Clean Coal Technology Advanced Materials Program

Overview of Steam Oxidation Task

Participants

UK

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Alstom Power: *Derek Allen*

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Oak Ridge National Laboratory: *Ian Wright*

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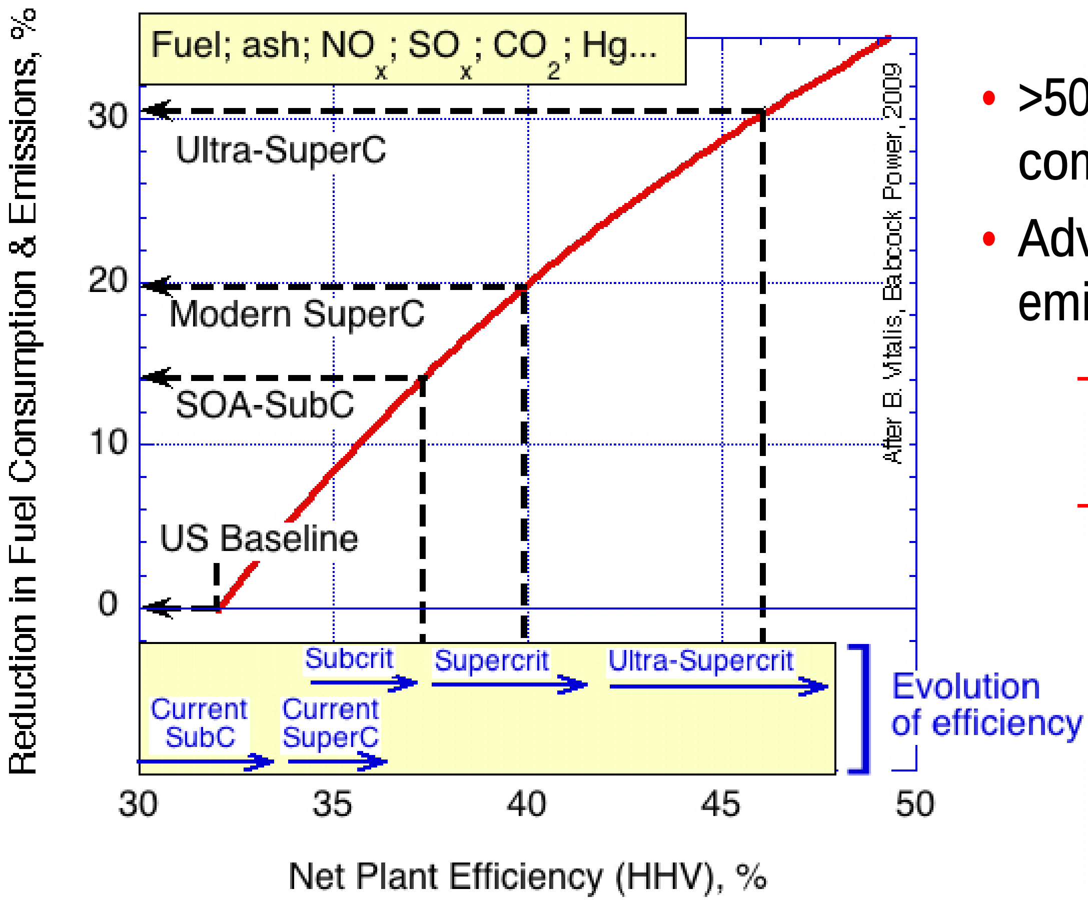
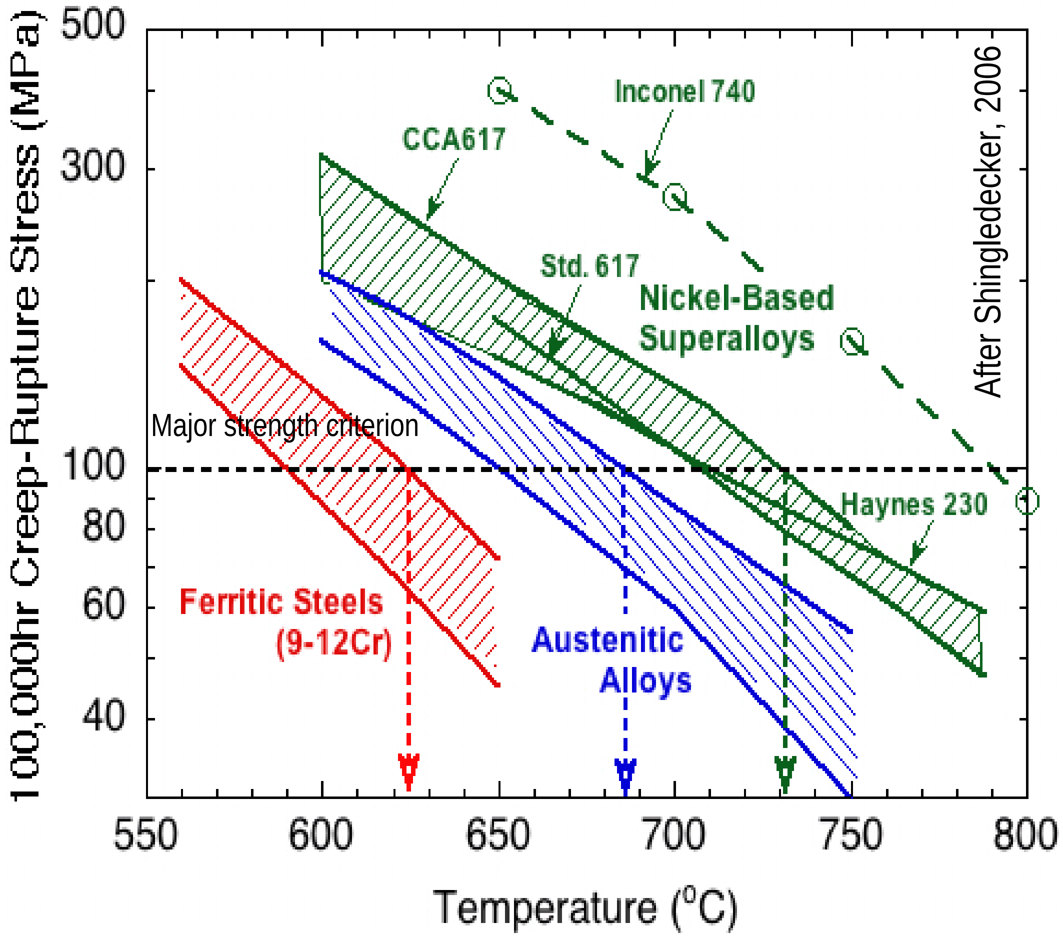
Background



