Carburisation by CO_2?

David Young

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REACTION WITH CO_2

Alloys: Fe-9Cr, P91, P92

Gas: Ar-20CO_2

T: 650^{o}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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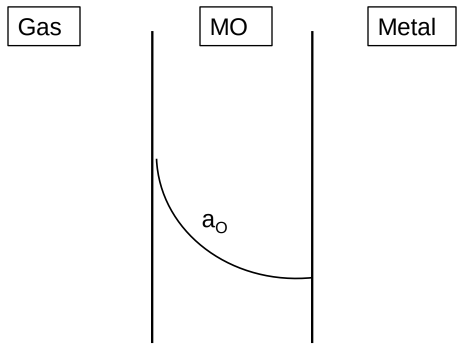
LOCAL EQUILIBRIUM: Growing Scale



Oxygen activity gradient

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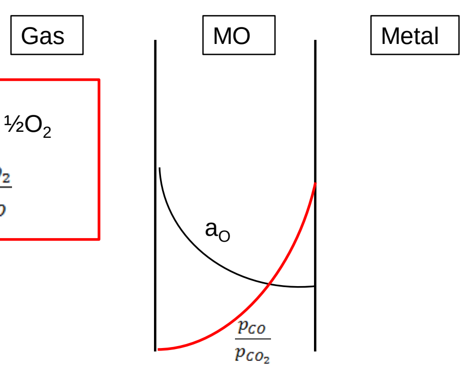
CARBON PENETRATION

$CO_2 = CO + ½O_2$

$$a_O = K\frac{p_{CO_2}}{p_{CO}}$$



Oxygen activity gradient corresponds to varying CO/CO_2 ratio

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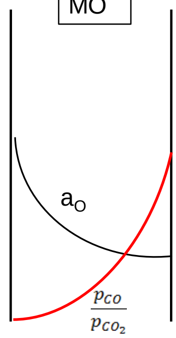
CARBON PENETRATION

Gas | MO | Metal

$CO_2 = CO + ½O_2$

$$a_O = K\frac{p_{CO_2}}{p_{CO}}$$



$$2CO = CO_2 + C$$

$$a_C = K\frac{p^2_{CO}}{p_{CO_2}}$$

Oxygen activity gradient corresponds to varying CO/CO_2 ratio

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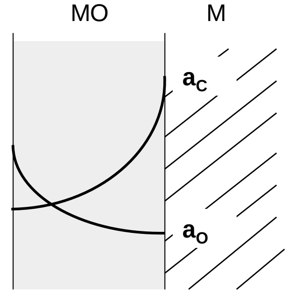
CARBON PENETRATION II

$$2CO = CO_2 + C \qquad a_C = K\frac{p^2_{CO}}{p_{CO_2}}$$

Gas MO M



CONCLUSION: Carbon activity increased within/beneath oxide scale

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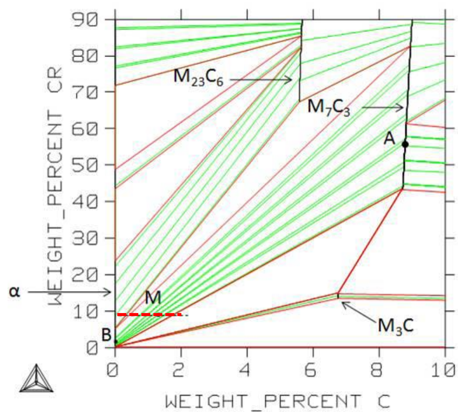
AMOUNT OF CARBIDE



Use measured f_v(carbide) and lever rule to select tie-line

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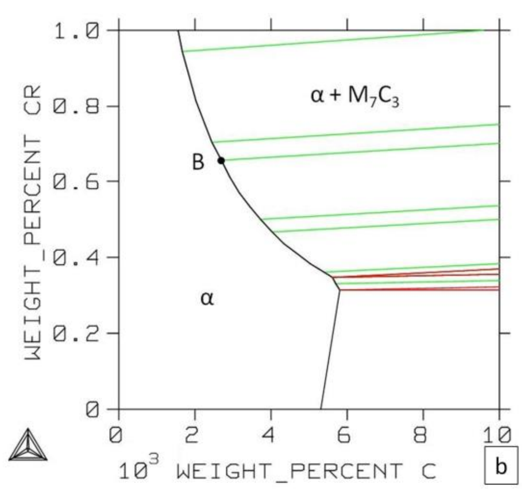
Fe-Rich Corner



