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Biomass Exacerbated Cyclic Oxidation of Steels in Steam

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Introduction

- Alloys undergo oxidation at high temperature.
  - Multilayered oxides of different compositions form.
  - Modification of the underlying alloy results.
- Rate of oxidation is exacerbated under steam conditions.
- On cooling stresses develop in the oxide layer resulting in loss of the oxide (spallation).
- On reheating oxides continue to reform.
- Load following biomass plants will lead to greater thermal cycling.

Introduction

- Spallation leads to:
  - Damage of components down stream,
  - Blockage of tubes,
  - Tube ruptures,
- Unscheduled / more frequent maintenance shutdowns.

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Questions

1. How will the cyclic nature of biomass power plants affect the oxidation behaviour of the heat exchanger tubing?

2. When does spallation become a big enough problem that maintenance is required?

Aims and Objectives

- **To investigate the cyclic steam oxidation and spallation behaviour of an austenitic stainless steel currently used as heat exchanger tubing.**

- To simulate the effect of the oxidation processes on the degradation of the alloy.

Materials

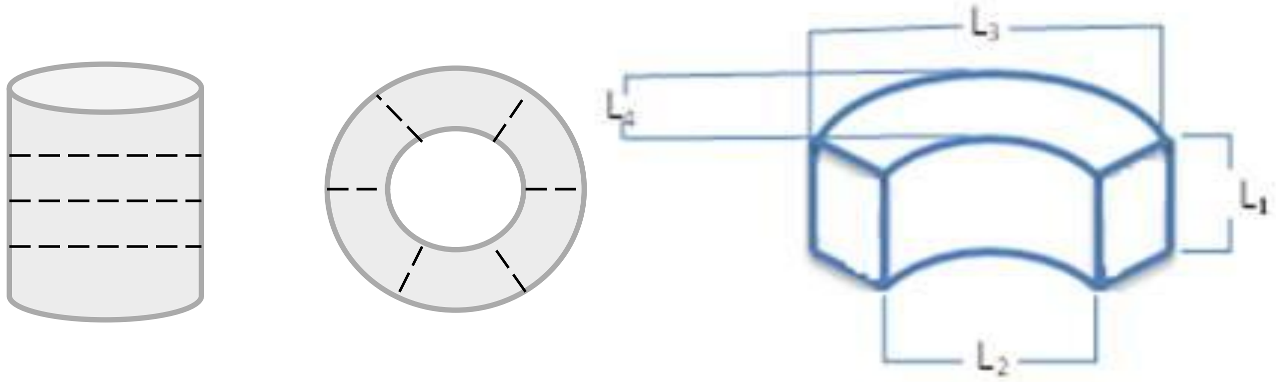
- Austenitic stainless steel TP347H FG.
  - Grain size = 20 µm
- Composition (wt.%):

C	Si	Mn	S	P	Ni	Cr	Nb	Fe
0.09	0.4	1.48	0.001	0.026	11.34	18.21	0.88	bal

- Commonly used as superheater and reheater tubing in fossil fired power plants.

Sample Preparation

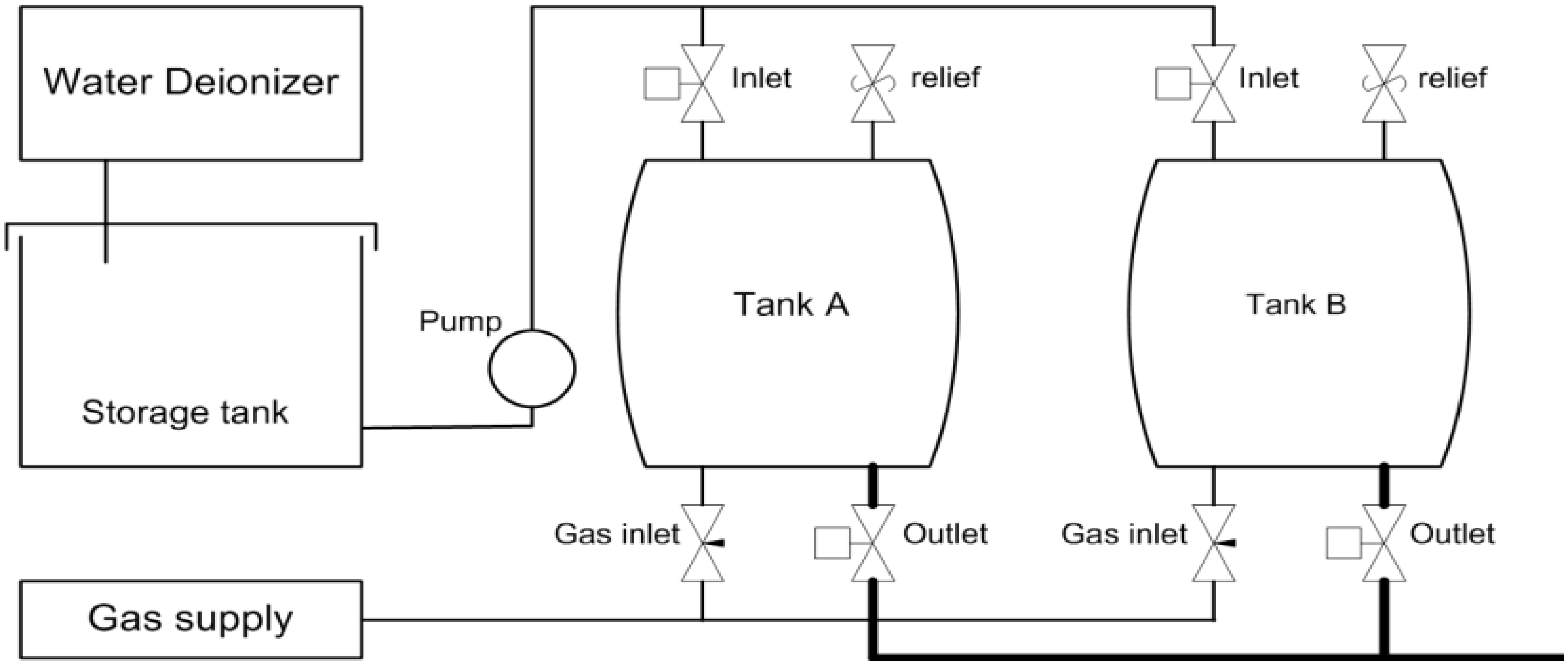
- Samples are sectioned from standard pipe as installed in plant.