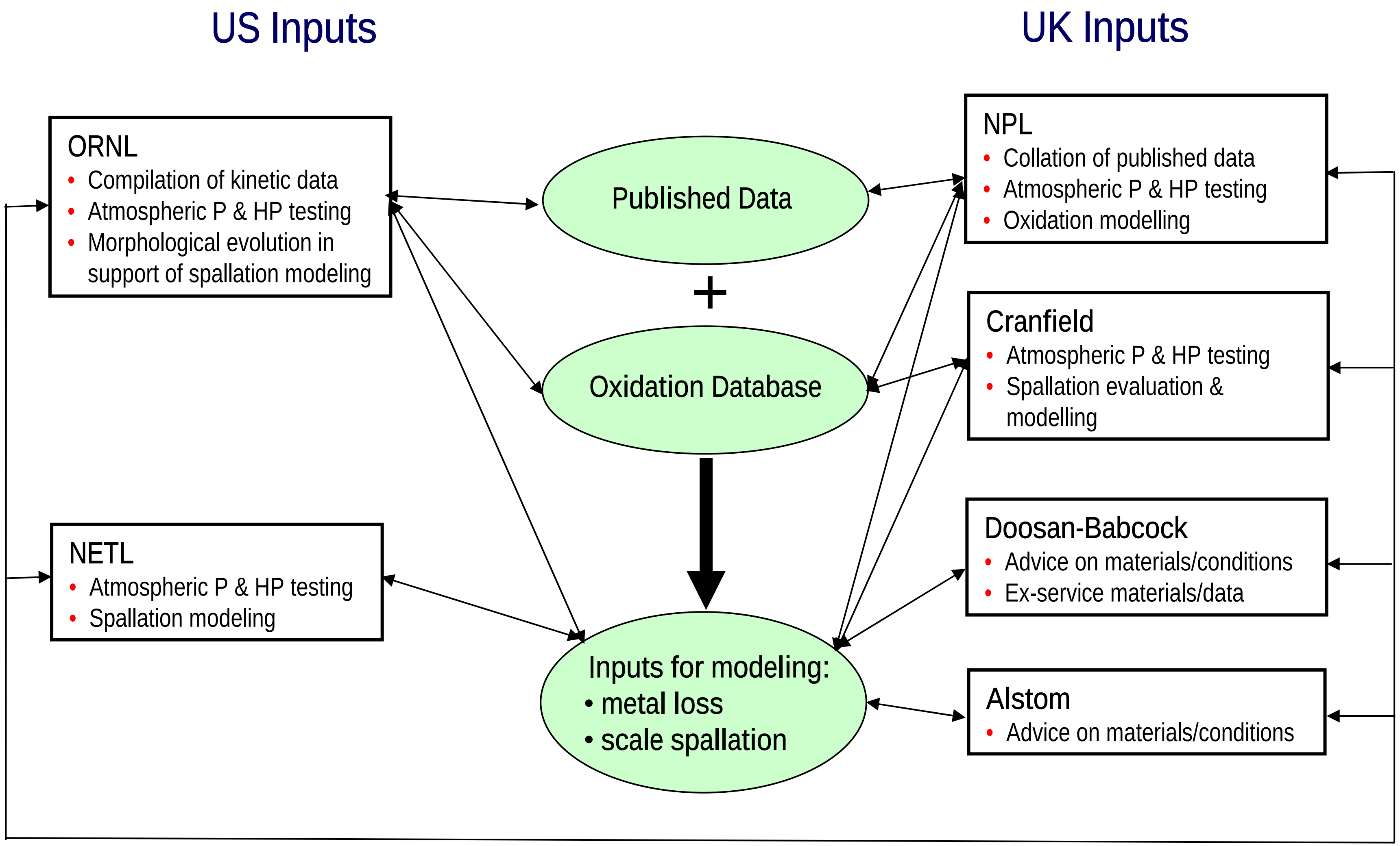
- >50% of US electricity involves coal combustion
- Advanced steam conditions can reduce emissions by 30-33%
  - 130 tonnes CO_2/h from a current US coal-fired 800 MWe supercritical plant
  - 396,922,158 tonnes CO_2/year from all US power plants (2007 data)

Advanced Steam Cycles

- USC targets:
  - Europe: 700°C/375 bar
  - US: 760°C/345 bar
- New alloys needed
- No reliable design data
- Potential failure modes unknown



