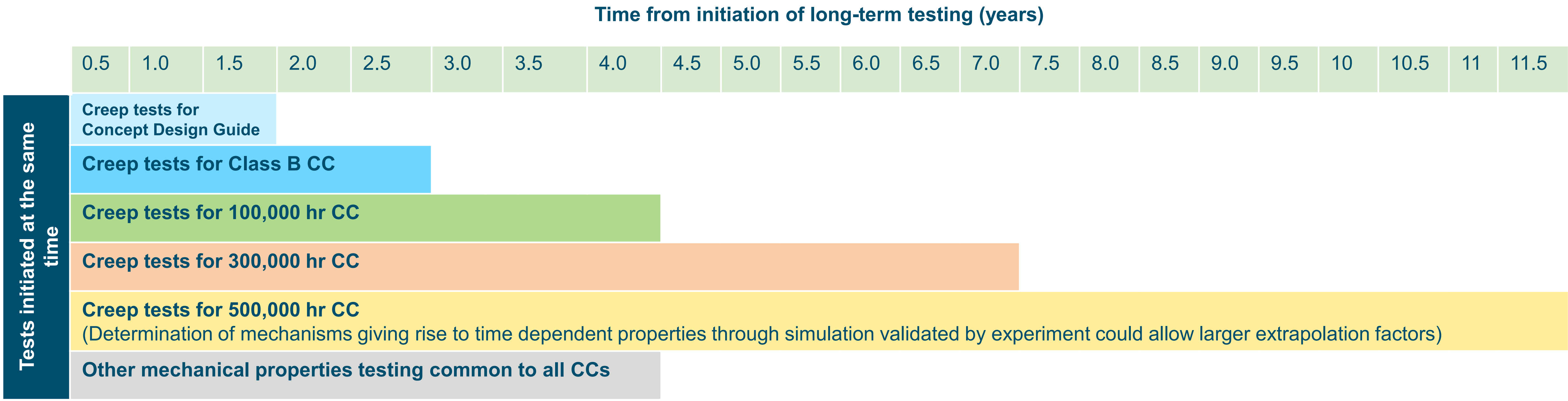
| A709 | C | Cr | Ni | Mn | Mo | N | Si | P | Ti | Nb | B | Fe |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Actual** | 0.066 | 19.93 | 24.98 | 0.91 | 1.51 | 0.148 | 0.44 | 0.014 | 0.04 | 0.26 | 0.0045 | Bal |

# Creep-Fatigue Performance of Alloy 709 (PT and Non-PT) and 316H

- ESR A709 Solution Anneal (SA) plus Precipitation Treatment (PT) has the greatest number of cycles to failure
- Followed by 316H and finally ESR A709-SA
- The ESR A709-SA heat exhibits a different creep-fatigue behavior than ESR A709-PT and 316H
- The overall peak stress of the ESR A709-SA and ESR A709-PT is greater than 316H



# A Staged Approach to Code Qualification




A four-year testing program, without resource constraints, would generate data package to support:

- Conceptual design
  - Conceptual Design Guide for 500,000-hour lifetime
- Preliminary design
  - 100,000-hour Class A code case
  - Class B material code case

Additional creep data at 7-year mark from start:

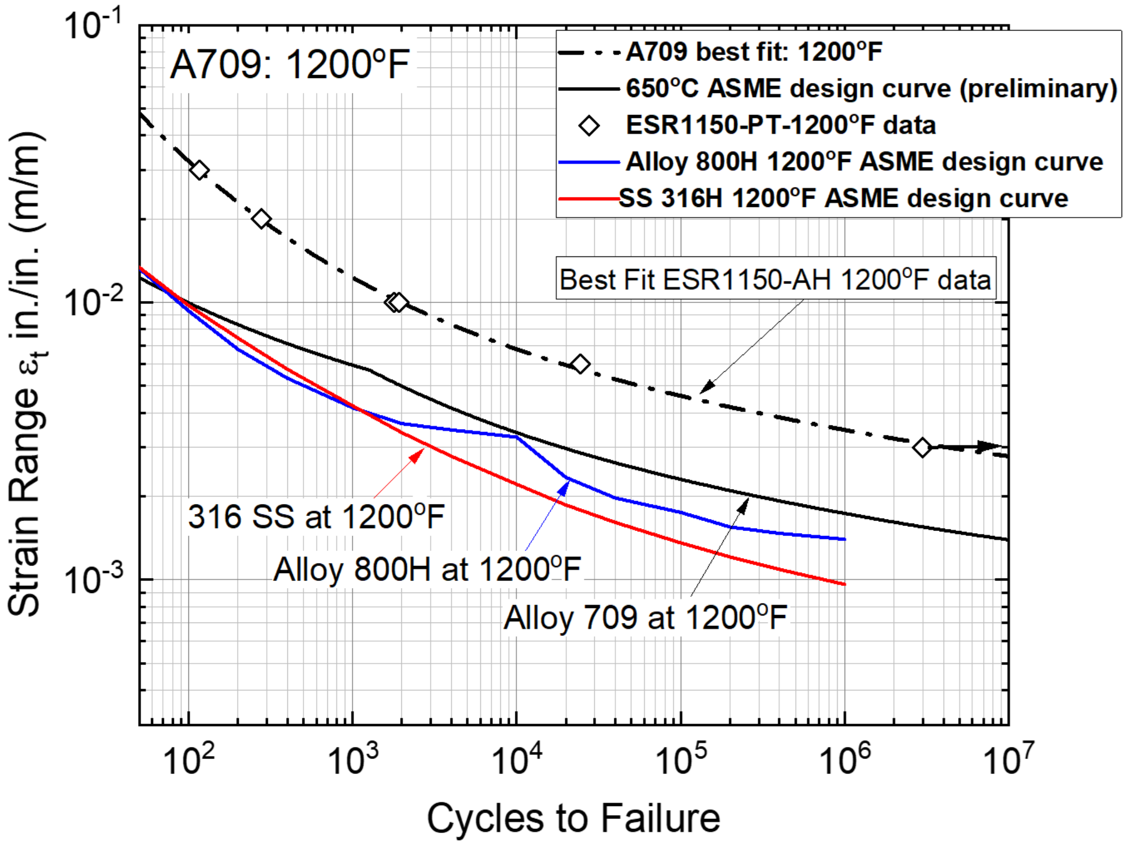
- Final design
  - 300,000-hour Class A code case