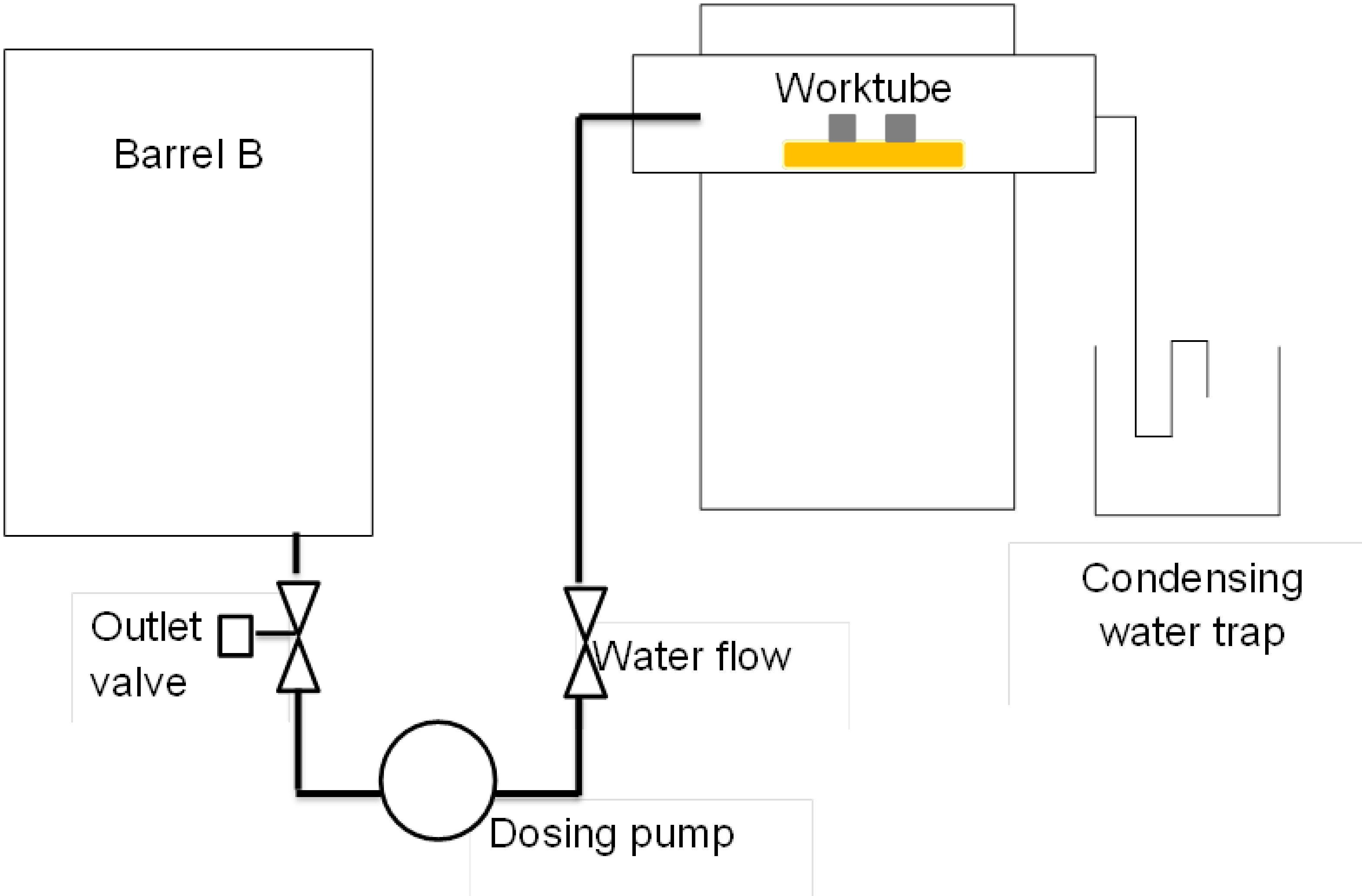
- L_1 = 10 mm; L_2 = 14 mm; L_3 = 18 mm; L_4 = 4.5 mm
- Inner surface is of interest – steam side of power plant.