Partners and Roles



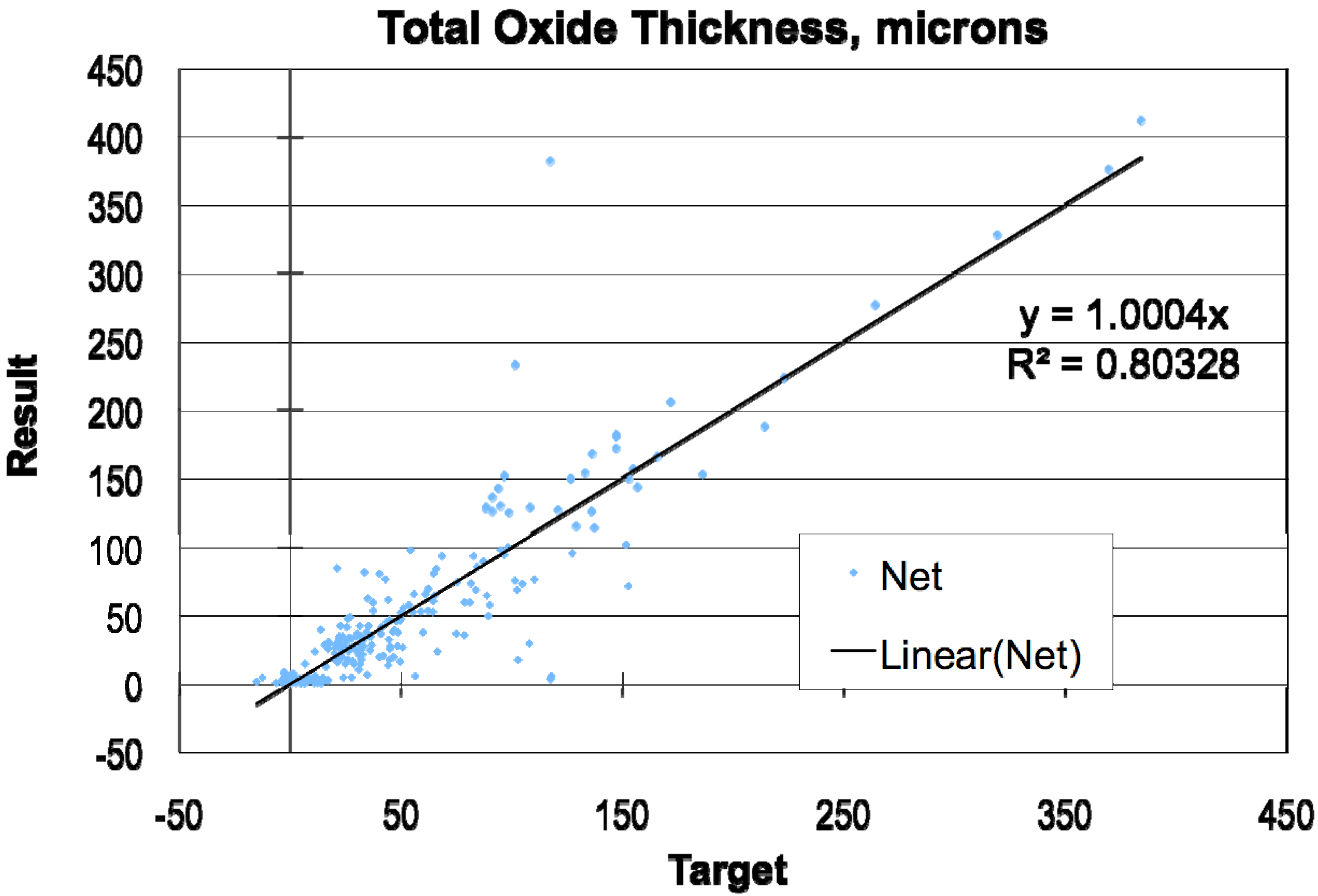
Objectives

- Establish current ‘state-of-knowledge’ of steam oxidation of alloys relevant to fossil-fueled advanced steam power plant
- Collate and analyse existing information to identify missing critical data
- Generate critical kinetic data as required
- Compile mechanistic descriptions of scale exfoliation behaviour for specific alloy classes
- Develop models for component lifetime prediction, especially scale exfoliation

State of knowledge

- Large body of data, but little in the way of coherent picture even for a single alloy class
- Steam oxidation is complex: need to define key factors and understand their influences
  - thick scales; interaction among oxide growth and stress-strain development
  - difficult to reproduce service conditions
- Influence of factors not usually considered in oxidation studies
  - thermal gradients
  - thermal conductivity
  - physical constraints
- Potentially large differences among research groups
  - little prior attention given to differences among test techniques
- For key alloys, subtle differences in composition can exert large influence

Goal: data compilation: T92



New oxidation data

<u>ENVIRONMENTS</u>

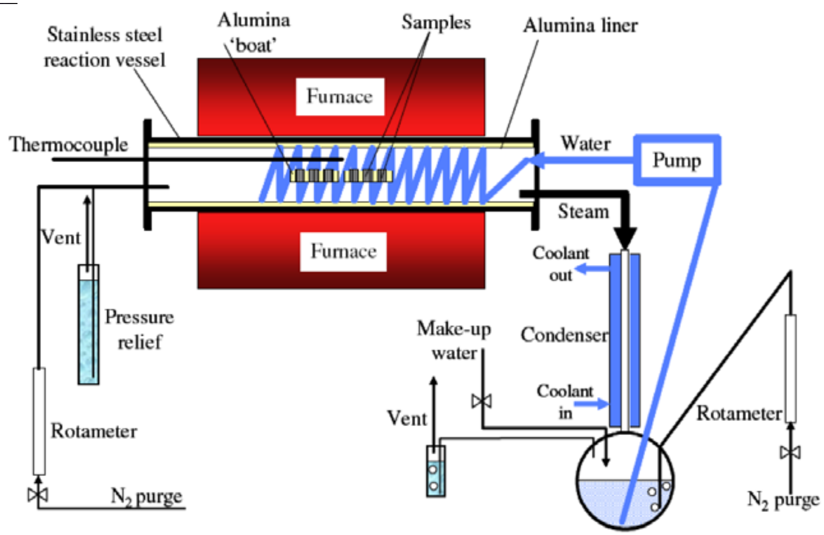
- Steam
  - 1 bar, 650-800ºC
  - 17 bar, 100 bar, 600-800ºC
  - 40 bar, flowing steam
- Ar-water vapor
  - 1 bar, 650-800ºC
- Air-water vapor
  - 1 bar, 650-800ºC
  - isothermal & cyclic

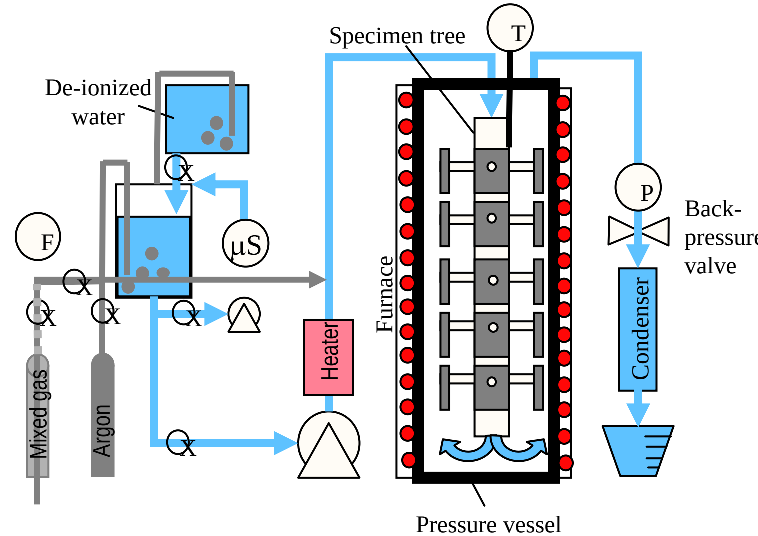
<u>ALLOYS</u>

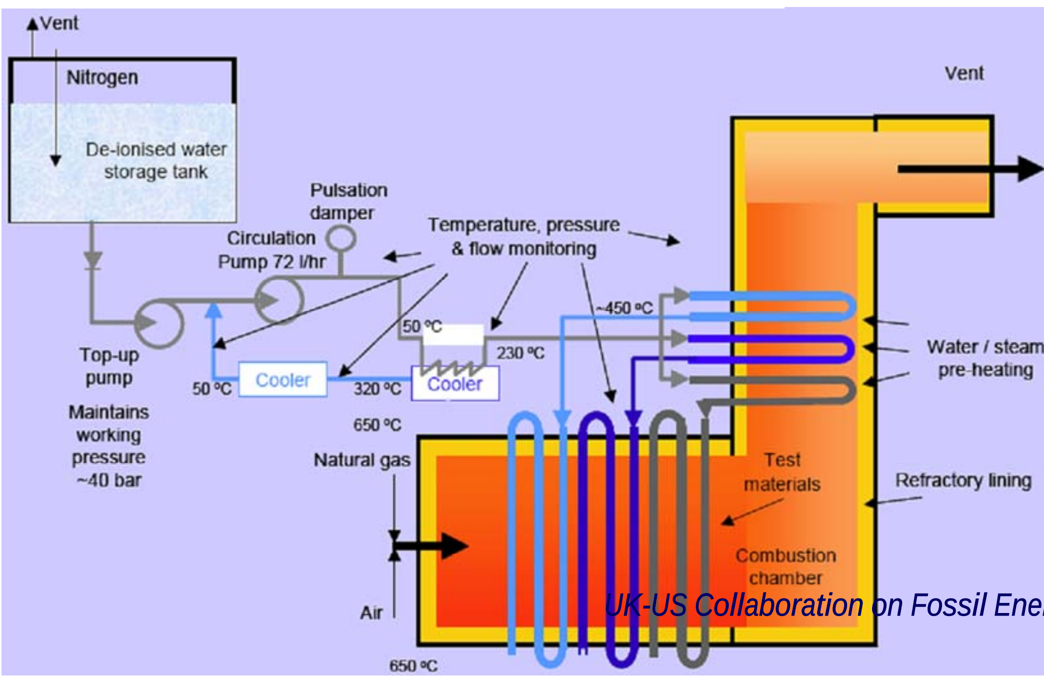
- Ferritic steels
  - 9-12Cr ferritic-martensitics
  - developmental 9-12 Cr
- Austenitic steels
  - 18Cr-12Ni ('advanced': TP347-based)
  - higher-Cr steels
- Ni-based alloys
  - conventional (solid soln-strengthened)
  - advanced (pptation-strengthened)

