FAST CARBON CORROSION: Reducing and Oxidising

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TECHNOLOGICAL RELEVANCE

- Hydrocarbons - Oil, Petrochemical Processing
- Syngas (CO + H_2) – Gasification
  NH_3 synthesis
  CH_3OH synthesis
- Combustion Gas (CO_2)
- CO_2 coolant

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TECHNOLOGICAL RELEVANCE

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- Combustion Gas (CO_2)

OXIDISE

CARBURISE

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REDUCING CONDITIONS

Hydrocarbons - Oil, Petrochemical Processing

- **Producing C_nH_m, H_2, CO**
- **Conditions are reducing**
- **Common metals not oxidised**
- **Consequence: carbon corrosion**

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THE PROCESS

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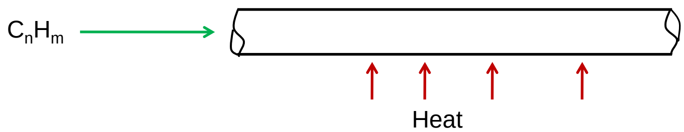

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THE PROCESS

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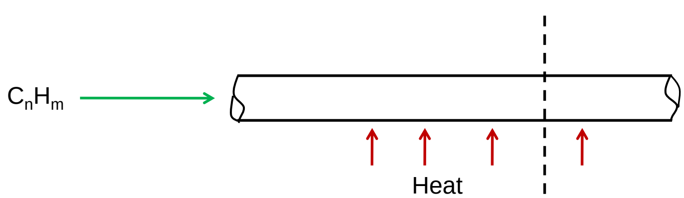

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THE PROBLEM: I

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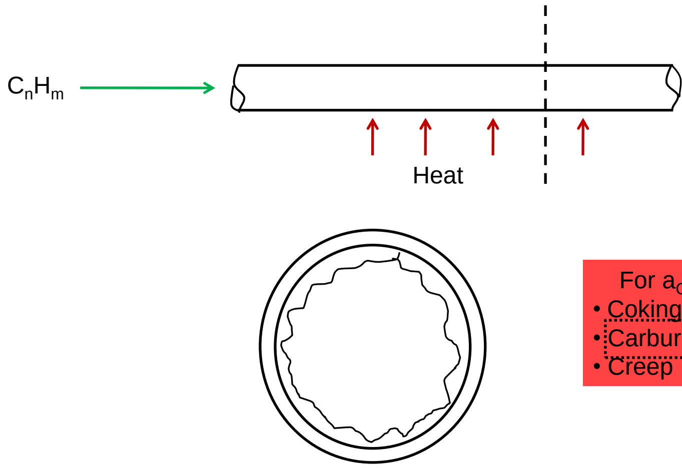

For $a_C \leq 1$
- Coking
- Carburisation
- Creep

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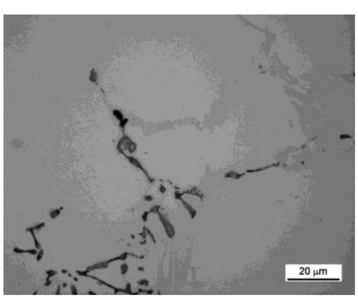
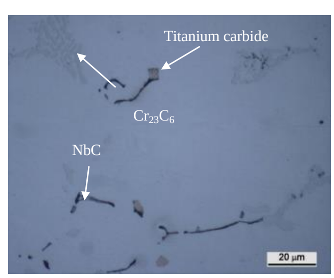
MATERIALS

Centricast Heat resisting Alloys





EXAMPLE: HP Mod Nb (Fe-25Cr-35Ni-Nb-Other)