Experimental Work

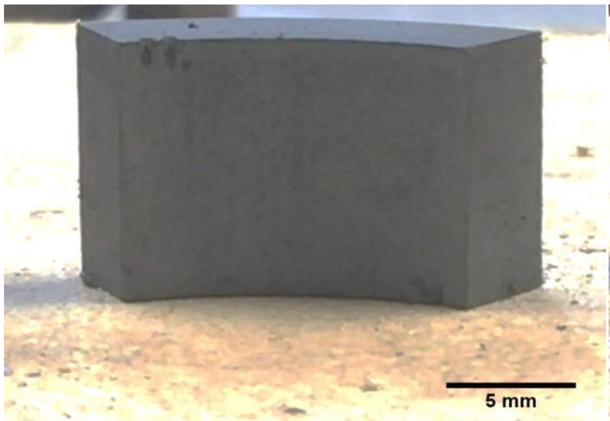
- Exposure to steam at 923 K for 50, 100, 300, 500, 750 and 1000 hours.
- Atmospheric pressure.



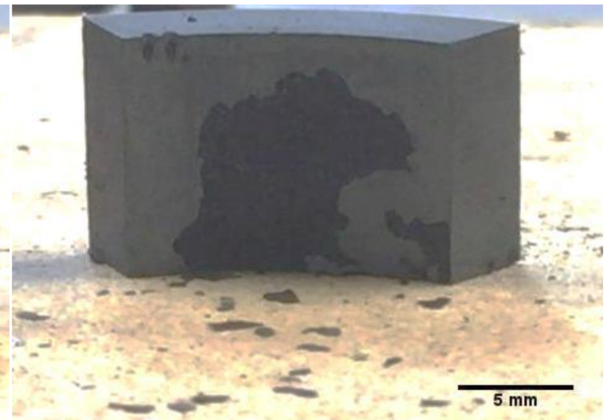
Experimental Work



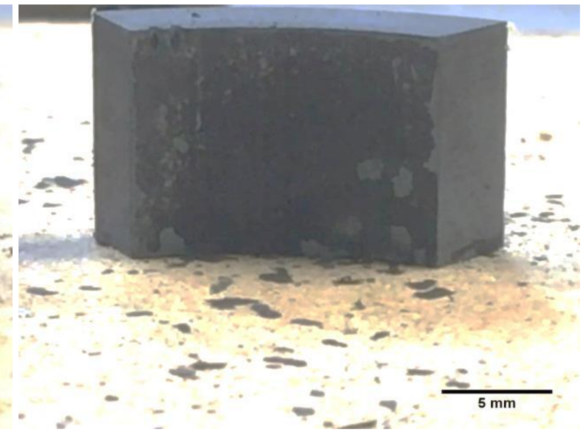
Spallation



Before spallation.
At temperature.



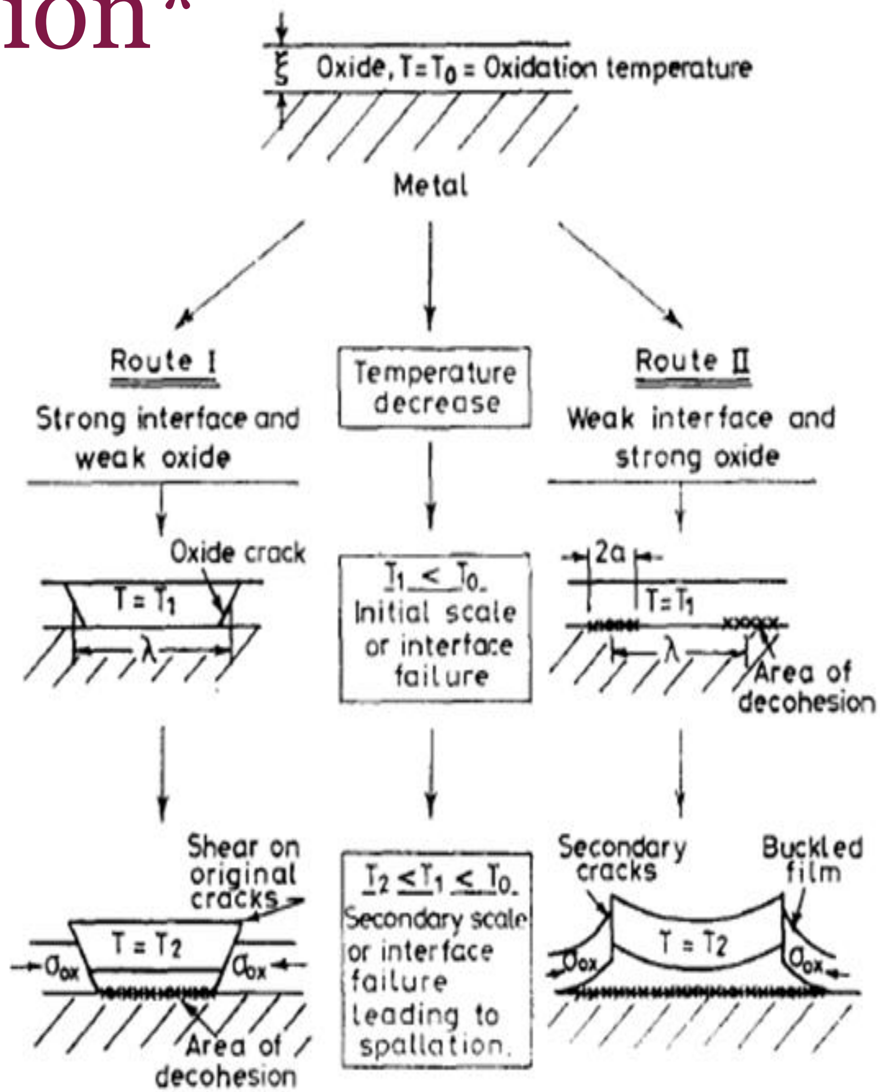
During spallation.
On cooling.