Over 1 million hours of steam oxidation data have been generated, covering 30 alloys and a range of temperatures

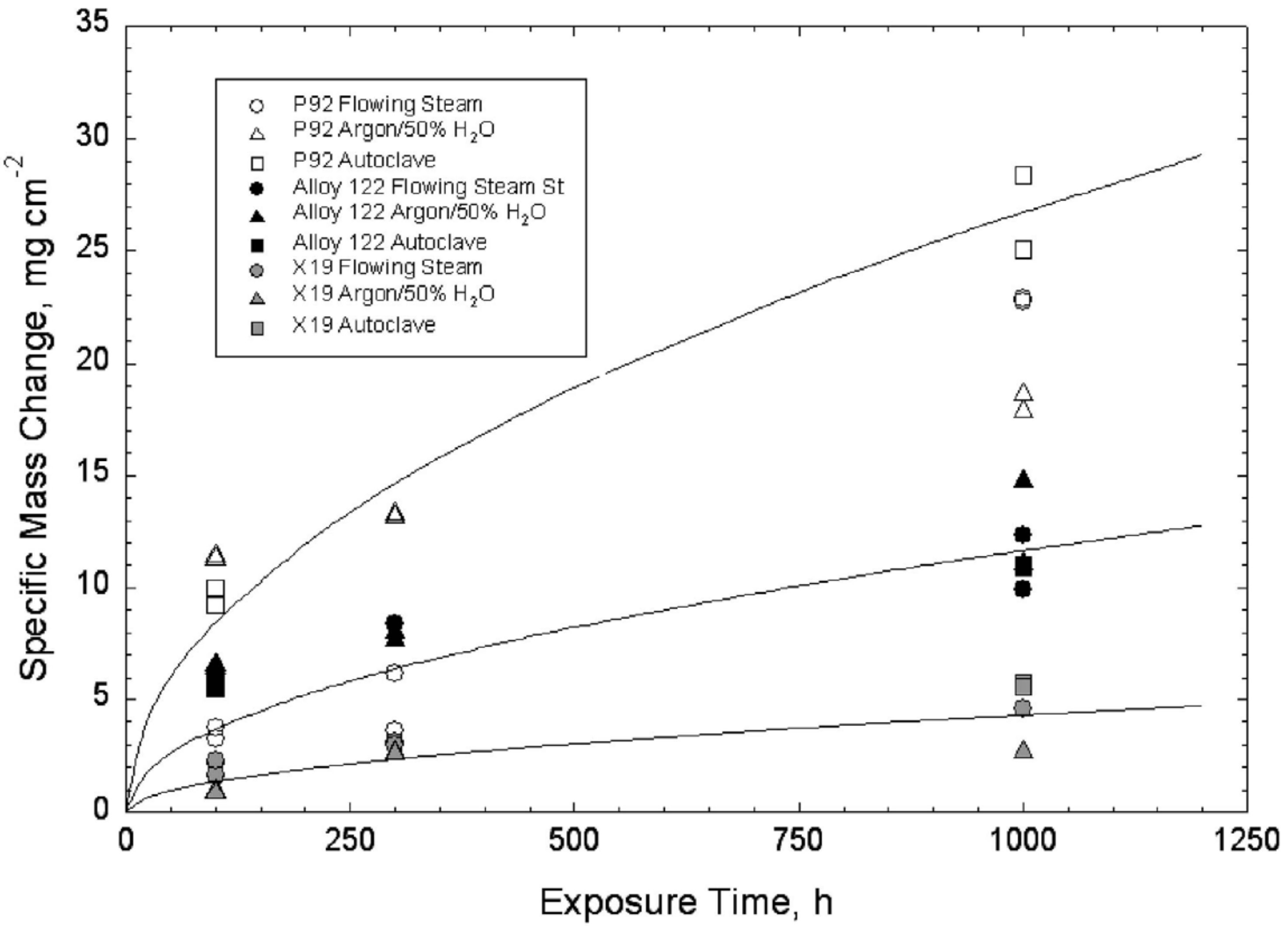
Range of test procedures



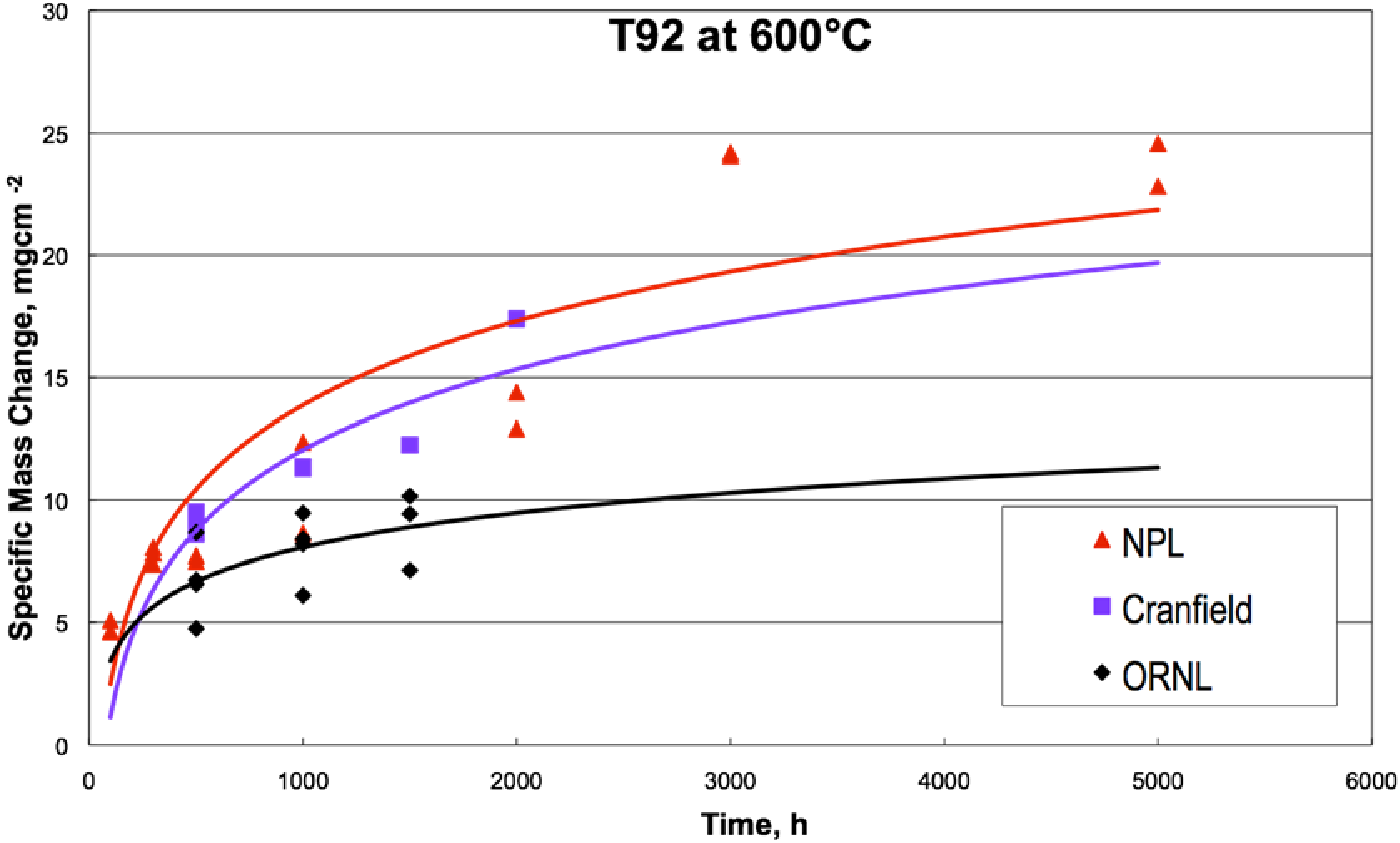