Tie-line defines alloy composition

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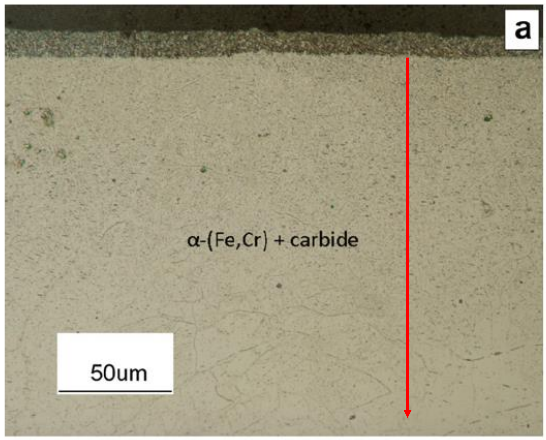
CARBIDE VOLUME FRACTION



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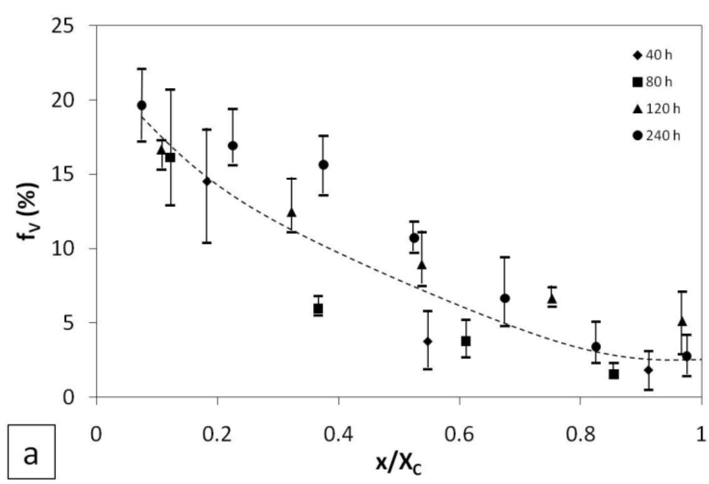
CARBIDE VOLUME FRACTION



Fe-9Cr reacted in dry CO_2 at 650°C

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TEST a_C CALCULATION

Method	a_C
Scale-alloy Equilibrium	0.47
From measured f_V	0.43

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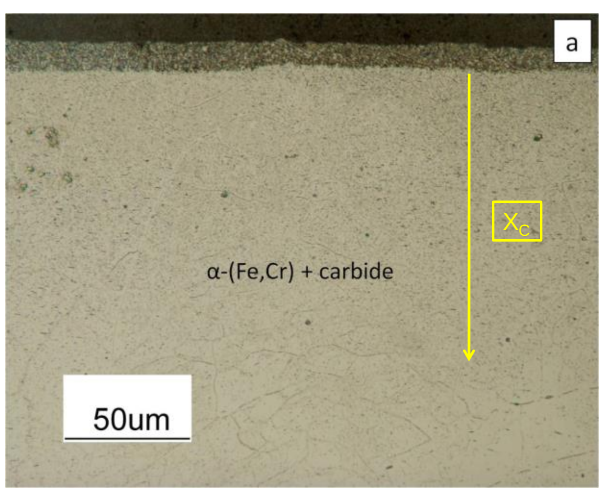
CARBURISATION KINETICS



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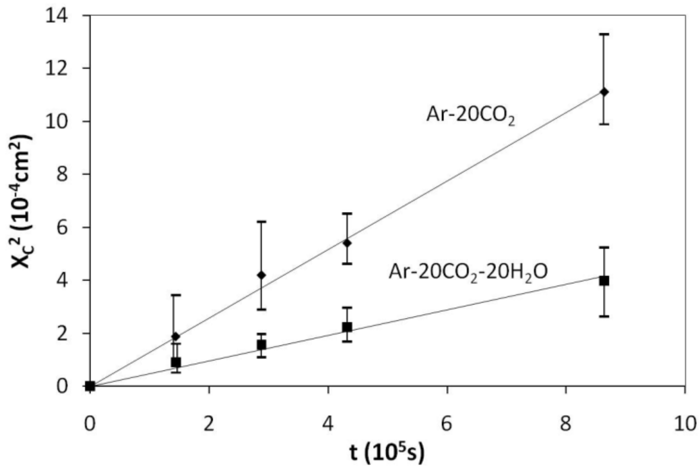
CARBURISATION KINETICS