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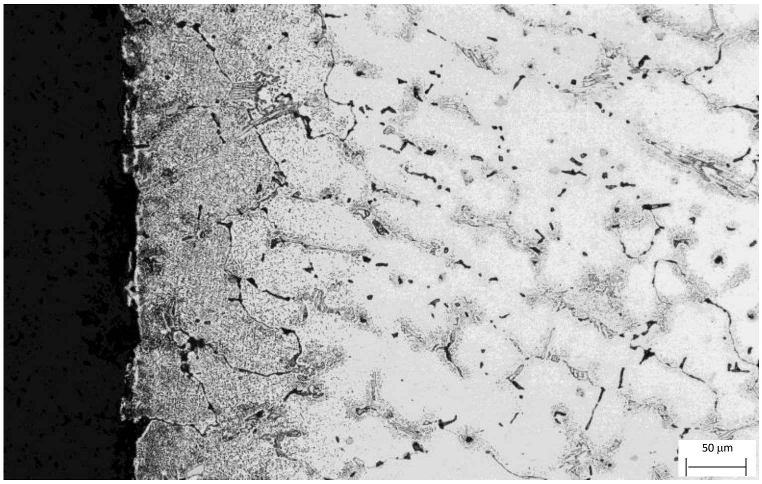
ALLOY CARBURISATION



Alloy ET45 (45 Ni 35 Cr) exposed to gas a_C = 1 for 24 h at 900ºC

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PRECIPITATE IDENTIFICATION

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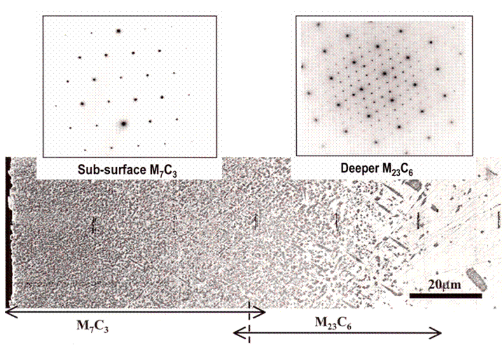

Internal carburisation

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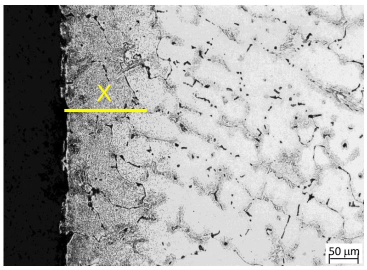
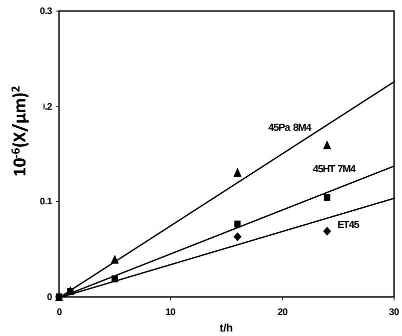
CARBURISATION KINETICS





CONCLUSION: Kinetics parabolic – diffusion controlled

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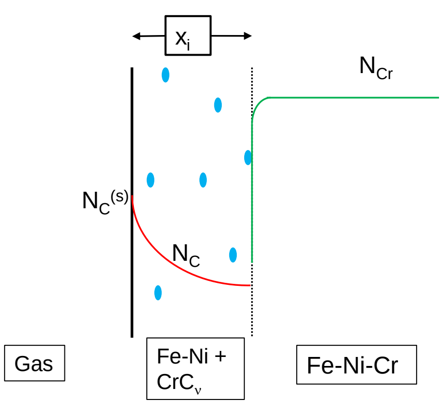
DIFFUSION CONTROLLED KINETICS



$$X_i^2 = 2k_p^{(i)} t$$

$$k_p^{(i)} = \frac{\varepsilon N_c^{(s)} D_c}{v N_{Cr}^{(o)}}$$

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CORROSION BY CO_2

- Hydrocarbons - Oil, Petrochemical Processing
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  NH_3 synthesis
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OXIDISE

CARBURISE

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TEST DIFFUSION MODEL

Carburisation rate constants

$$(10^7 k_p / cm^2 s^{-1})$$

	(1100°C)		(1000°C)		(900°C)	
	measured	*calc*	*measured*	*calc*	*measured*	*calc*
G4868	1.45	2.05	0.13	0.33	0.10	0.11
Fe-35Cr-45Ni	0.44	0.50	0.10	0.08	0.04	0.03
45HT	0.63	0.62	0.10-0.15	0.15	0.04-0.05	0.023

