Metal Dusting – Catastrophic Corrosion by Carbon

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Lesson 3 Class 1

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TECHNOLOGICAL RELEVANCE

Hydrocarbons - Oil, Petrochemical Processing

Syngas ($CO + H_2$) – Reforming, Gasification

NH_3 synthesis

CH_3OH synthesis

Combustion Gas (CO_2)

OXIDISE

CARBURISE

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GRAPHITE CAUSES METAL DUSTING

Graphite deposition causes metal loss rates of cm per year

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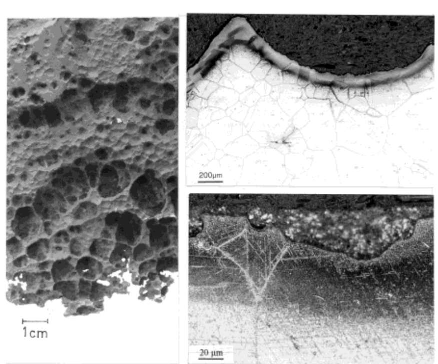
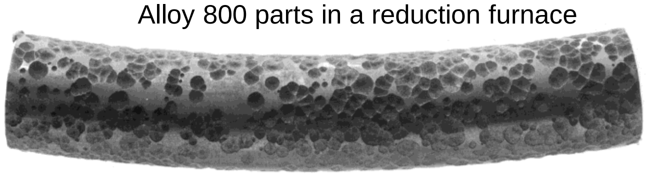
METAL DUSTING, ALLOY 800



Alloy 800 parts in a reduction furnace



Alloy 800 in synthesis gas at about 600°C

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METAL DUSTING

- Occurs at intermediate T
- Requires gas with $a_C > 1$
- Depends on gas composition (not just a_C)
- Mechanism varies with alloy type: Fe- or Ni-base

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METAL DUSTING OF Fe AND FERRITICS

Start with simplest system: Fe

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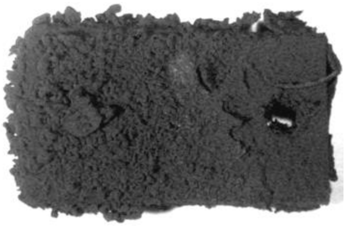
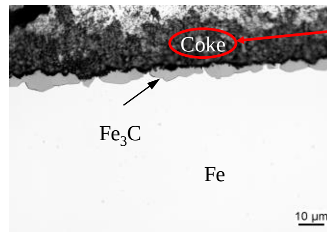
THE IRON DUSTING REACTION



Fe

Surface view



Cross-section

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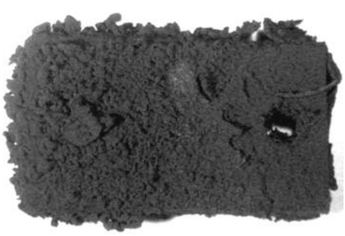
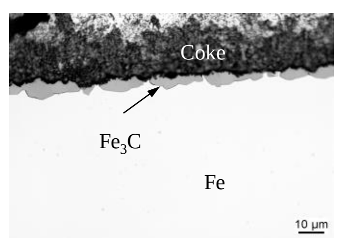
THE IRON DUSTING REACTION



Fe



Source of Carbon: Supersaturated gas

$$\left.\begin{aligned} CO + H_2 &= H_2O + C(s) \\ 2CO &= CO_2 + C(s) \\ CH_4 &= 2H_2 + C(s) \end{aligned}\right\} \quad a_C>1$$

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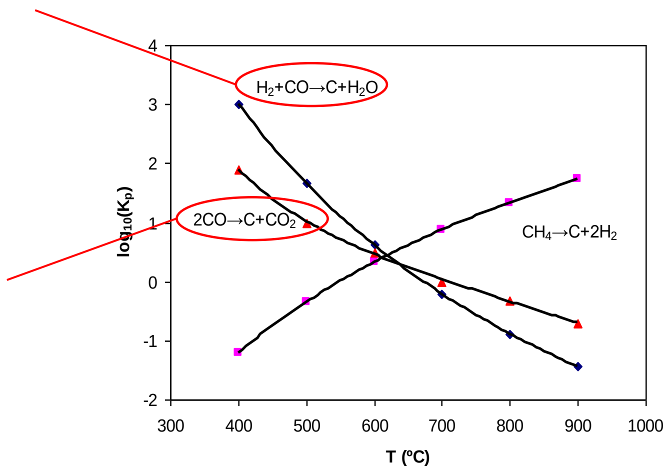
T EFFECT ON GAS EQUILIBRIA



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Rate of C(s) Production

- In gas phase, Syngas and Boudouard reactions do not occur
- Need solid catalysts: Fe, Ni, Co

Catalysis Sites?