Diffusion-controlled: calculate carbon permeability

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CARBON PERMEABILITY

$$X_C^2 = 2k_p t$$

$$k_p = \varepsilon \frac{N_C^{(s)} D_C}{\nu N_{Cr}^{(0)}}$$

$N_C^{(s)} D_C$ = 6.5 x 10^{-11} cm^2 s^{-1}

Use independently measured D_C to calculate N_C, hence a_C

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VERIFY a_C CALCULATION

Method	a_C
Scale-alloy Equilibrium	0.47
From measured f_V	0.43
From carburisation rate	0.25

CONCLUSION: Carbon beneath oxide scale supersaturates with respect to gas, but represents local equilibrium

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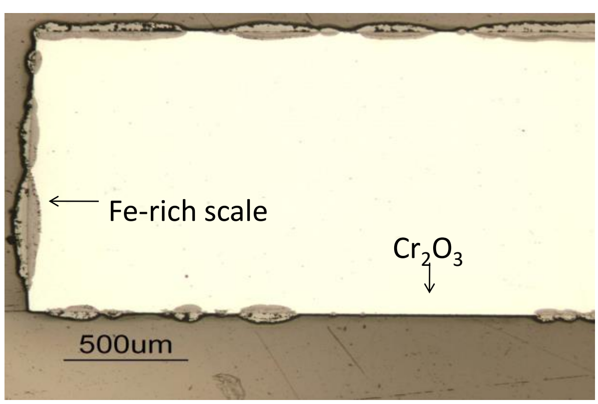
HIGHER Cr ALLOYS?



Fe-20Cr, Ar-CO_2, 650^oC

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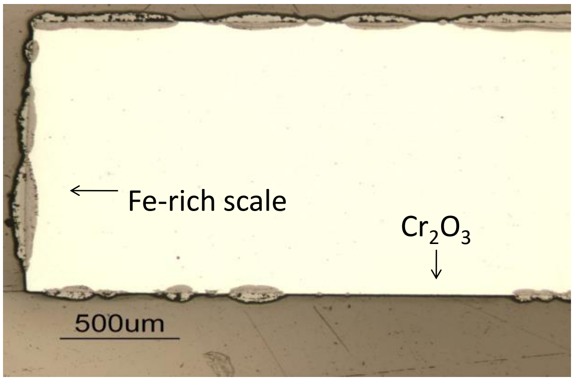
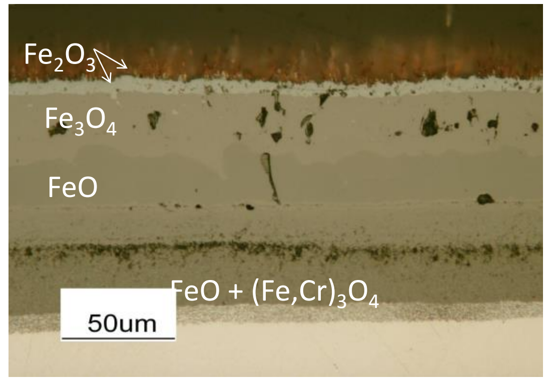
HIGHER Cr ALLOYS?