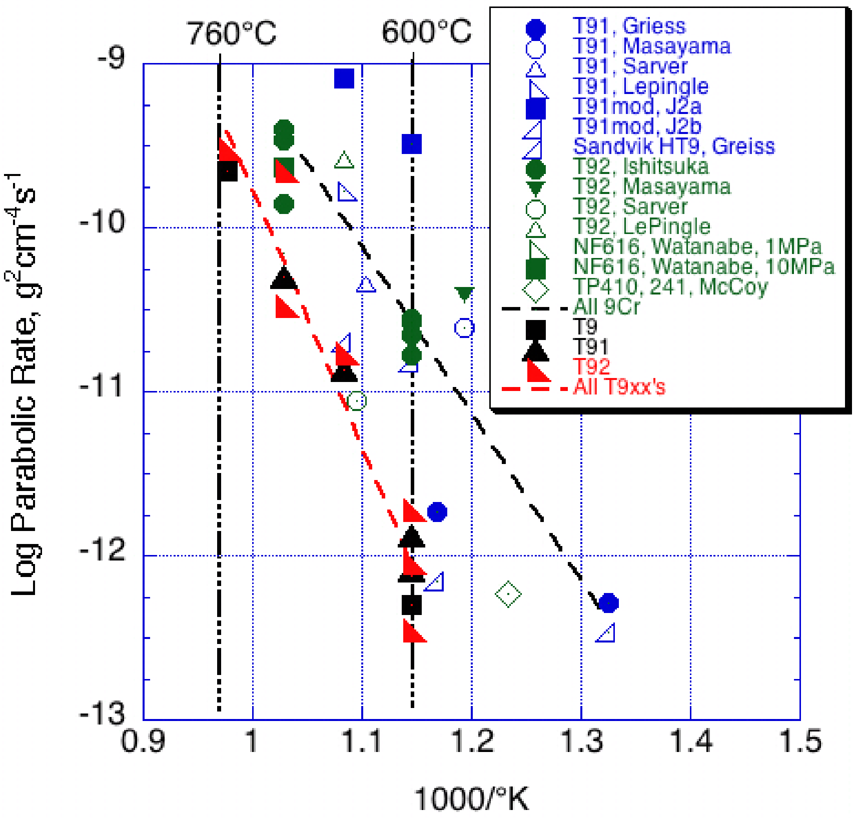
Comparison of test methods

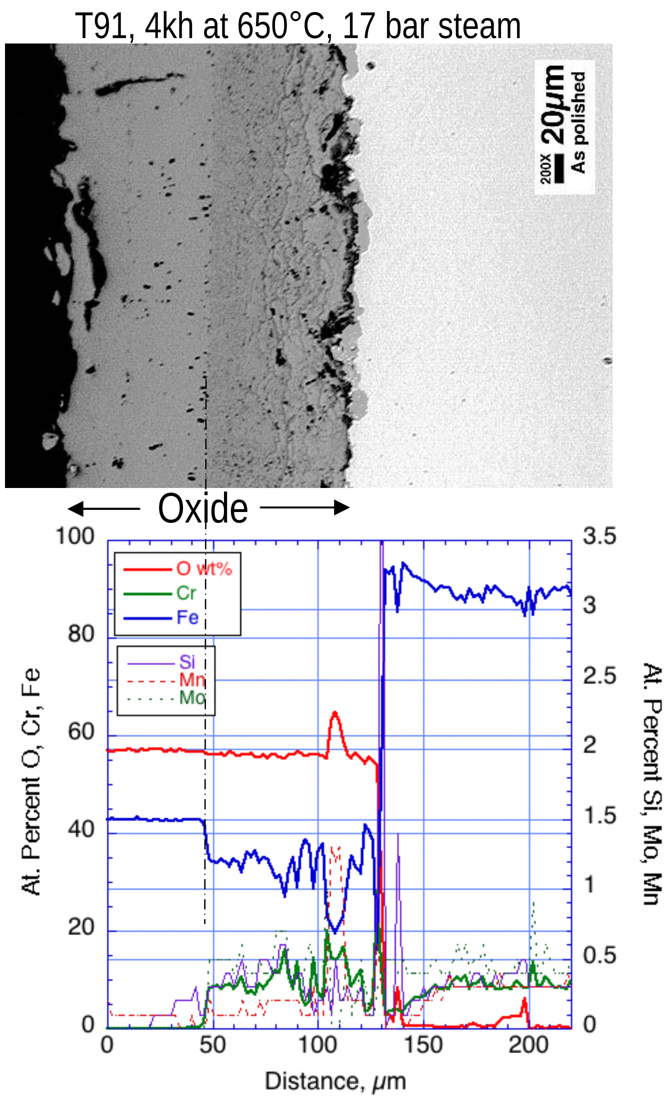


Inter-lab comparisons



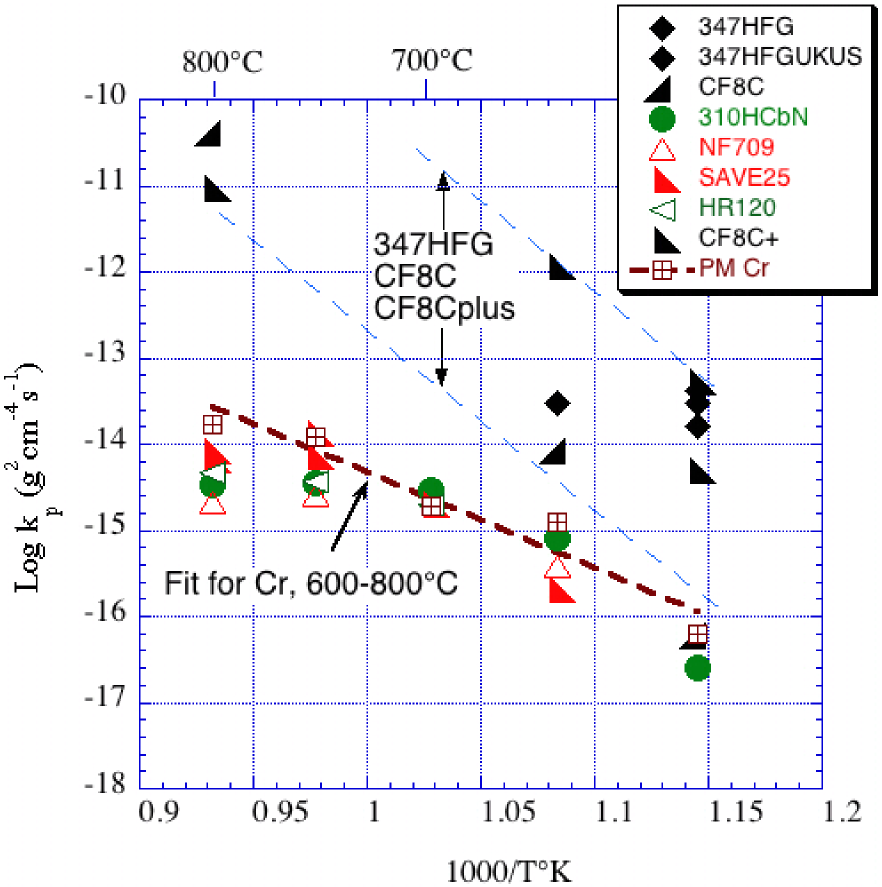
'9-Cr' ferritic steels



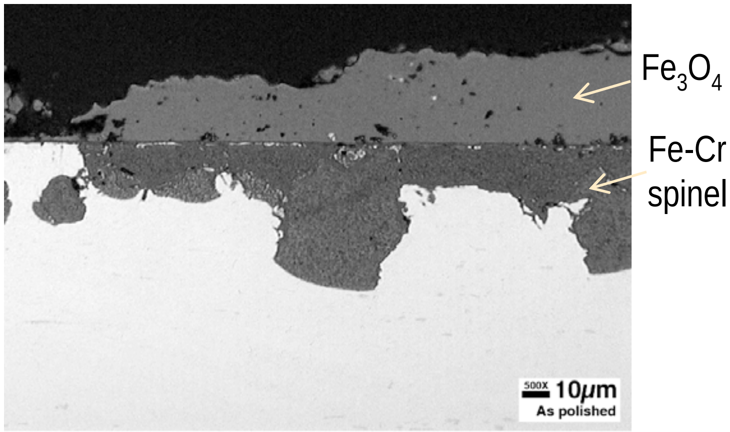