Additional creep data at 12-year mark from start:

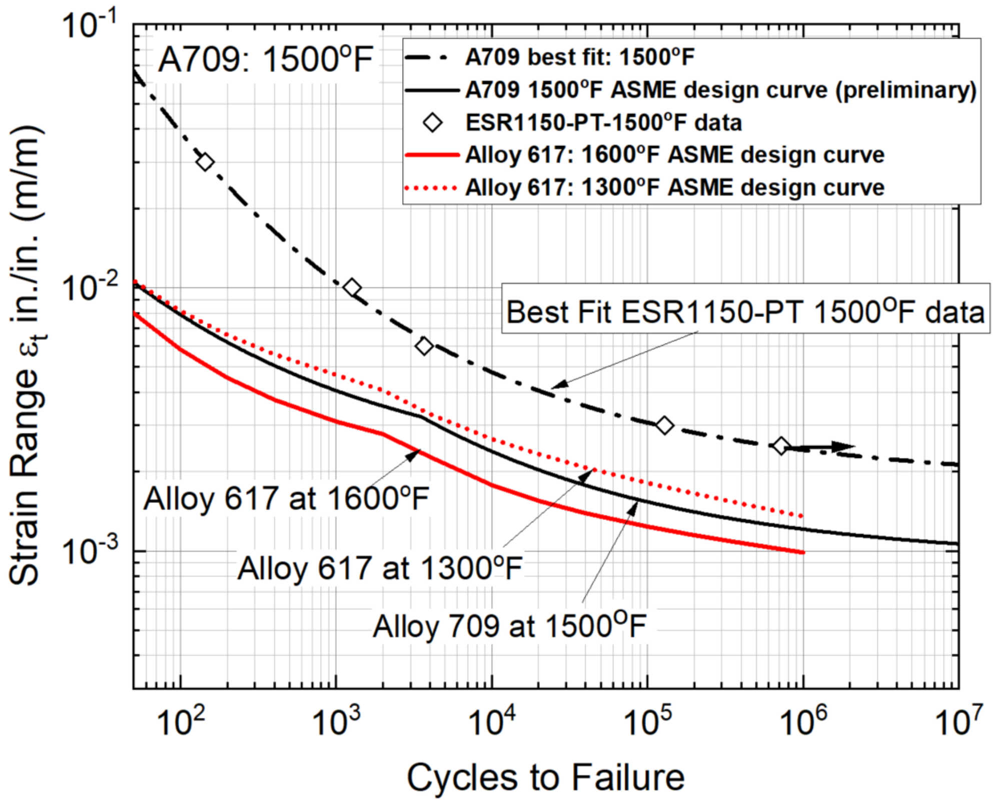
- Nth-of-a-kind
  - 500,000-hour Class A code case