After spallation.
Room temperature.

Routes to Spallation*

- Two things are necessary to initiate spallation:
  - Decohesion along the spallation interface (delamination)
  - Cracks through the oxide layer to the interface.



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*H.E. Evans, "Stress effects in oxidation of metals", International Materials Review, 1995, 40, pp 1-40

Routes to Spallation*

- Route I: Wedging.

$$\Delta T_W = \sqrt{\frac{\gamma_F}{\xi E_{ox}(\alpha_m - \alpha_{ox})^2(1 - \nu_{ox})}}$$

$$\gamma_F = W^*(\Delta T)^2(\Delta\alpha)^2 E_{ox}(1 - \nu_{ox})$$

- Route II: Buckling.

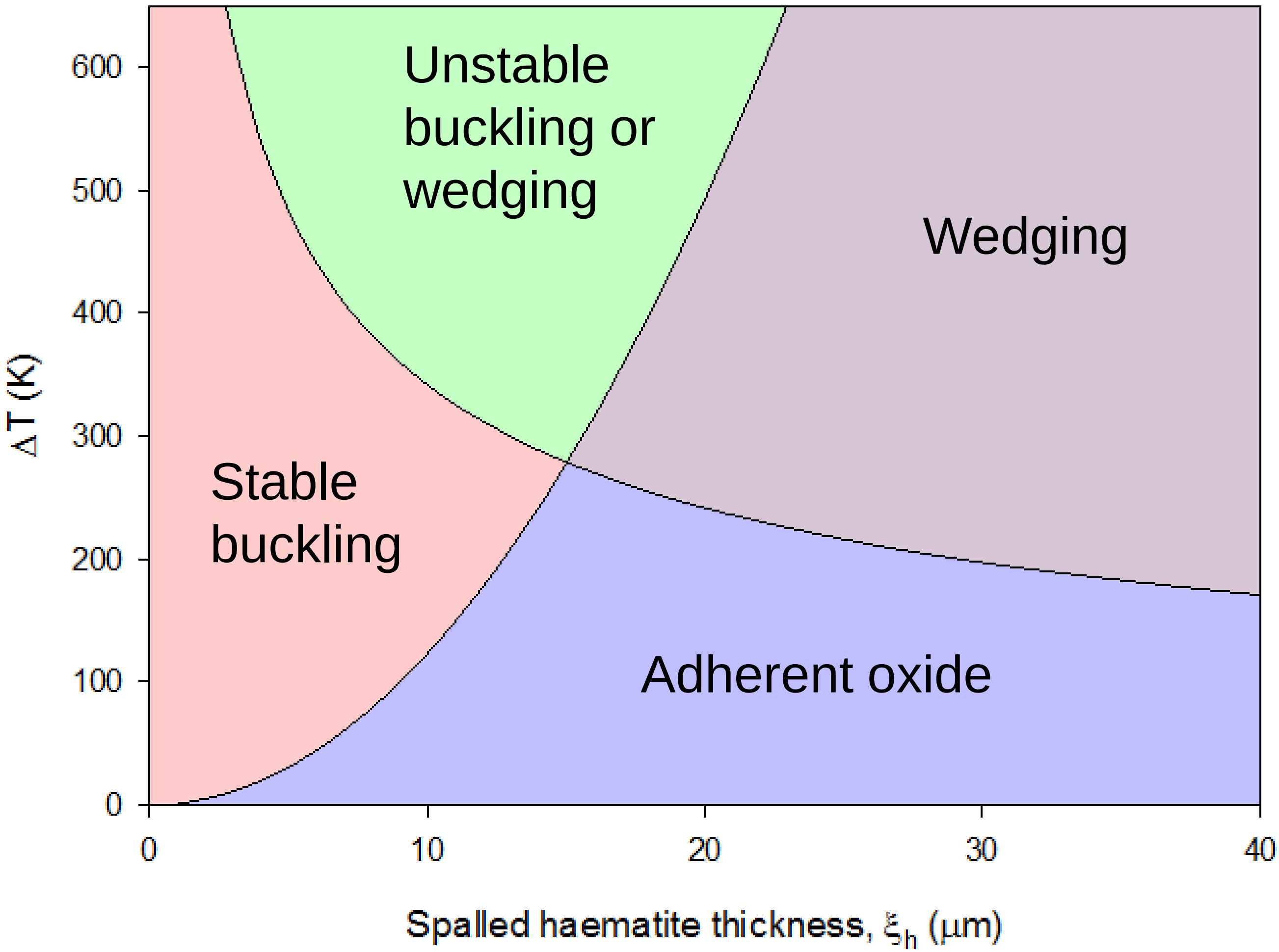
$$\Delta T_b = \frac{1.22}{(\alpha_m - \alpha_{ox})(1 - \nu_{ox}{}^2)}\left(\frac{\xi}{R}\right)^2$$