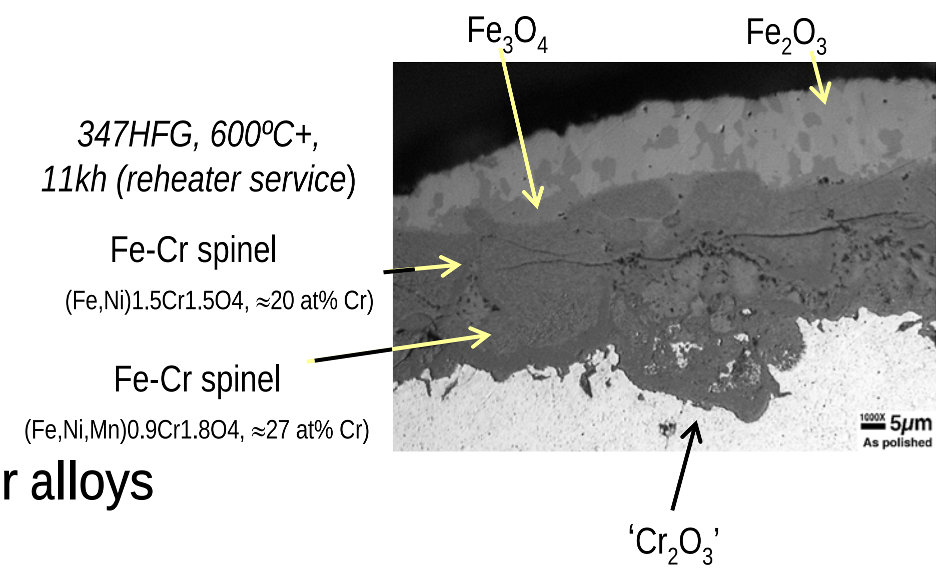
- New data self-consistent
- Slower rates, different activation energy to literature data

Austenitic steels



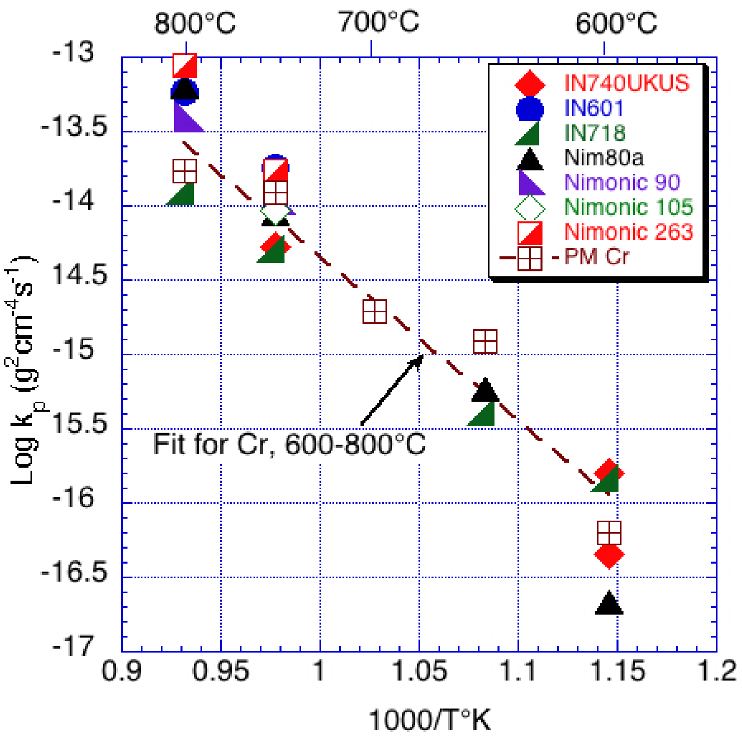
347HFG, 650ºC, 4kh (Lab)