Fe-20Cr, Ar-CO_2, 650°C



Fe-9Cr, Ar-CO_2, 650°C

Higher Cr: partial protection

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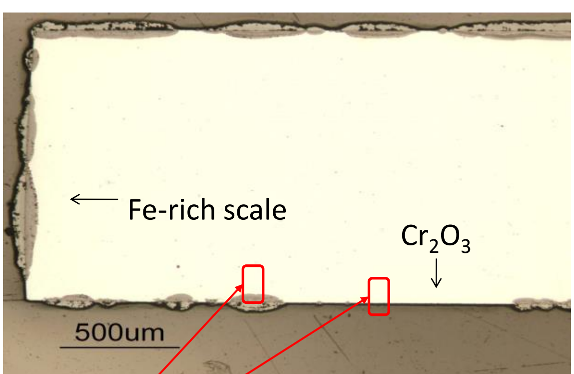
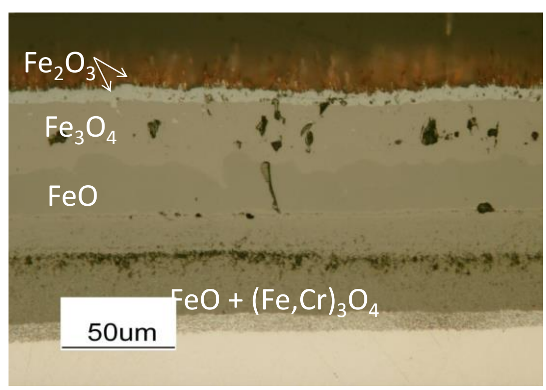
HIGHER Cr ALLOYS?



Internal carbides?

Fe-20Cr, Ar-CO_2, 650°C



Fe-9Cr, Ar-CO_2, 650°C

Higher Cr: partial protection

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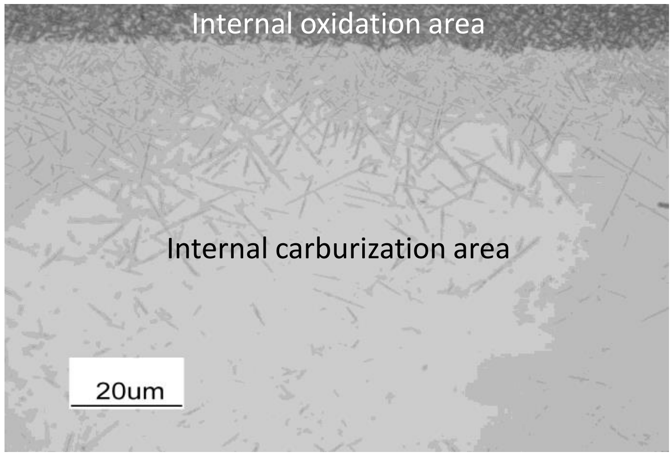
Carbides in Fe-20Cr at 650°C



Under iron-rich oxide nodule

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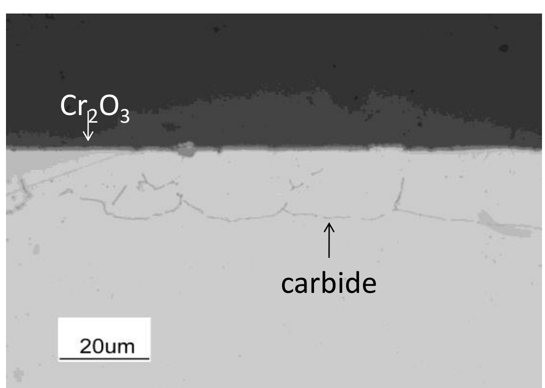
Carbides in Fe-20Cr at 650°C



Under chromia scale

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IINTERFACE a_C UNDER Cr_2O_3

Method	a_C(Dry)
FeO-alloy Equilibrium	0.47
Cr_2O_3-alloy Equilibrium	$>10^4$
From measured f_V	0.1
From carburisation rate	0.01

CONCLUSION: Oxide scale provides partial, transient protection against carburisation

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How Does C Penetrate Oxide Scale?

BACKGROUND KNOWLEDGE

- Diffusion of Cr or O in Cr_2O_3 along grain boundaries
- C is "insoluble" in Cr_2O_3
- PROPOSAL: C moves via oxide grain boundaries

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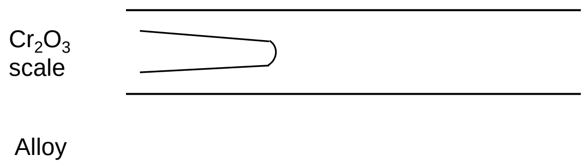
Atom Probe Tomography