Eox = Young's modulus, α_m and α_{ox} = thermal expansion coefficients of metal and oxide,ν_{ox} = Poisson's ratio.

ΔT = oxidation temperature - event temperature, R = radius of delamination site, W* = strain energy, γ_F = fracture energy, ξ = oxide thickness.

*H.E. Evans, "Stress effects in oxidation of metals", International Materials Review, 1995, 40, pp 1-40

Spallation Map



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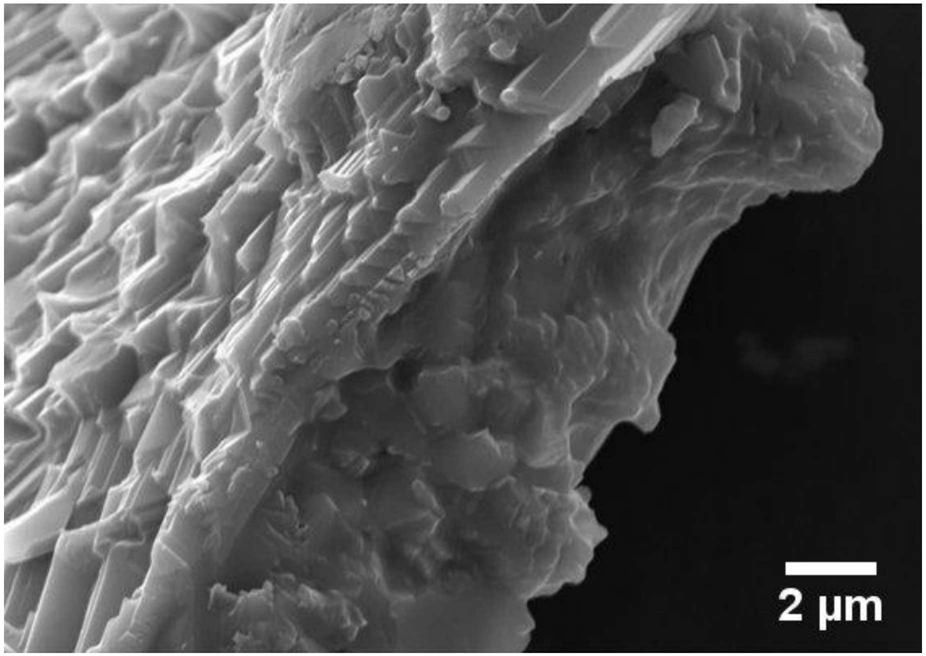
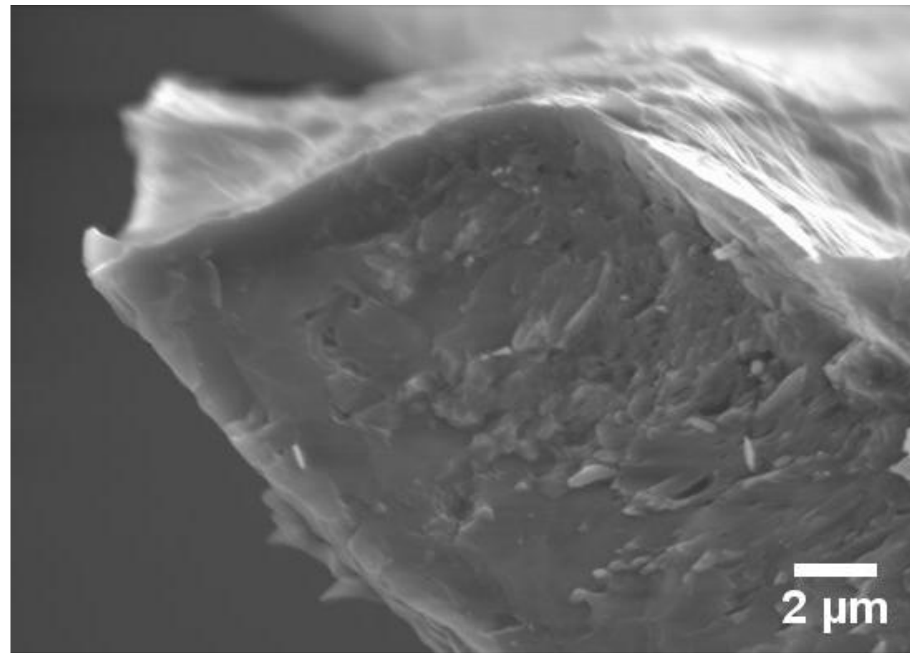
Imaging Spall Particles