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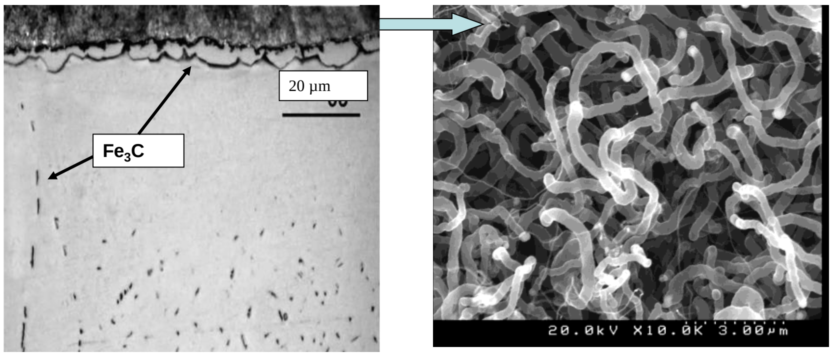
EXAMINE REACTION MORPHOLOGY

T = 680^{o}C, CO/H_2/H_2O, a_C = 2.9, p_{O2} <Fe/FeO



CONCLUSION: Cementite does form at Fe surface and Fe-rich particles found in coke

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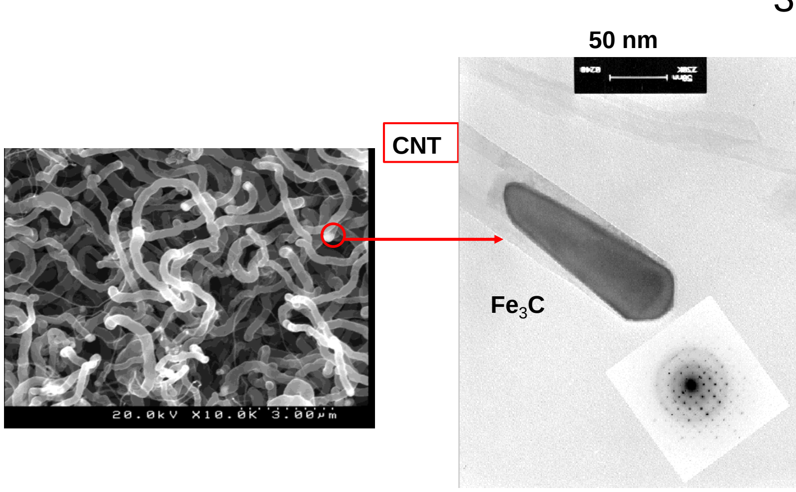
NANOPARTICLES ARE Fe_3C



CONCLUSION: Carbon filaments are nanotubes

Cementite does NOT decompose

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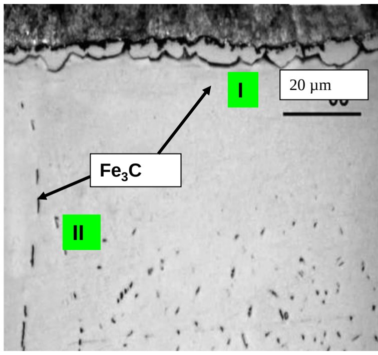
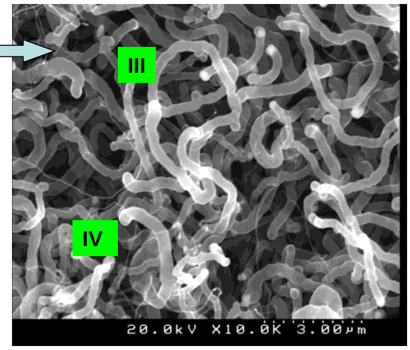
EXAMINE REACTION MORPHOLOGY