# Alloy 709-PT Has Enhanced Fatigue Properties

## Alloy 709-PT better than Alloy 800H and 316H at 1200F (650C)

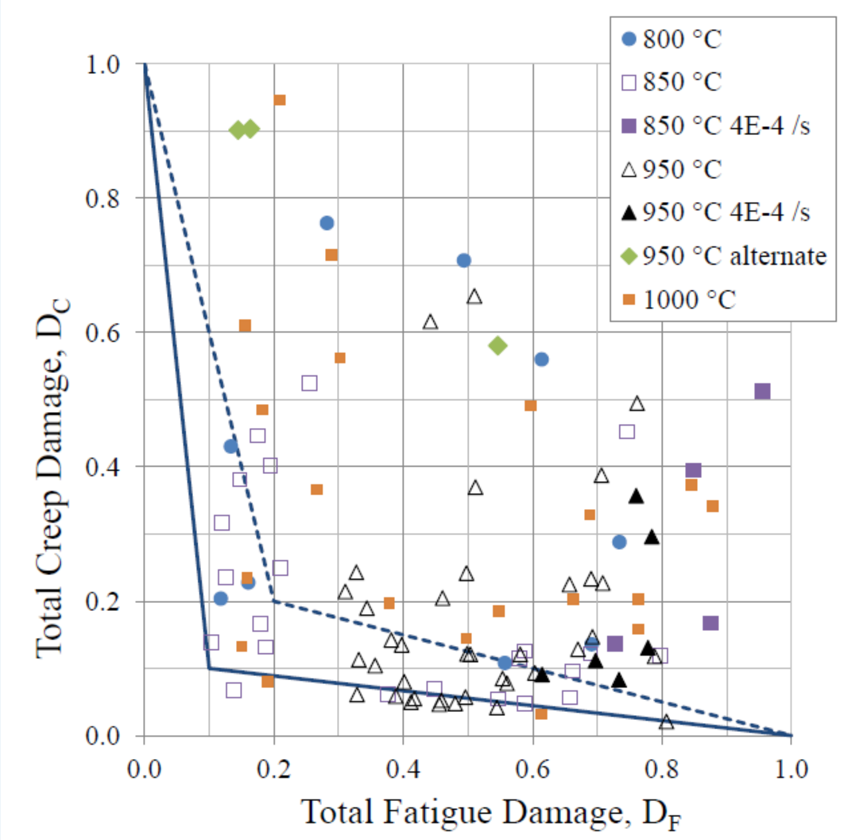



## Alloy 709-PT comparable to Alloy 617 at 1500F (816C)

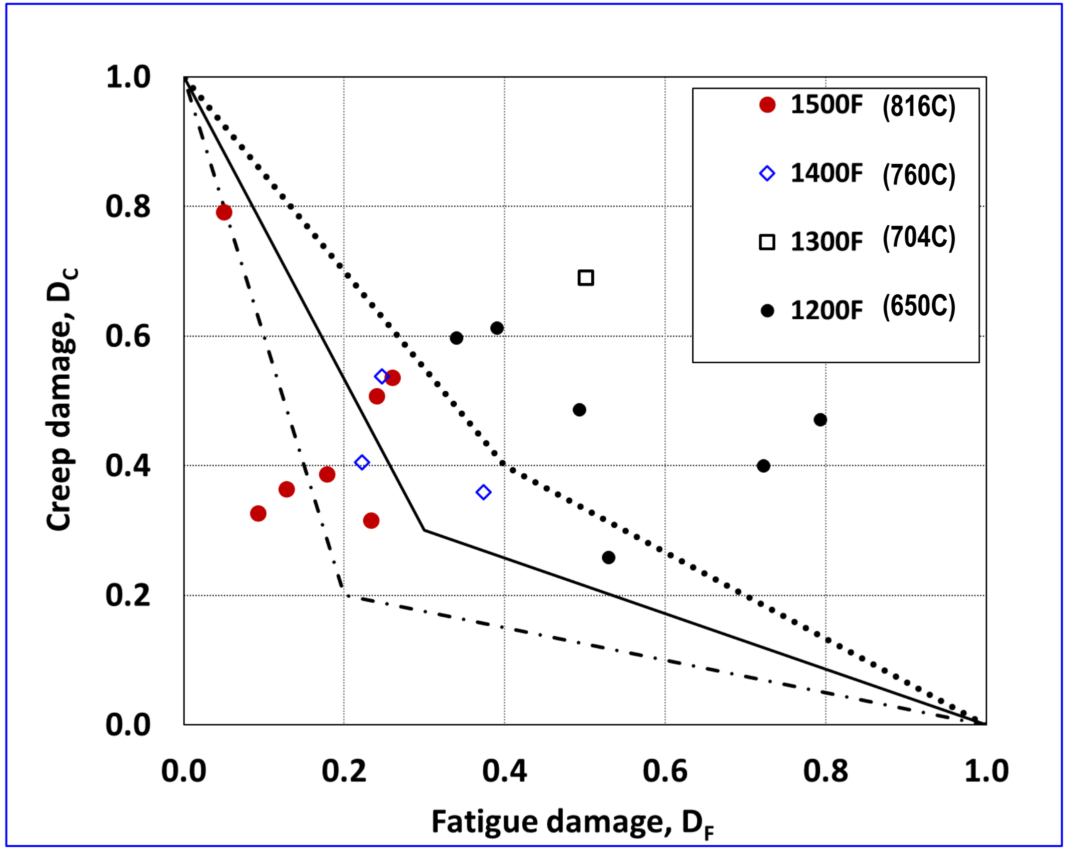


# Alloy 709-PT Has Very Good Resistance to Creep-Fatigue Interaction

Alloy 617 Creep-Fatigue Interaction




Alloy 709-PT Creep-Fatigue Interaction



# Extrapolated 100,000-Hour Minimum Rupture Stress

| Temp, C | Minimum Rupture Stress Values | | | |
|---|---|---|---|---|
| | High Temperature Alloys | | Stainless Steels | |
| | A617 | A800H | 316H | A709-PT |
| 650 | 127.1 | 63.0 | 58.2 | 99.8 |
| 675 | 102.5 | 51.2 | 45.1 | 80.2 |
| 700 | 82.6 | 41.6 | 34.6 | 64.2 |
| 725 | 66.5 | 33.8 | 26.3 | 51.1 |
| 750 | 53.5 | 27.5 | 19.6 | 40.4 |
| 775 | 43.0 | 22.3 | 14.5 | 31.8 |
| 800 | 34.6 | 18.1 | 10.4 | 24.8 |
| 825 | 27.7 | 14.8 | 7.4 | 19.3 |
| 850 | 22.3 | 12.0 | 5.1 | 14.8 |
| 875 | 17.8 | 9.8 | 3.4 | 11.3 |
| 900 | 14.3 | 7.9 | 2.1 | 8.5 |
| 925 | 11.4 | 6.5 | 1.2 | 6.4 |

| Temp, C | Minimum Rupture Stress Ratios (Relative to A617) | | | |
|---|---|---|---|---|
| | High Temperature Alloys | | Stainless Steels | |
| | A617 | A800H | 316H | A709-PT |
| 650 | 1.0 | 0.50 | 0.46 | 0.78 |
| 675 | 1.0 | 0.50 | 0.44 | 0.78 |
| 700 | 1.0 | 0.50 | 0.42 | 0.78 |
| 725 | 1.0 | 0.51 | 0.39 | 0.77 |
| 750 | 1.0 | 0.51 | 0.37 | 0.76 |
| 775 | 1.0 | 0.52 | 0.34 | 0.74 |
| 800 | 1.0 | 0.53 | 0.30 | 0.72 |
| 825 | 1.0 | 0.53 | 0.27 | 0.69 |
| 850 | 1.0 | 0.54 | 0.23 | 0.67 |
| 875 | 1.0 | 0.55 | 0.19 | 0.63 |
| 900 | 1.0 | 0.56 | 0.15 | 0.60 |
| 925 | 1.0 | 0.56 | 0.11 | 0.56 |