Mill very fine tips from oxide



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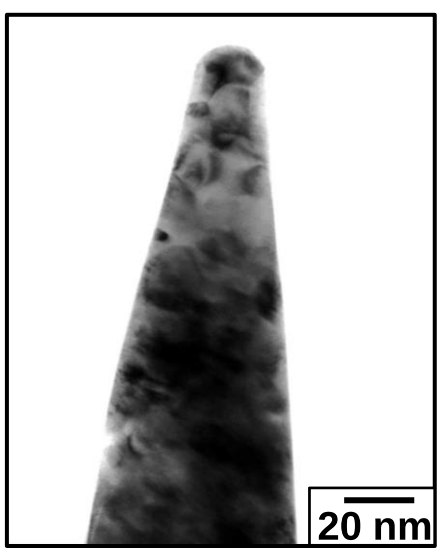
FIB MILLED TIP FOR ATOM PROBE



Bright field TEM view

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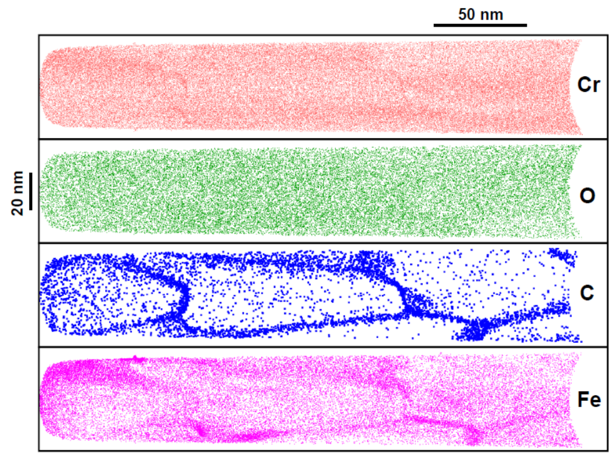
APT Results



Carbon is on chromia grain boundaries

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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? OK

How fast is it, and what controls its rate? OK

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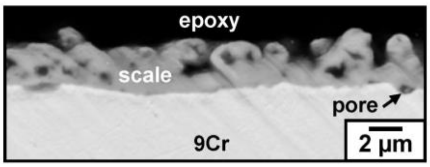
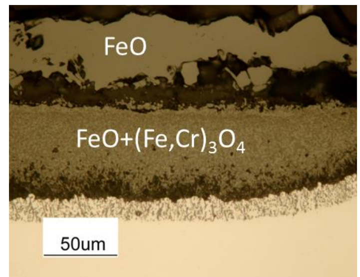
Rates in Air and CO_2



120 h in Air



30 h in Ar-CO_2

Protective behaviour in air
Non-protective (breakaway) in CO_2

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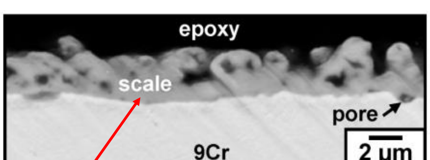
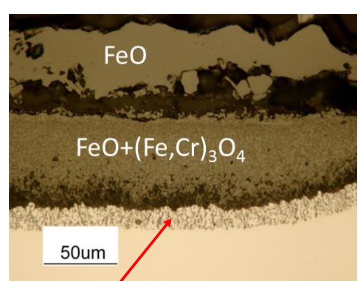
Rates in Air and CO_2



120 h in Air



30 h in Ar-CO_2

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External or Internal Cr Oxide

$$N_{Cr}(\text{crit}) = \left(\frac{\pi g N_O^S D_O V_m}{3 D_{Cr} V_{OX}}\right)^{1/2}$$

Same alloy, same T, but:

N_{Cr}

N_{Cr}

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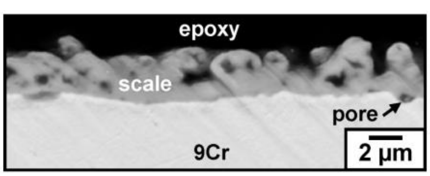
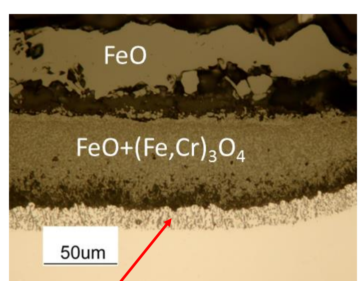
Rates in Air and CO_2