<u>Mass Transfer Processes</u>

I. Cementite layer growth

II. Internal precipitates

III. Filament growth

IV. Particles

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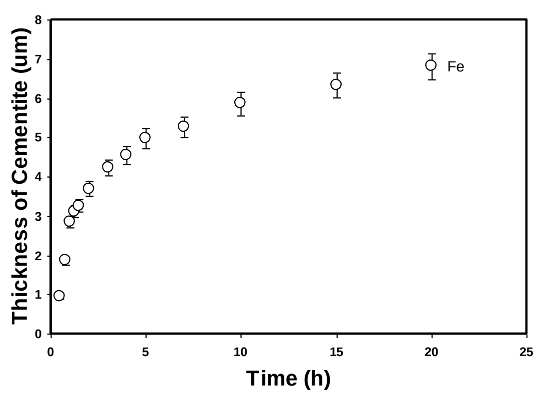
CEMENTITE SCALING



CONCLUSION: a_C>1 at Fe_3C/Coke interface

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Fe_3C SCALE GROWTH AND DISINTEGRATION

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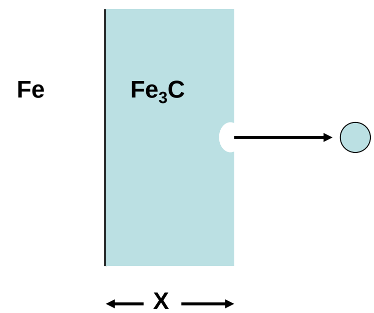

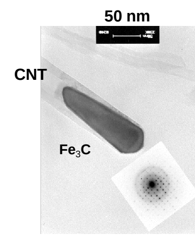

$$\frac{dX}{dt} = \frac{k_p}{X} - k_d$$

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EVALUATION OF k_d

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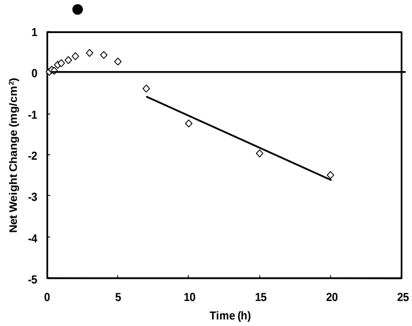

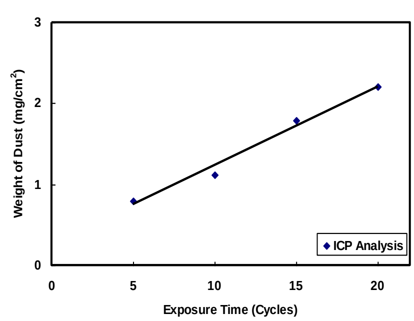

Measure metal loss

Measure Fe content of coke deposit

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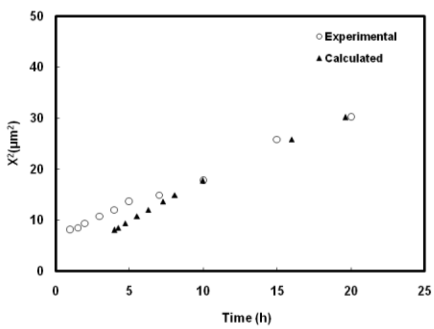
EVALUATION OF D IN Fe_3C

$$\frac{dX}{dt} = \frac{k_p}{X} - k_d$$



- Measure X = f(t)
- Measure k_d independently
- Fit to Eqn
- Extract k_p
- Calculate D_C

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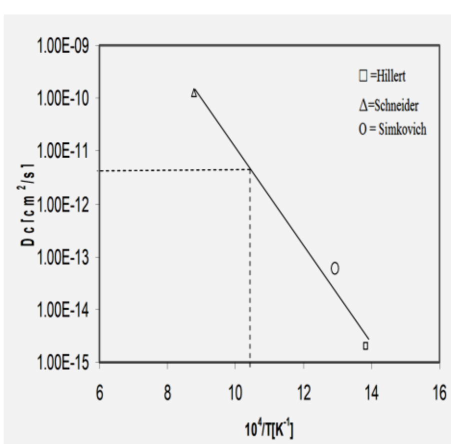
D in CEMENTITE LAYER



Kinetics:

^{12} cm^2 s^{-1}

Diffusion Measurements:

$D_C (Fe_3C) = 5x10^{-12}$ cm^2 s^{-1}

CONCLUSIONS: Fe_3C scale growth diffusion controlled

a_C>1 at Fe_3C/Coke interface

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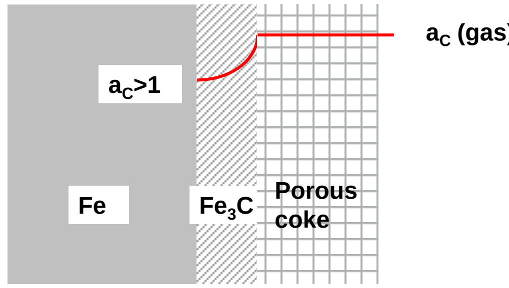
CONCLUSIONS: I



- Fe_3C grows – $a_c > 1$
- Scaling diffusion controlled
- Carbon diffuses inwards

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CARBON FILAMENT GROWTH

50 nm

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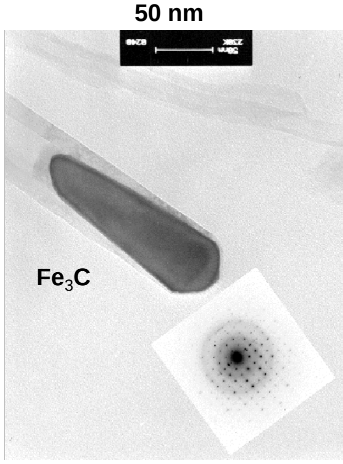
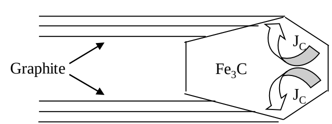
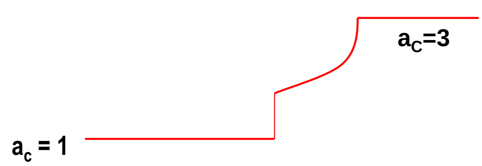
CNT







PROPOSAL: Same mechanism for Fe_3C Particles & Scale: C Diffusion

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PREDICT CNT GROWTH RATE

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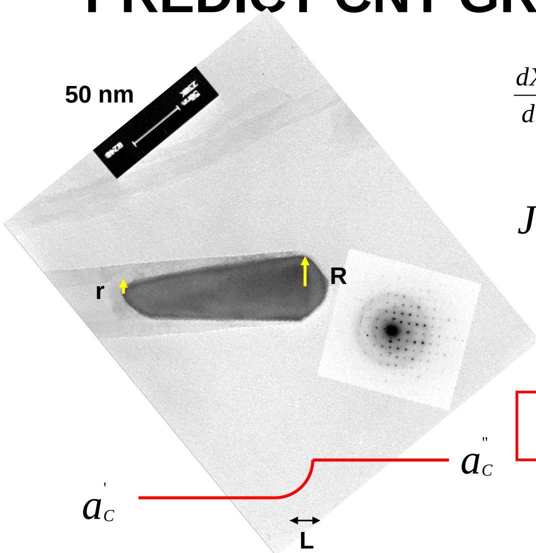

$$\frac{dX}{dt} = J_C V_C \frac{R^2}{(R^2 - r^2)}$$

$$J_C = \frac{D_C}{L V_{Fe3C}} \ln \frac{a_C''}{a_C'}$$

T = 680°C, a_C = 2.9, D_C = 8x10^{-12} cm^2 s^{-1}

Predict dX/dt = 20 nm s^{-1}

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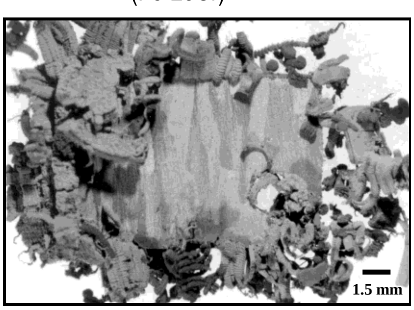
NANOTUBE GROWTH RATES

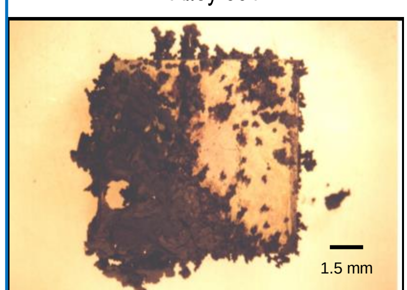
Cementite Catalysed
(Fe-25Cr)