# Chemical Compositions (in wt %)

| | A617 N06617 | A800H N08810 | 316H S31609 | A709 S31025 |
|---|---|---|---|---|
| C | 0.05-0.15 | 0.05-0.10 | 0.04-0.10 | 0.10 max |
| Ni | 44.5 min | 30.0-35.0 | 10.0-14.0 | 23.0-26.0 |
| Cr | 20.0-24.0 | 19.0-23.0 | 16.0-18.0 | 19.5-23.0 |
| Co | 8.0-10.0 | - | - | - |
| Mo | 8.0-10.0 | - | 2.0-3.0 | 1.0-2.0 |
| Ti | 0.6 max | 0.15-0.6 | 0.04 max * | 0.2 max |
| Fe | 3.0 max | 39.5 min | balance | balance |
| Mn | 1.0 max | 1.5 max | 2.0 max | 1.5 max |
| Si | 1.0 max | 1.0 max | 0.75 max | 1.0 max |

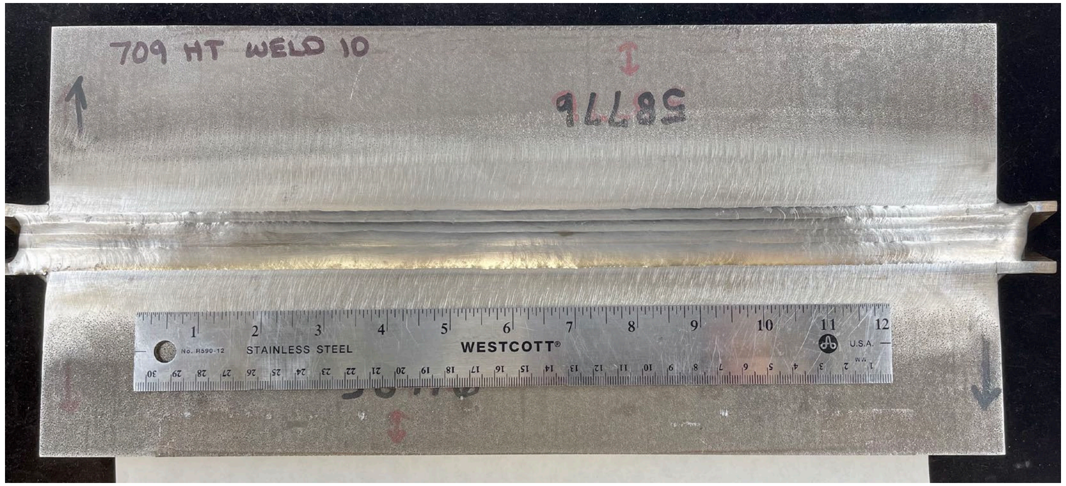
* ASME Section III, Division 5 additional requirement

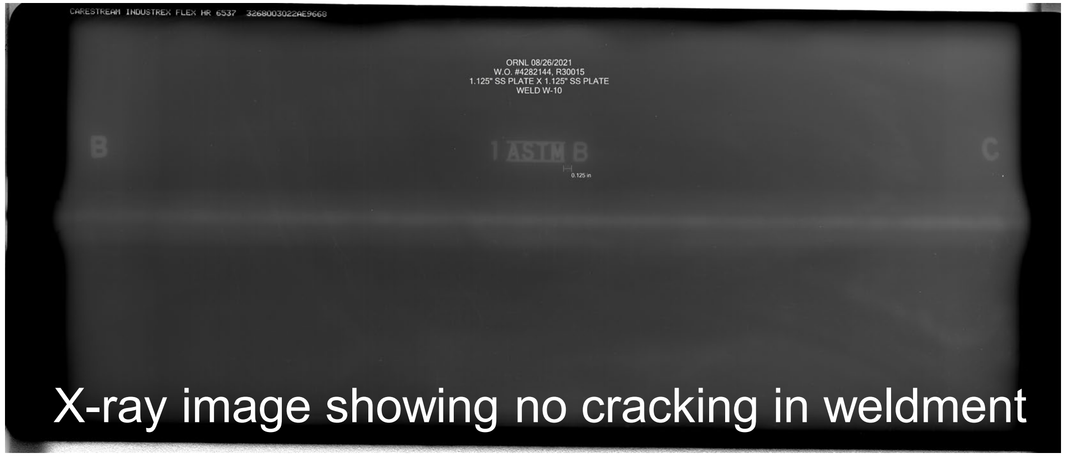
| | A617 N06617 | A800H N08810 | 316H S31609 | A709 S31025 |
|---|---|---|---|---|
| Cu | 0.5 max | 0.75 max | - | - |
| Al | 0.8-1.5 | 0.15-0.6 | 0.03 max * | - |
| P | - | 0.045 max | 0.045 max | 0.03 max |
| S | 0.015 max | 0.015 max | 0.03 max | 0.03 max |
| B | 0.006 max | - | - | 0.002-0.010 |
| Nb | - | - | - | 0.1-0.4 |
| N | - | - | 0.05 min * | 0.1-0.25 |