- Close agreement
- T-effect well predicted
- Diffusion model works

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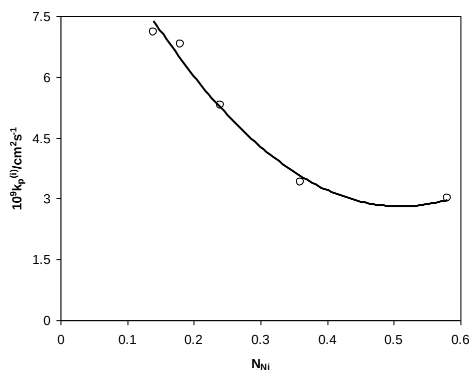
PUT DIFFUSION MODEL TO USE

- Vary Ni/Fe ratio to minimise $D_C N_C$



BENEFIT: Factor of 2 or 3

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PUT DIFFUSION MODEL TO USE

- Increase Si to reduce $D_C N_C$
- Works, but metallurgical limits on N_{Si}

- SOME MYSTERIOUS EFFECTS
- Increase Nb: reduces rate by factor of 2
- Add RE: small decrease to rate

CONCLUSION: need to STOP carbon penetration, not slow it

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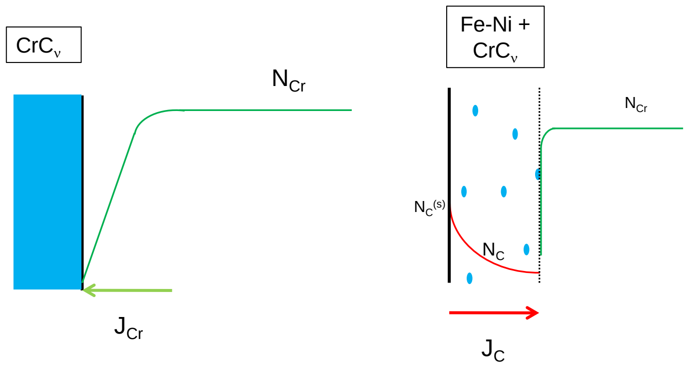
I. CARBIDE SCALE, NOT INTERNAL PRECIPITATES



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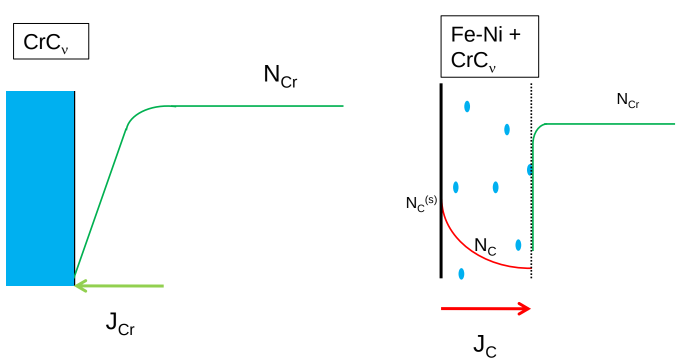
CONDITION FOR CARBIDE SCALE



Critical N_{Cr} for external rather than internal carbide:

$$N_{Cr}^{(o)} = \left(g_{CrCv} \ \frac{\pi}{2v} \ \frac{V_A}{V_{CrCv}} \ \ \frac{N_c^{(s)} D_c}{D_{Cr}} \right)^{\frac{1}{2}}$$

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PUT DIFFUSION MODEL TO USE

$$N_{Cr}^{(o)} = \left(g_{CrCv} \frac{\pi}{2v} \frac{V_A}{V_{CrCv}} \quad \frac{N_c^{(s)} D_c}{D_{Cr}} \right)^{\frac{1}{2}}$$

CrC_v scale formation on model Ni-Cr at 1000ºC

Carbide	**N_{Cr}(crit.)**
Cr_3C_2	15
Cr_7C_3	20
$Cr_{23}C_6$	37

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PUT DIFFUSION MODEL TO USE

$$N_{Cr}^{(o)} = \left(g_{CrCv} \frac{\pi}{2v} \frac{V_A}{V_{CrCv}} \quad \frac{N_c^{(s)} D_c}{D_{Cr}} \right)^{\frac{1}{2}}$$

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CONCLUSION: This is not good!