120 h in Air



30 h in Ar-CO_2

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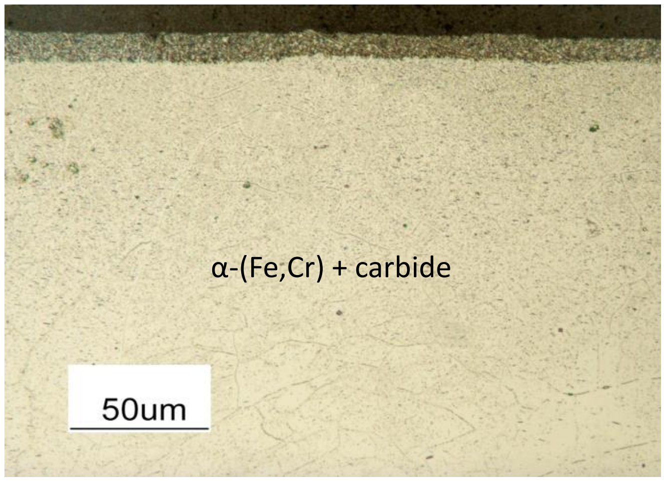
Fe-9Cr at 650^{o}C

CONCLUSIONS:



Internal Cr-rich oxide

Internal Cr-rich carbide

Internal carburisation (dry CO_2)

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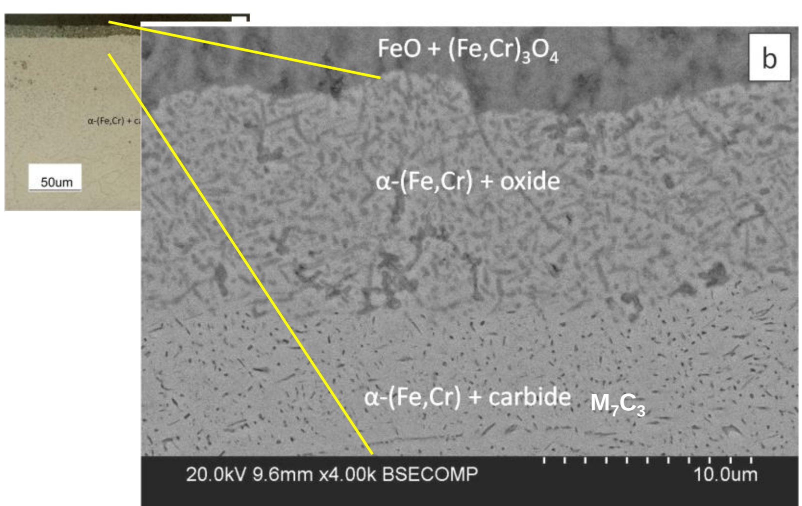
INTERNAL REACTION, 650^{o}C



Gheno et al.,
Corros. Sci. (2011)

Precipitates identified by XRD:

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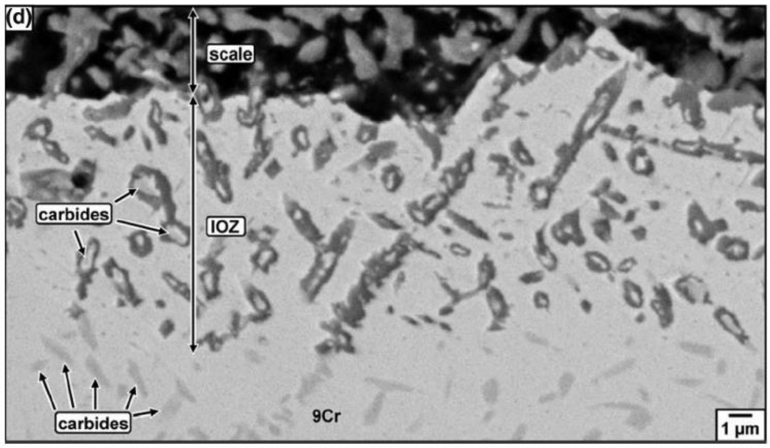
Oxidation of Internal Carbides

$Fe + M_3O_4 + O \rightarrow FeO + M_3O_4$

$\boxed{M_7C_3 + \underline{O} \rightarrow M_3O_4 + \underline{C}}$



Carbides oxidised in place; Cr-rich oxides end up in inner scale

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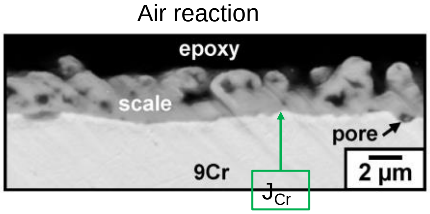
Explains why 9Cr alloy nonprotective in CO_2