* ASME Section III, Division 5 additional requirement

# Alloy 709 Weldment

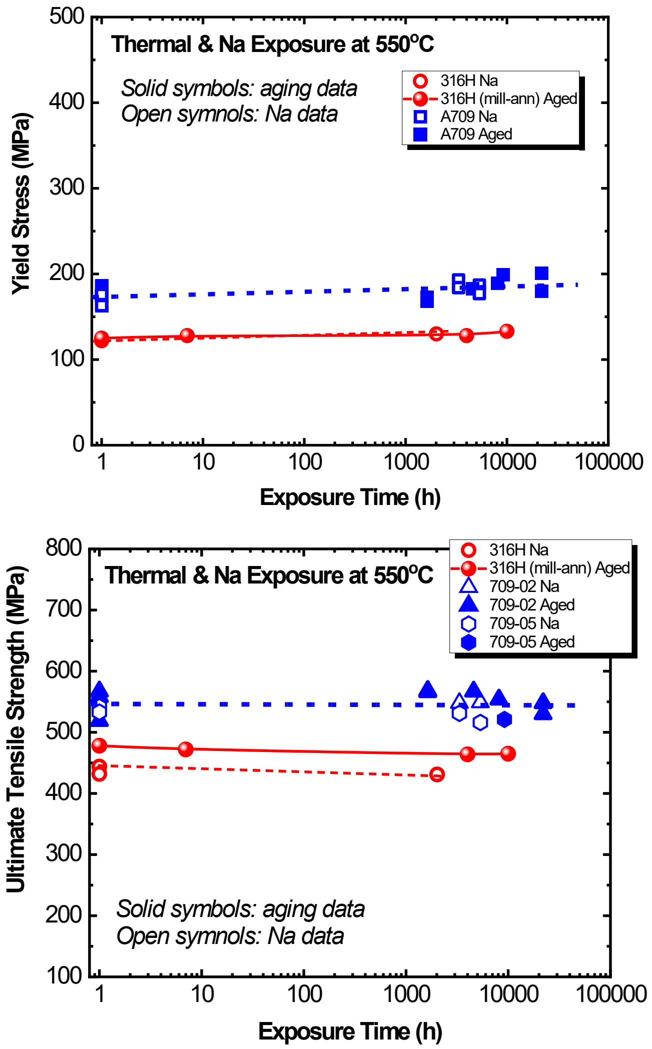
- Weld consumable: Matching filler metal
- Welding process: Gas tungsten arc (GTA)
- Completed optimizing Alloy 709 GTA welding parameters for matching filler metal weld consumable
- Fabricated ASME Section IX qualified weldment using Carlson ESR1150-PT base metal and weld wire with low phosphorus ( < 20 ppm)
- Ongoing – fabricating production welds to support Alloy 709 Code Case testing using the second commercial Alloy 709 heat from ATI Specialty Rolled Products