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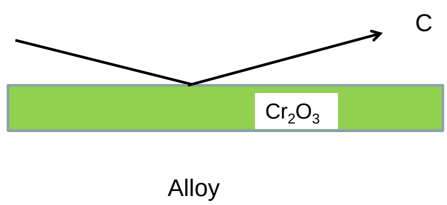
PROTECTIVE OXIDE SCALE

If process gas is oxidising to chromium



Chromia known to have “zero” solubility for C

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CONCLUSIONS: CARBURISATION

- Cr carbides precipitate inside heat resisting steels
- Process is fast
- Mechanism: inward diffusion of solute C
- Parabolic kinetics
- $k_p = k \frac{N_C^{(s)} D_C}{N_{Cr}}$
- Control by alloy chemistry unsuccessful
- Protective oxide scale can work

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CORROSION BY CO_2

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CO_2 Corrosion: Practical Examples

• Oxyfuel process	Possible
• Concentrated solar thermal	On-line now
• Advanced nuclear reactors	Potential ??
• AGR – British nuclear reactors	Mature technology

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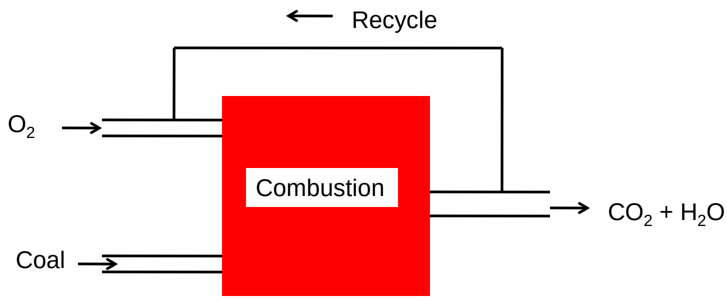
MOTIVATION: I

- **Oxyfuel process for CO_2 capture**



CONCEPT: Burn coal in O_2, not air

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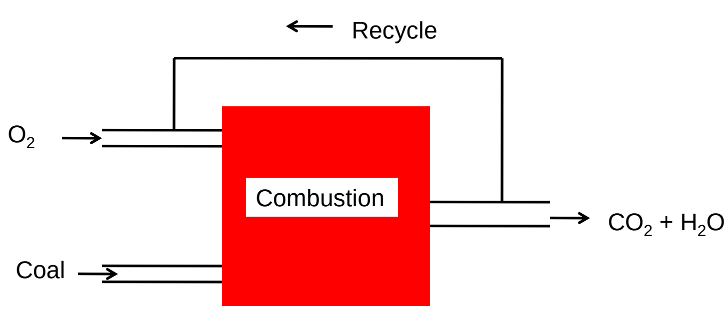
MOTIVATION: I

- **Oxyfuel process for CO_2 capture**



PROBLEM: Hot gas rich in CO_2 + H_2O – corrosion!

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MOTIVATION: II

- **Concentrated Solar Thermal**

Heat transfer fluid: supercritical CO_2

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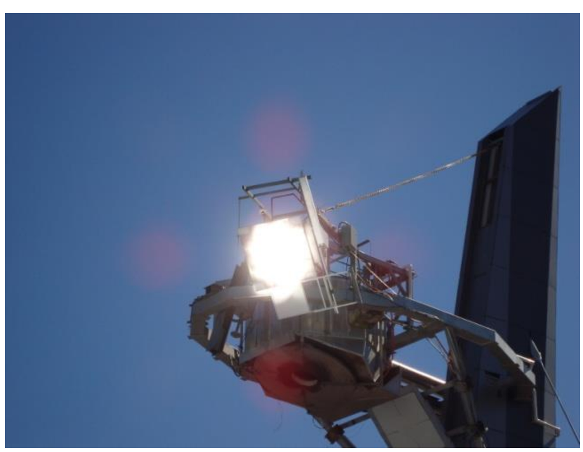
MOTIVATION: II