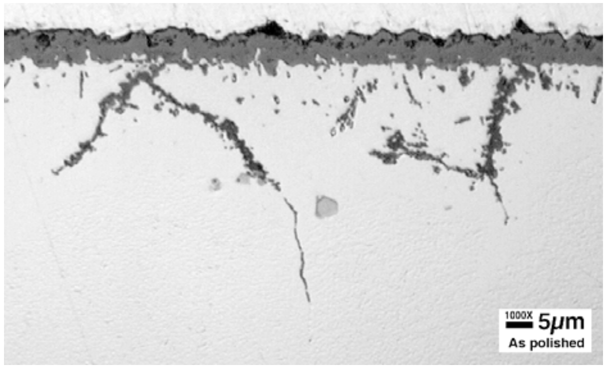


- Distinction between 18Cr-12Ni and higher alloys
- On 18Cr-12Ni lab vs plant comparison:
  - outer layer is Fe_3O_4 in lab test, Fe_2O_3 in plant

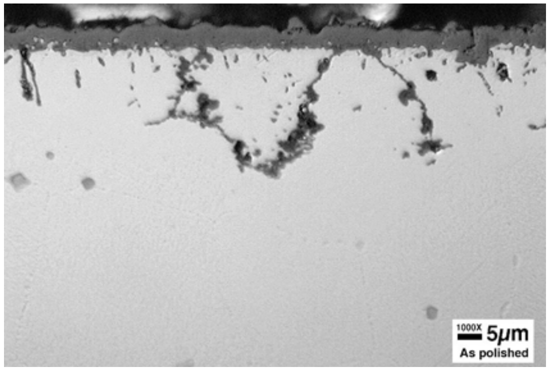
Ni-based alloys



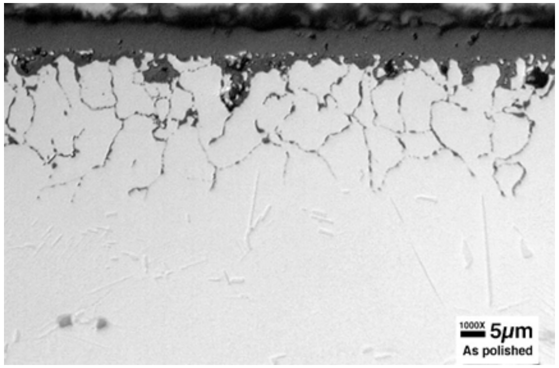
- Increased mass gain wrt PMCr indicative of increasing extent of internal oxidation
- Similar mass-gain kinetics, different corrosion morphologies
- Need thickness measurements



Nimonic 80A



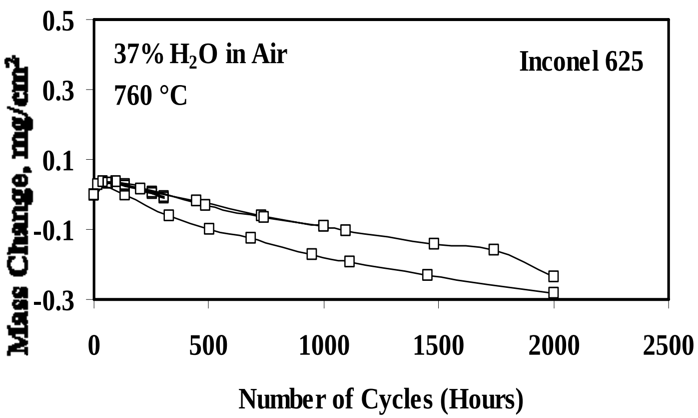
Nimonic 90



Nimonic 263

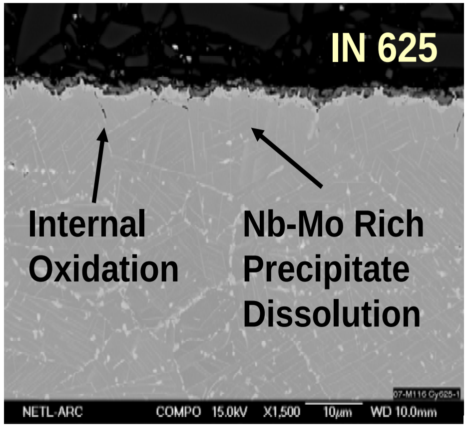
Steam vs air-water vapor

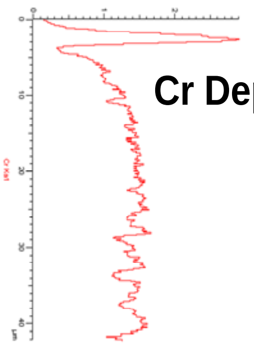
$$1/2Cr_2O_3(s) + H_2O(g) + 3/4O_2(g) = CrO_2(OH)_2(g)$$