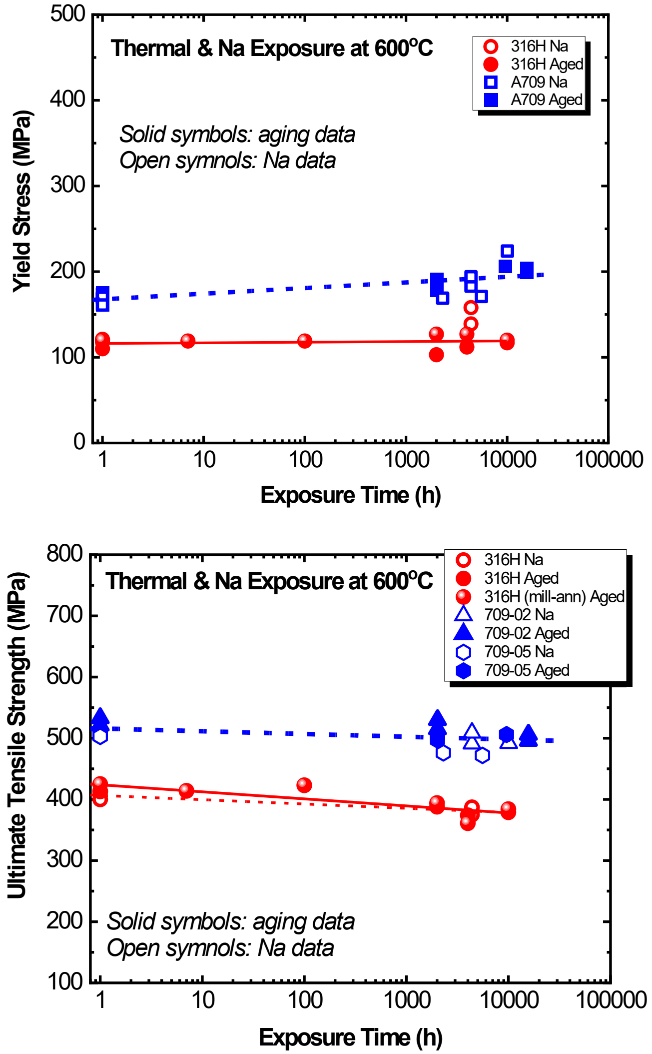




X-ray image showing no cracking in weldment

# Sodium Compatibility of Alloy 709

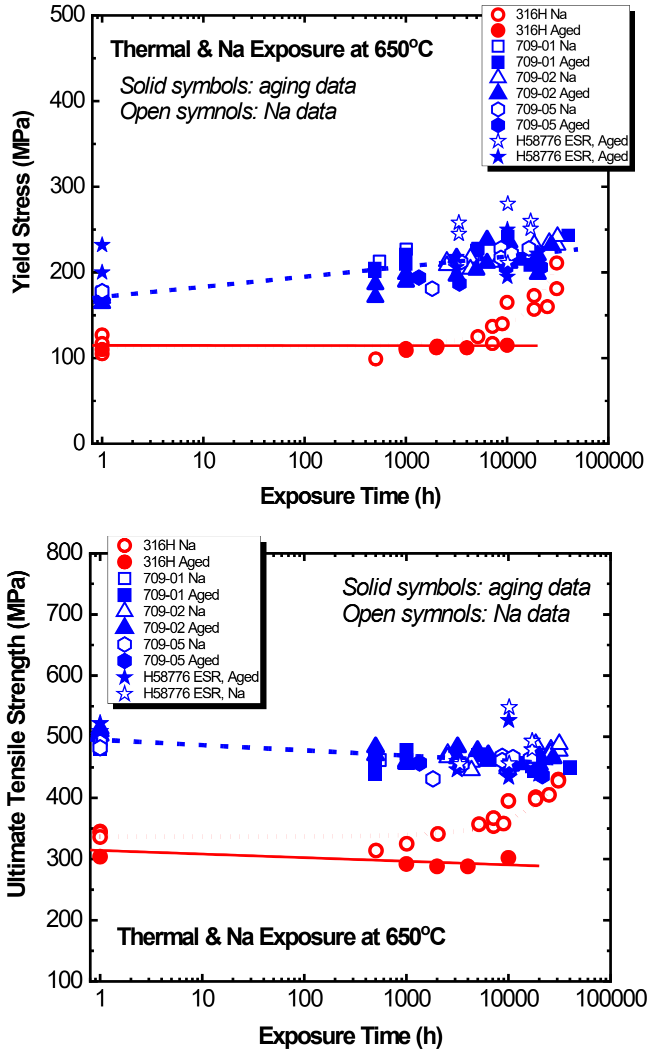



550C Exposure




600C Exposure

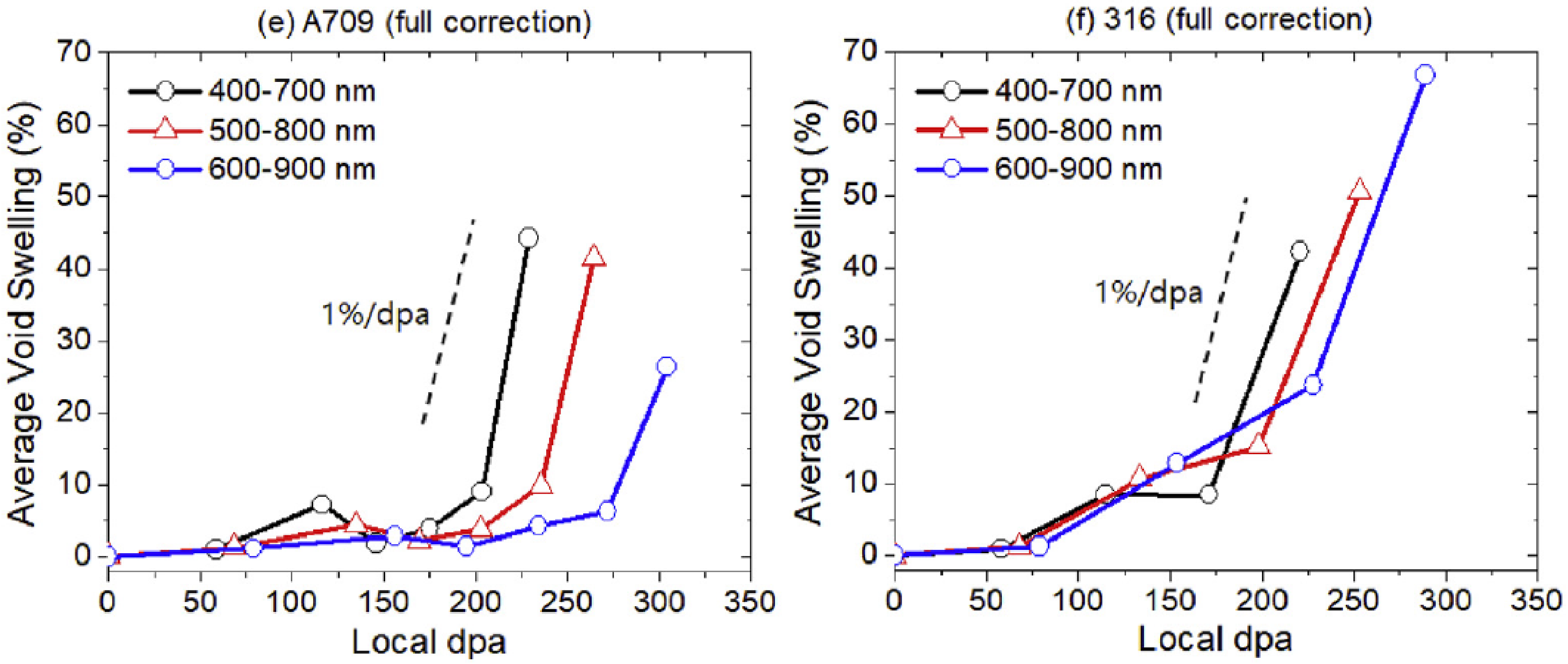
650C Exposure



# Swelling Scoping Study Through Ion Irradiation [1]

- Ion irradiation results for Alloy 709 and Type 316 stainless steel (~5% cold work) show that Alloy 709 had a significantly longer swelling transient regime
- Demonstrate enhanced swelling resistance of Alloy 709 over 316 under heavy ion irradiation (3.5 MeV $Fe^{+2}$ ions)