- **Concentrated Solar Thermal Receiver**



Heat transfer fluid: supercritical CO_2

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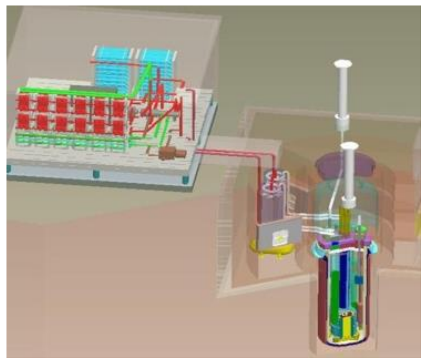
MOTIVATION: III

- **Advanced Nuclear Reactors: closed Brayton cycle increases efficiency**



Working fluid, supercritical CO_2

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Motivation IV: UK Nuclear Reactors (AGR)

- Primary coolant is pressurised CO_2 (p = 20-40 atm)
- Gas circulates between reactor core and heat exchanger
- Heat exchanger produces steam to drive turbines
- Steel (T91) in heat exchanger corrodes

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Motivation IV: UK Nuclear Reactors (AGR)

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Use this as prime example

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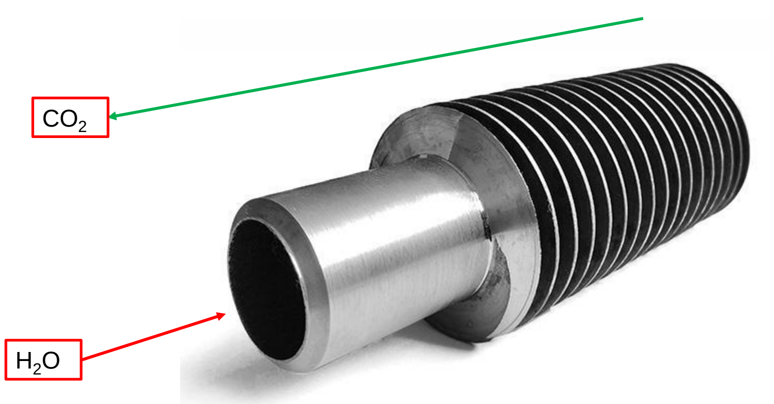
HEAT EXCHAGER REACTION WITH CO_2



Outer finned tube wall exposed to hot CO_2

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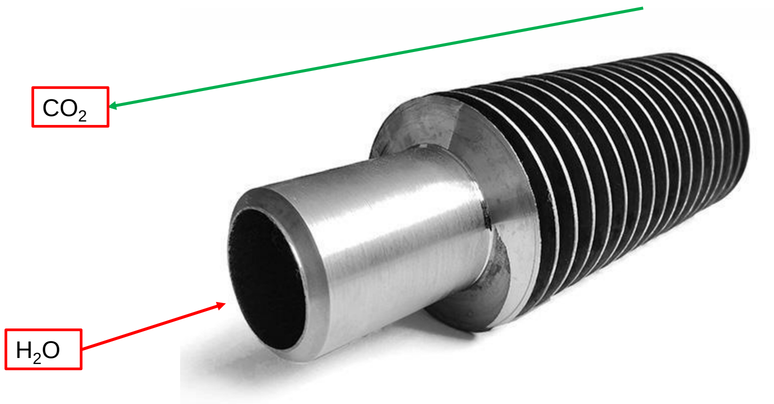
HEAT EXCHAGER REACTION WITH CO_2



Material: P91
Ferritic-martensitic steel
Fe-9Cr-1Mo-C

Outer finned tube wall exposed to hot CO_2

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INITIAL PROBLEM

When reactors commissioned, creep data available for P91
But, no long term data for corrosion of P91 in CO_2!

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But, no long term data for corrosion of P91 in CO_2!