Air reaction



Enough Cr to diffuse to surface and form:

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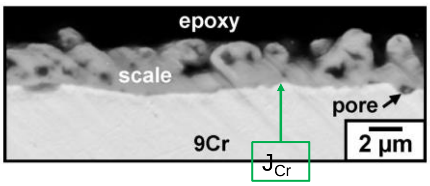
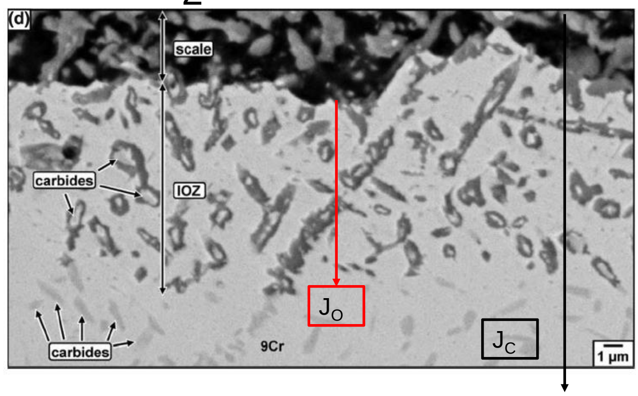
Explains why 9Cr alloy nonprotective in CO_2

Air reaction



Enough Cr to diffuse to surface and form: External Cr-rich scale



- Fast inward C diffusion
- C reacts with:
- Result:
- Consequence:

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CO_2 Corrosion of 9Cr Steels: Questions

What is the rate compared with air oxidation? OK

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? OK

How fast is it, and what controls its rate? OK

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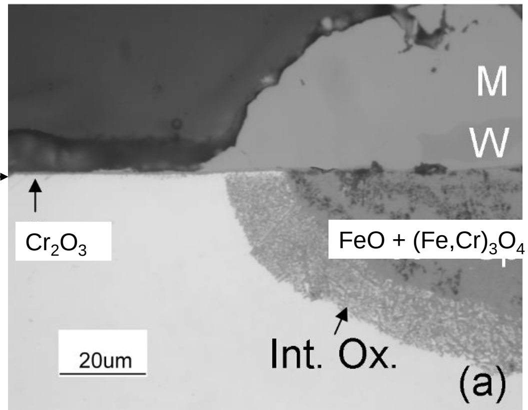
Original Alloy Surface

Alloy surface



Alloy Cr precipitated internally as:
Immobile, marks original location in alloy
Therefore – two oxide layers

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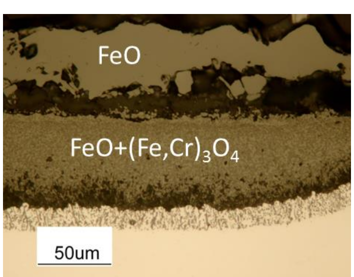
Mass Transport



J_O J_{Fe} J_C

- Inward O diffusion confirmed by tracer experiments (^{16}O then ^{18}O)
- Outward Fe diffusion from alloy via cation vacancies in FeO
- Inward C diffusion?

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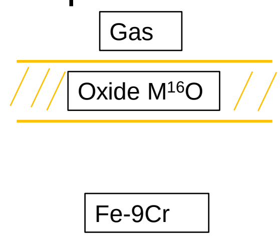
Tracer Diffusion Experiment

I. Expose to ^{16}O



II.

First part of 2-stage experiment

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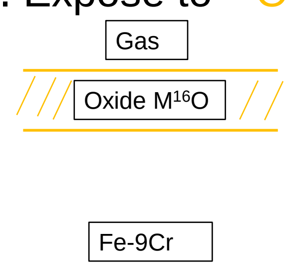
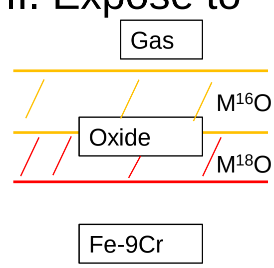
Tracer Diffusion Experiment