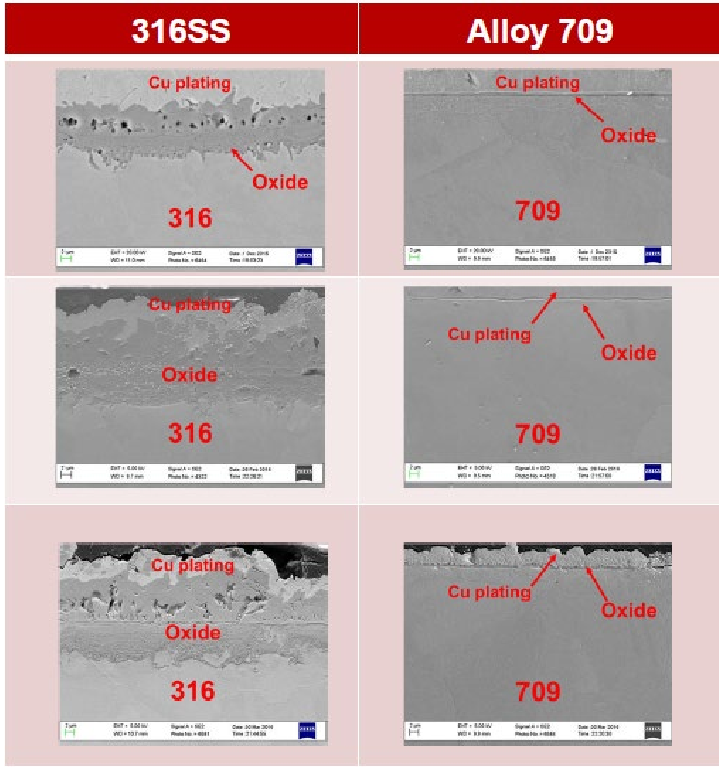
Heavy ion irradiation results at 575C, the peak swelling temperature



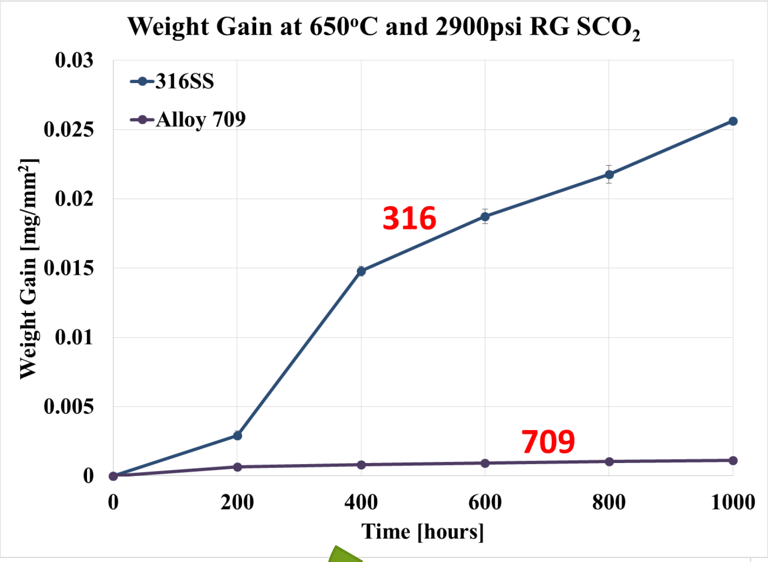

[1] Kim et al., Journal of Nuclear Materials, 527 (2019) 151818

# Short-term Supercritical CO2 Compatibility Scoping Study [1]

2900 psi, research grade (99.998% pure) CO2, 650C

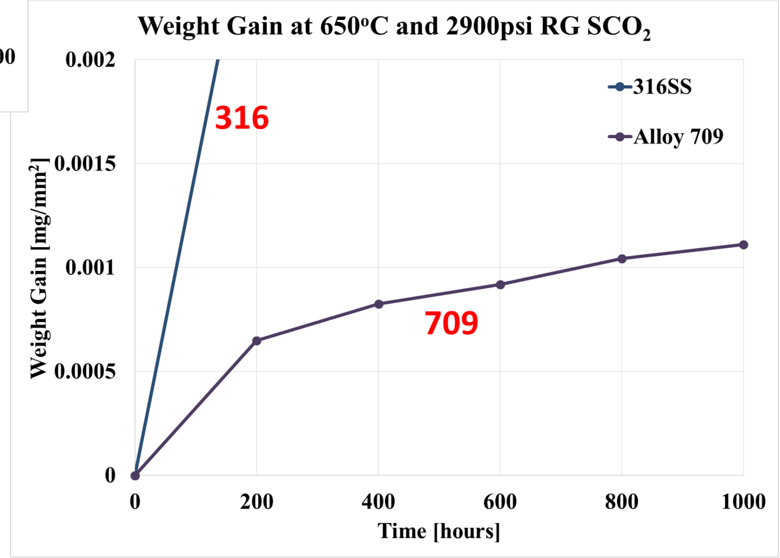



SEM Cross-Sectional Image after Testing




Need longer term exposures on tensile specimens to determine effects on mechanical properties