SOLUTION
Install in-plant accelerated corrosion test unit

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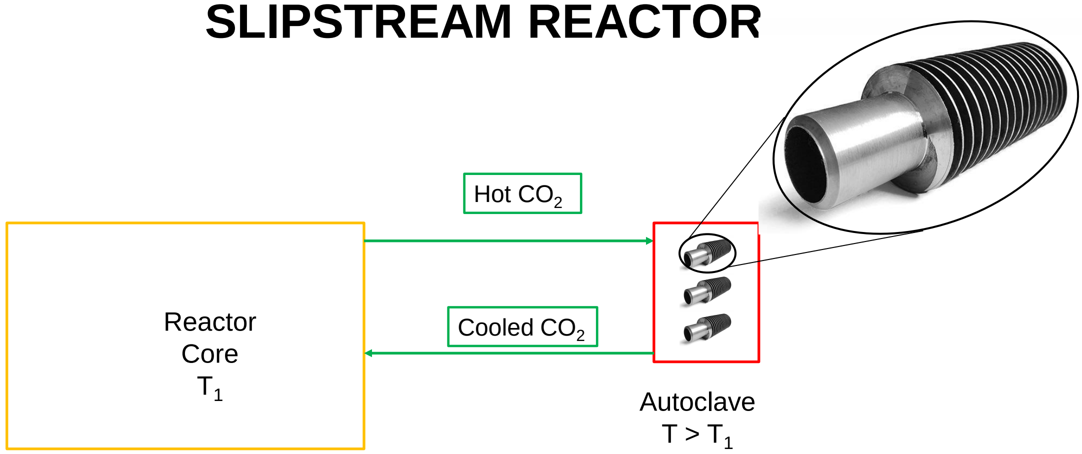
SLIPSTREAM REACTOR



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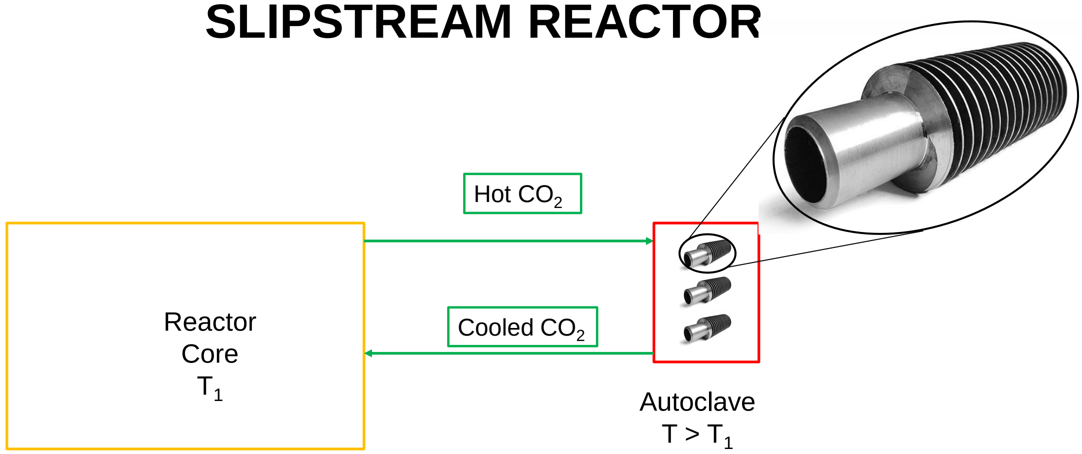
SLIPSTREAM REACTOR



Reaction in autoclave accelerated by higher T
Samples taken out at different times

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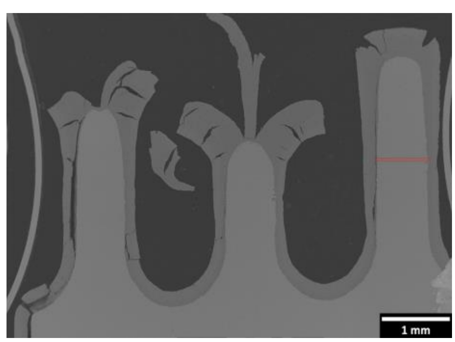
Sample from Slipstream Reactor



Cross-section through fins and part of tube wall
Exposed at T= 600ºC, p(CO_2) = 42 atm, for 19,924 h

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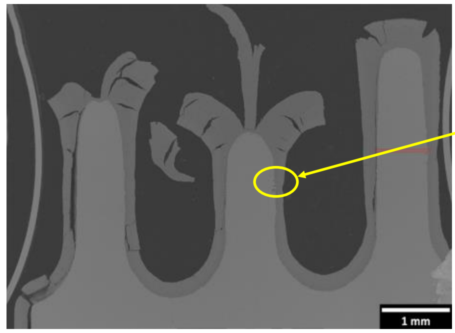
Sample from Slipstream Reactor