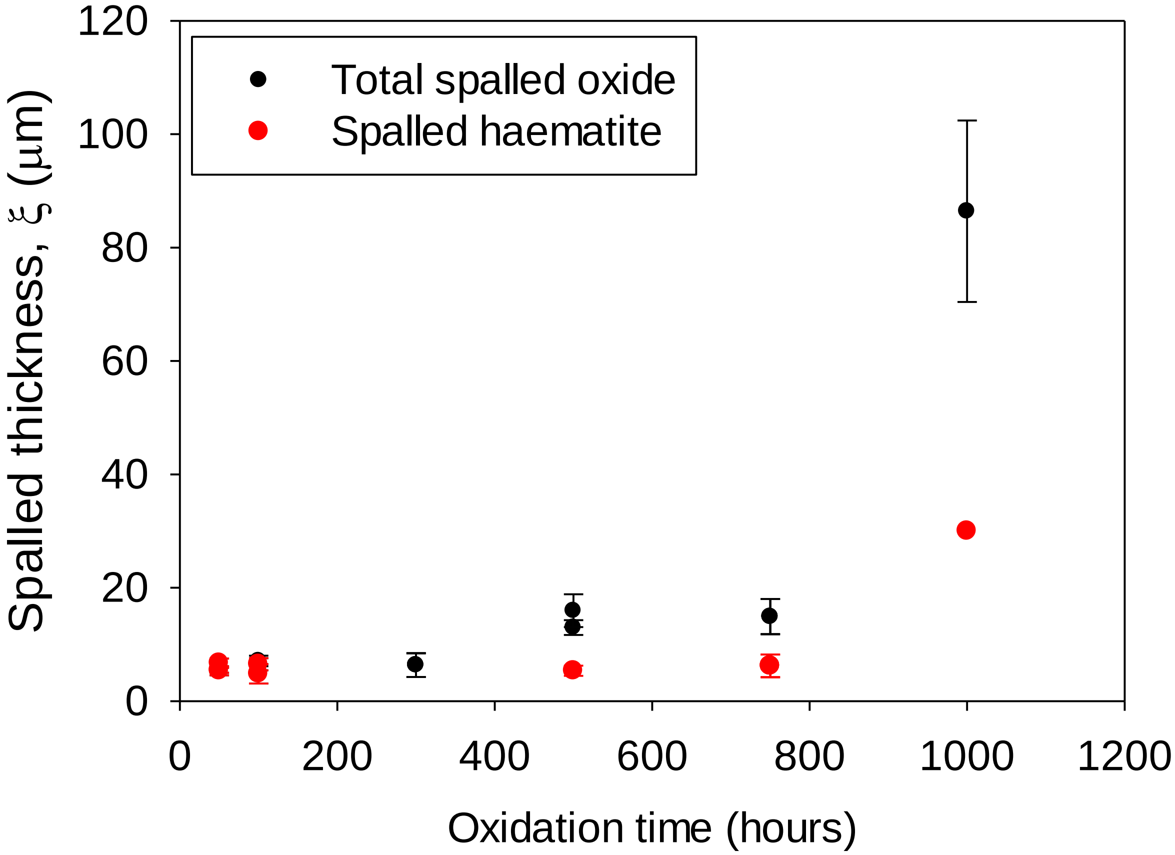


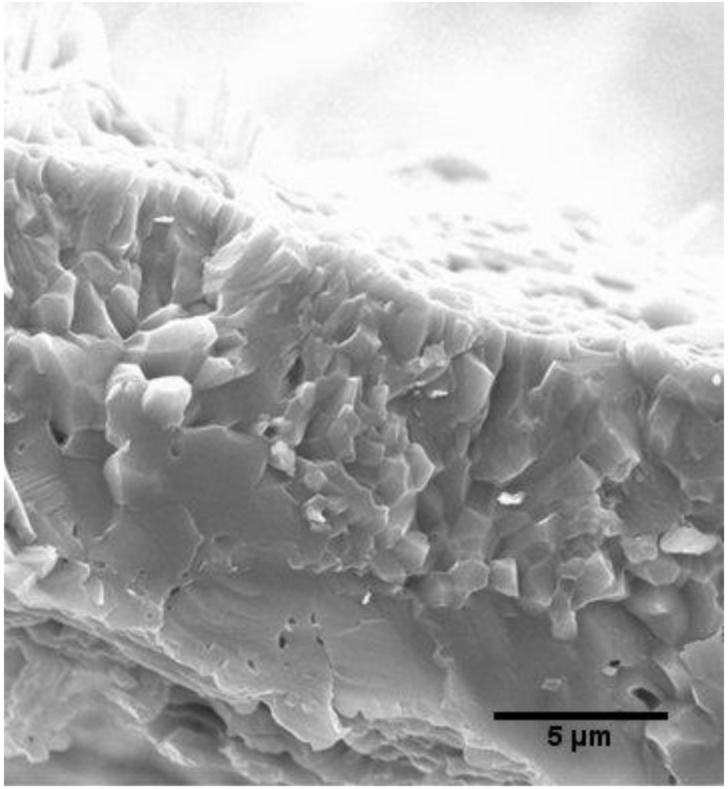
100 hours, 923 K



500 hours, 923 K

Spalled Oxide Thickness, ξ





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R and ΔT Measurements

- Synchronised IR and video camera.
- Able to detect delamination and spallation sites.
- Provide localised ΔT and R values.