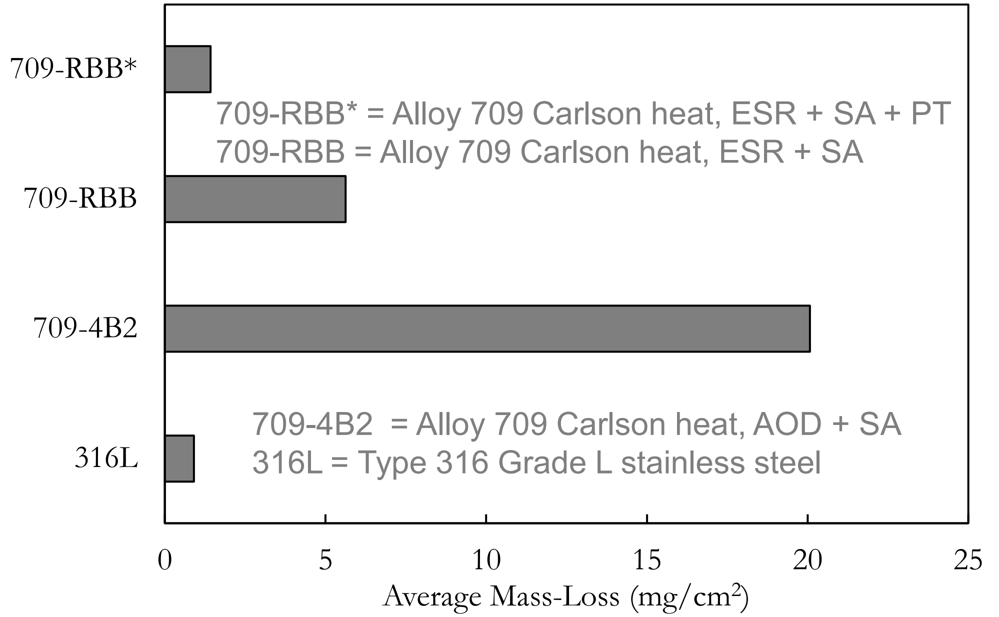
Magnified Scale




[1] Kumar Sridharan, NEUP Project 13-4900, University of Wisconsin-Madison

# Alloy 709 Chloride Salt Compatibility Scoping Study [1]

- Chloride salt: Purified $MgCl_2$-NaCl-KCl (45-53-2 wt.%)
- Uncoated materials
  - Corrosion exposure at 800C for 100 hours in static capsule
  - Average corrosion rate (slowest to fastest)
    1. 316L (0.91 $mg/cm^2$)
    2. 709-RBB* (1.42 $mg/cm^2$)
    3. 709-RBB (5.63 $mg/cm^2$)
    4. 709-4B2 (20.07 $mg/cm^2$)




- Selected Alloy 709 material with processing condition that gave the worst corrosion performance, 709-4B2 (AOD + SA), for boronization surface treatment
  - Chloride salt exposure at 700C for 120 hours in static capsule
  - Preliminary examination of pre-exposure and post-exposure coated sample
    - Boronization surface treatment is effective in preventing chloride salt corrosion for the worst performing uncoated Alloy 709 processing condition (709-4B2)

[1] Results courtesy of J. Zhang, Virginia Tech

# Nuclear Energy University Projects (NEUPs) on Alloy 709

| Project # | Title | PI, Affiliation |
|---|---|---|
| 14-6346 | Integrated computational and experimental study of radiation damage effects in Grade 92 Steel and Alloy 709 | Haixuan Xu, University of Tennessee, Knoxville |
| 14-6762 | Microstructural evolution of advanced ferritic/martensitic alloys under ion irradiation | Jim Stubbins, University of Illinois, Urbana-Champaign |
| 15-8308 | Creep and creep-fatigue crack growth mechanisms in Alloy 709 | Afsaneh Rabiei, North Carolina State University |
| 15-8432 | Multi-scale experimental study of creep-fatigue failure initiation in a 709 Stainless Steel alloy using high resolution digital image | John Lambros, University of Illinois, Urbana-Champaign |
| 15-8548 | Assessment of Aging Degradation Mechanisms of Alloy 709 for Sodium Fast Reactors | Kip Findley, Colorado School of Mines |
| 15-8582 | Mechanistic and Validated Creep/Fatigue Predictions for Alloy 709 from Accelerated Experiments and Simulations | Korukonda Murty, North Carolina State University |
| 15-8623 | Characterization of Creep-Fatigue Crack Growth in Alloy 709 and Prediction of Service Lives in Nuclear Reactor Components | Gabriel Potirniche, University of Idaho |

# Summary

- Alloy 709 is an advanced austenitic alloy, has very high creep rupture strength among austenitic stainless steels
- Alloy 709-PT (Precipitation Treatment) has balanced creep vs. creep-fatigue performance
- Creep strength of Alloy 709-PT is lower than nickel alloys such Alloy 617 but has significant advantage over Type 316 stainless steel
- Alloy 709-PT maintains reasonable creep strengths up to 925C to accommodate short-term elevated temperature excursions under some postulated accident scenarios
- Fatigue and creep-fatigue performance of Alloy 709-PT is excellent
- Data package generation sponsored by DOE-NE is ongoing to codify Alloy 709-PT in ASME Boiler and Pressure Vessel Code, Section III, Division 5 for high temperature reactor applications
- Alloy 709 has good compatibility with sodium and supercritical CO2 (very short-term data) as compared with Type 316 stainless steel
- Limited heavy ion irradiation data showed that Alloy 709 has higher swelling resistance than Type 316 stainless steel
- While Alloy 709 is not optimum for molten salt resistance, boronization surface treatment shows potential
  - Longer term exposure and high temperature mechanical properties testing are required to confirm the beneficial effect of surface treatment for Alloy 709-PT in molten salts
- In addition to SFR and MSR, Alloy 709 is a potential candidate for HTGR applications for outlet temperatures in the range 1400 to 1500F