I. Expose to ^{16}O



II. Expose to ^{18}O



Part 2: ^{18}O

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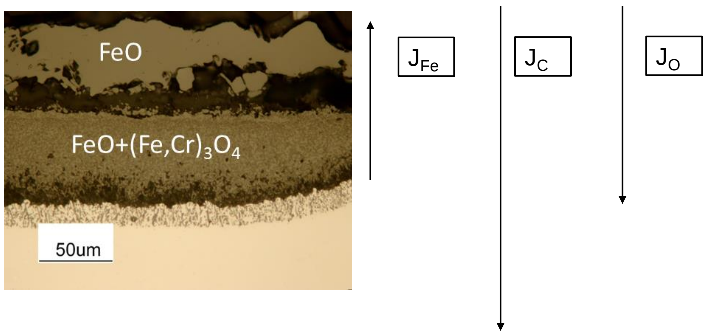
Mass Transport Mechanisms



- Inward O diffusion confirmed by tracer experiments (^{16}O then ^{18}O)
- Outward Fe diffusion from alloy via cation vacancies in FeO
- Inward C diffusion?

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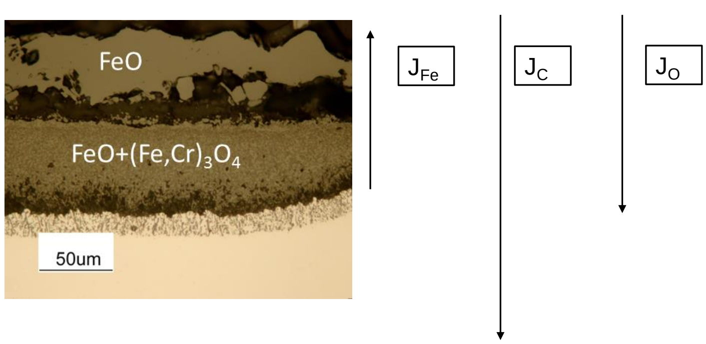
Mass Transport Mechanisms



- Outward Fe diffusion from alloy via cation vacancies in FeO
- Inward C diffusion?
- Inward O diffusion?

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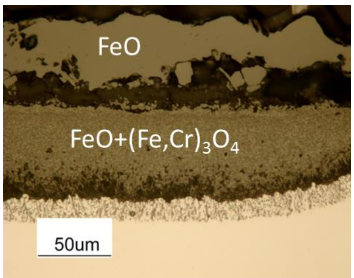
Mass Transport Mechanisms: Outer layer



J_{Fe} J_C J_O

- Background: O lattice diffusion in FeO does not happen
- C is not soluble in FeO

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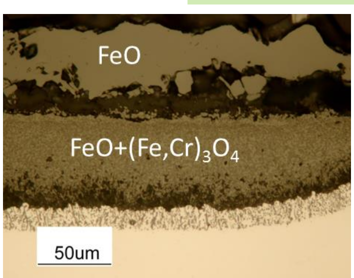
Mass Transport Mechanisms: Outer layer

- Background: O lattice diffusion in FeO does not happen
- C is not soluble in FeO



J_{Fe} J_C J_O

PROPOSAL:
Diffusion of C, O

EVIDENCE:
Diffusion of C, O

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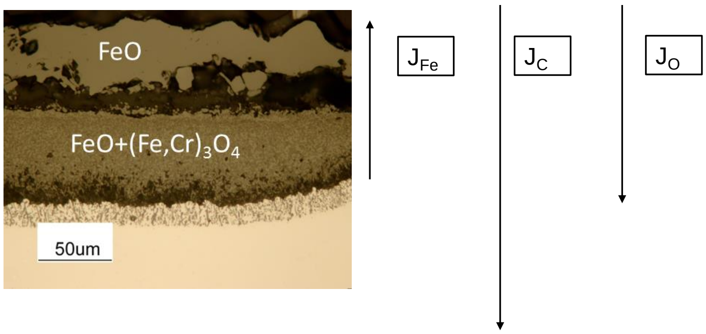
Mass Transport Mechanisms: Inner Layer



- Inner layer is fine-grained, 2-phase and porous

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CO_2 Corrosion of 9Cr Steels: Questions

What is the rate compared with air oxidation? **OK**

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? **OK**

How fast is it, and what controls its rate? **OK**

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Next Time

Alloy design to resist CO_2 attack

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