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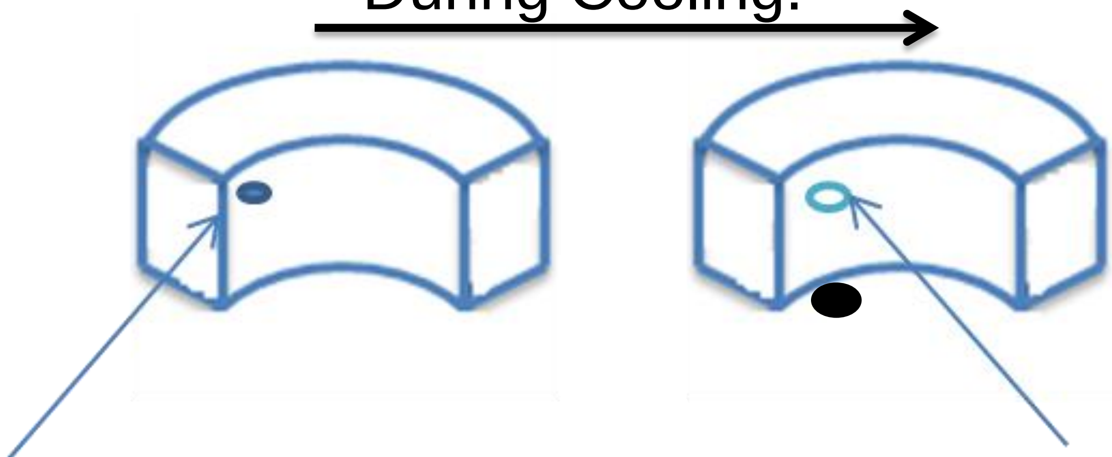
The Measurements

During Cooling.



Initial local delamination:

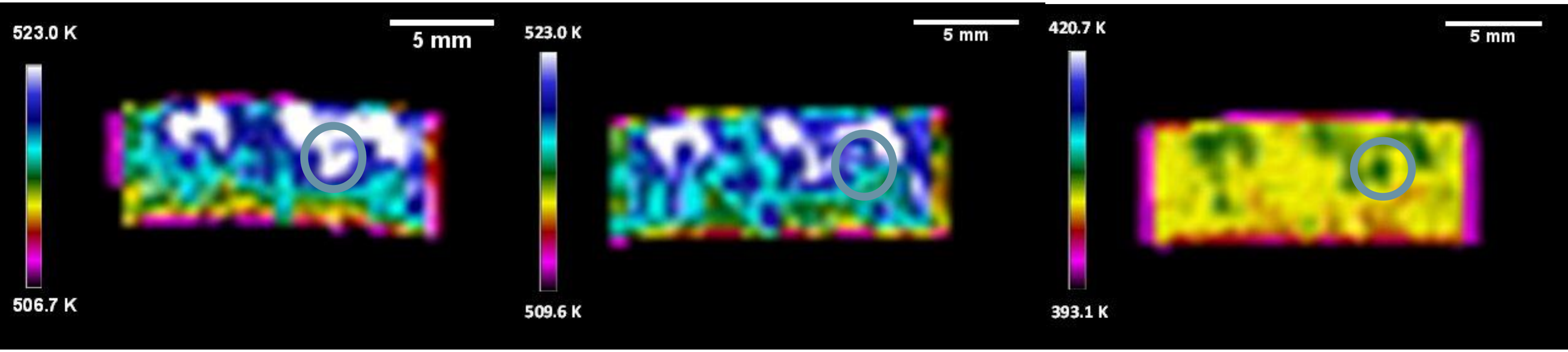
- Detectable with IR camera
- T_D = temperature at which delamination occurs.

Complete local spallation:

- Detectable with video and IR camera
- T_{SP} = temperature at which spallation occurs.