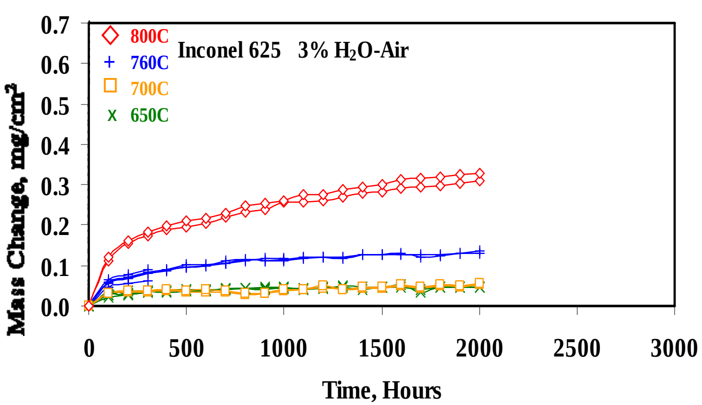


Cyclic Oxidation
2000 Cycles
760°C
Air + 37% H_2O
Low Gas Flow
Boldly Exposed

Cr Evaporation

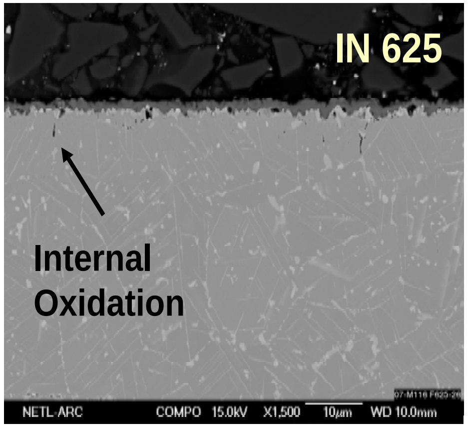


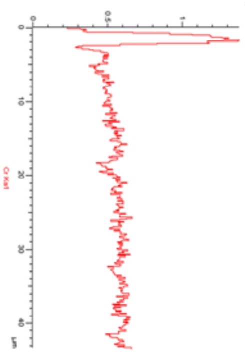




Furnace Exposure
2000 Hours
800°C
Air + 3% H_2O
Low Gas Flow
Sheltered Exposure

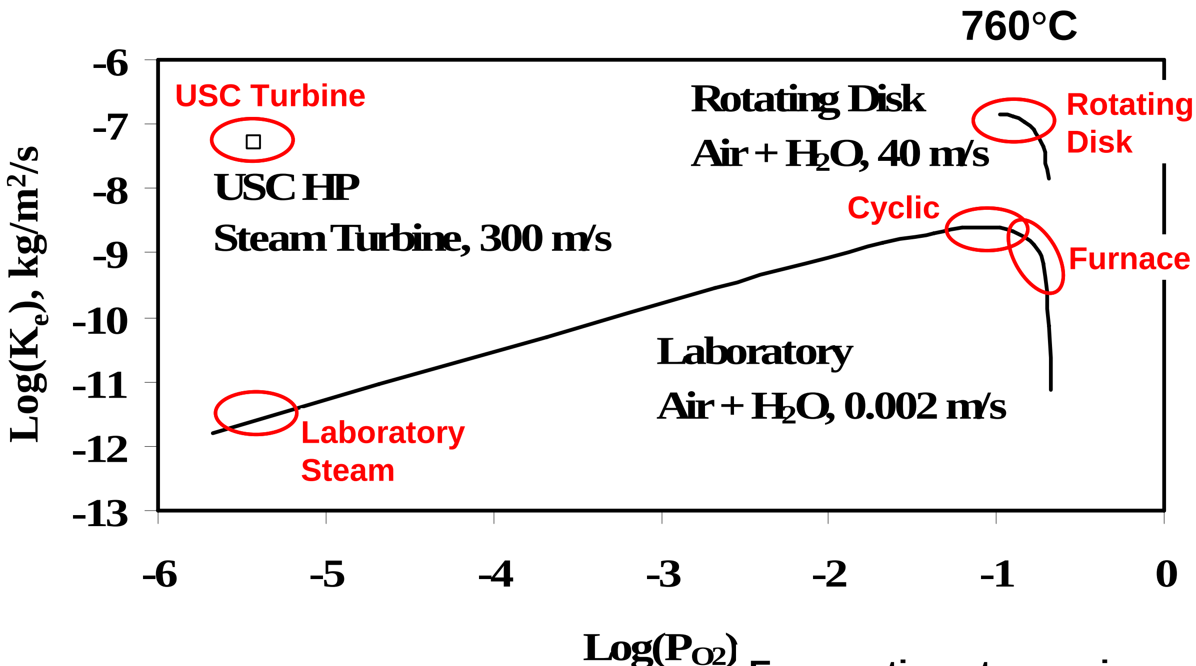
Suppressed Cr Evaporation





USC steam turbine issues

- Difficult to duplicate USC steam turbine conditions in the laboratory
- Air-water vapor mixtures provides evaporation effects
- NETL developed a model to relate rate of Cr loss to lifetimes of Cr-forming alloys



Evaporation at a maximum at 57% H_2O

- Air-wv as a substitute for high-pressure steam?
- Need to better understand differences

Modeling of scale spallation

- Many contributing factors need thorough evaluation:
  - oxide growth in a thermal gradient
  - oxide growth during thermal cycling
  - strain development during oxide grown on the inside of a tube
  - strain resulting from differences in CTE between oxide and alloy
  - contribution to strain development from oxide growth
  - effect of creep (alloy <u>and</u> oxide) on stress relaxation
  - strain distribution in multi-layered scales
  - criteria for scale failure (exfoliation?)
  - external parameters determined by the boiler operation
- Importance of reliable oxidation kinetics
- Evolution of scale morphologies key to stress-strain accommodation & scale failure
- NPL and ORNL are developing models using these inputs

Future activities

- Develop a unified test method with a view to future standardization

- Better understanding of:
  - factors causing uncertainty in metal loss and oxide thickness data from lab. exposures
  - effect of steam pressure on oxidation kinetics and scale morphology

- Measure oxidation kinetics of alloy T91 for compositions within the full specification range
  – provide a measure of the scatter likely from different alloy melts

- Understand the effects of specimen geometry and heat flux

- Further develop and validate models for:
  – oxidation kinetics when accompanied by chromia evaporation
  – scale exfoliation

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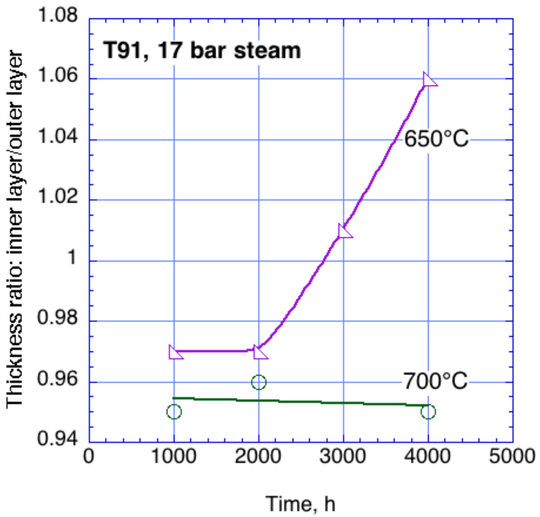
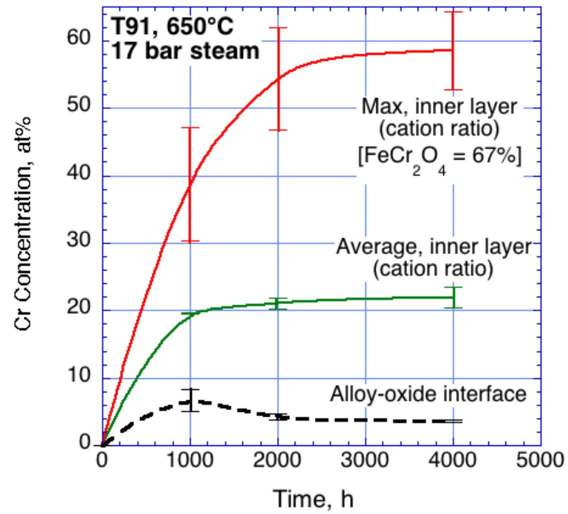
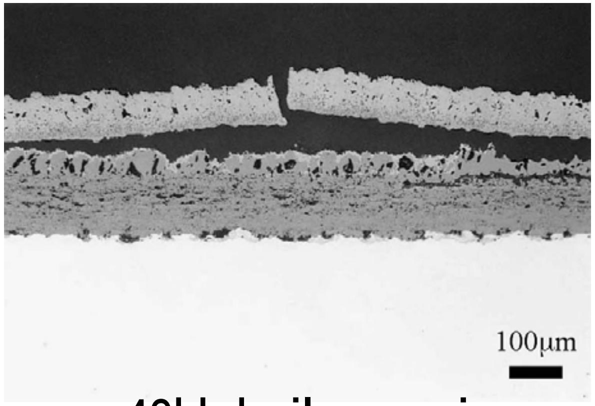
Mechanistic input: 9Cr

Measurement of Cr concentration profile--basis for understanding







40kh boiler service (reheater)