Examine this region

Cross-section through fins and part of tube wall
Exposed at T= 600ºC, $p(CO_2)$ = 42 atm, for 19,924 h

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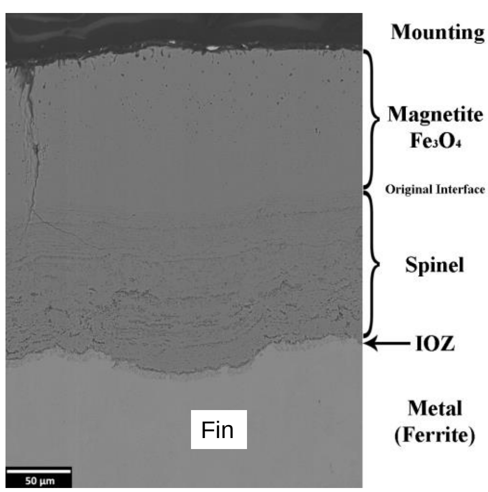
Microscopic Examination of Corrosion Products



SEM image of cross-section at oxide-metal interface

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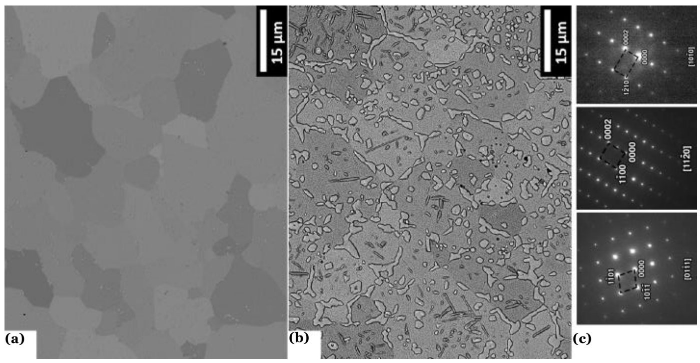
Metal Fin Interior



Before reaction After reaction

Cr-rich carbides precipitated inside steel

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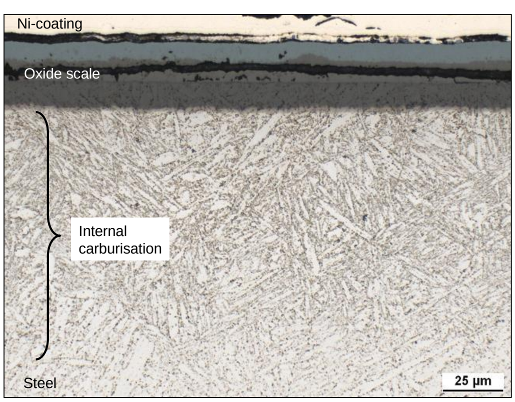
Overall Reaction



External oxide

Internal carbide

P92 exposed to CO_2 at 550oC for 150 h

Internal carburisation is very rapid!

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CARBURISATION: THERMODYNAMIC CHECK

- **Gas at Equilibrium**
- **$CO_2 = CO + ½O_2$**
- **$p(O_2) = 1.6 \times 10^{-7}$ atm**

- **$2CO = CO_2 + C$**
- **$a_C = 8 \times 10^{-14}$**

PROBLEM: a_C required for $Cr_{23}C_6$ is ~ 10^{-2}

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CO_2 Corrosion of 9Cr Steels: Questions

- What is the rate compared with air oxidation?
- Why is the oxide scale in two layers?
- Why is the interface between them at the former steel surface?
- What transports across the scale, metal or oxygen?
- What controls the scaling rate?
- Why does internal carburisation occur?
- How fast is it, and what controls its rate?

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Is it expected thermodynamically?

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REACTION WITH CO_2

Alloys: Fe-9Cr, P91, P92

Gas: Ar-20CO_2

T: 650°C

p_{O_2} = 10^{-7} atm, a_C = 10^{-15}

$7\underline{Cr} + 3\underline{C} = Cr_7C_3$

For 9 Cr steel, need $a_{Cr} \sim 10^{-2}$

The required carbon activity is 10^{13} times higher than the gas can provide!

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