IR Camera Results

- Images shown are the same sample on cooling after 100 hours in steam at 923 K.

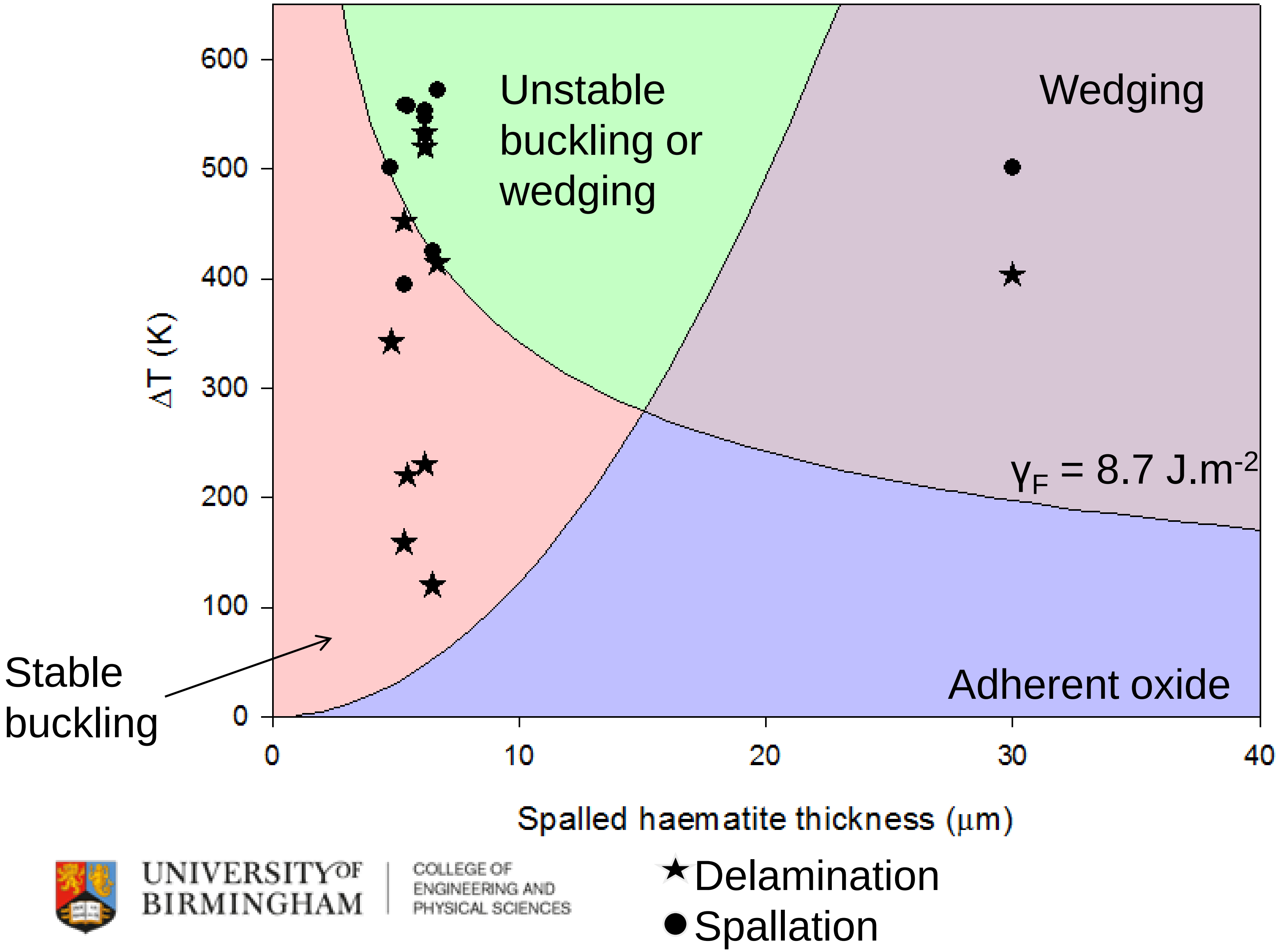


Before delamination.
ΔT = 398.6

- At time of delamination.
- ΔT_D = 405.5

- At time of spallation.
- ΔT_{SP} = 508.9

Spallation Map



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Conclusions

- A unique combination of infrared and video camera techniques has been used to obtain critical data to input into the spallation model.
- Delamination and formation of buckles at oxide interfaces occurs – illustrated by IR camera.
- Spalled oxide thickness measurements have been obtained using high resolution scanning electron microscopy.
- An approach using fracture energy of the oxide has been shown to predict the onset of spallation.

Future Work

- Planned publication for this section of the work.

- Ongoing analysis of the degradation occurring in the alloy due to oxidation processes.

- The effect of thermal cycling.
  - Including accelerated degradation techniques.

Acknowledgements.

BF2RA, EPSRC, Technical support provided by the UoB EM centre, Sumitomo Metal Industries Ltd for alloy, Dr Chris Cooper, Mr Tim Perry.