Coking onset	1 cycle
Experiment end	81 cycle
Duration	80h

$\overline{V}$ = 20 nm s^{-1}

Austenite Catalysed
Alloy 601



Coking onset	81 cycle
Experiment end	234 cycle
Duration	153h

$\overline{V}$ = 3 nm s^{-1}

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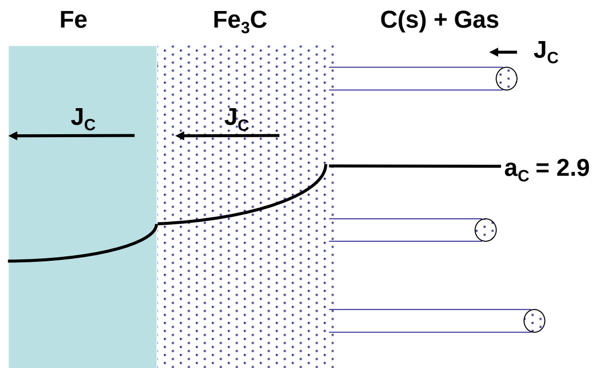
CONCLUSIONS: DUSTING OF Fe



- Gas in contact with Fe_3C layer
- Carbon diffuses inward
- Fe highly supersaturated

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CEMENTITE DISINTEGRATION

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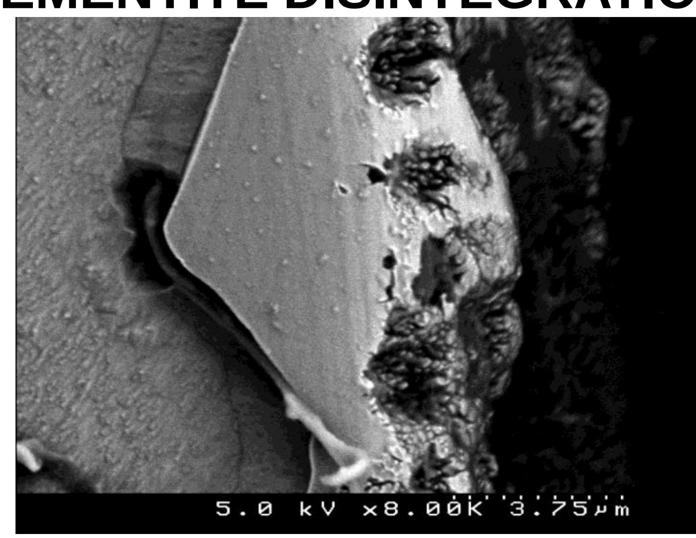

CONCLUSION: Graphite nucleates inside Fe_3C

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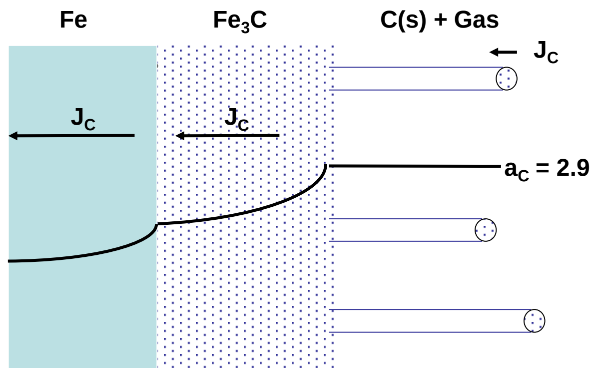
CONCLUSIONS: DUSTING OF Fe



- **Gas in contact with Fe_3C layer**
- **Carbon diffuses inward**
- **Fe highly supersaturated**

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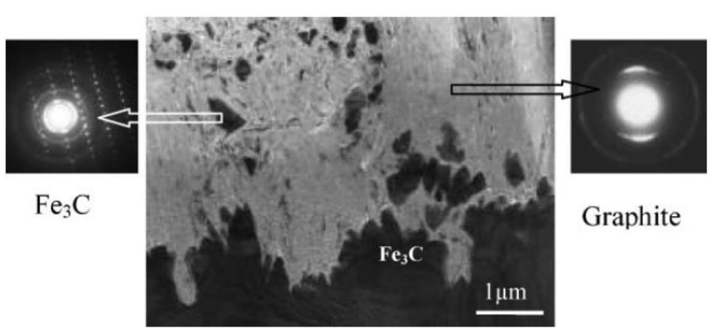
C(gr) Nucleation: Fe_3C Disintegration



Interface between coke and Fe_3C layer grown on iron

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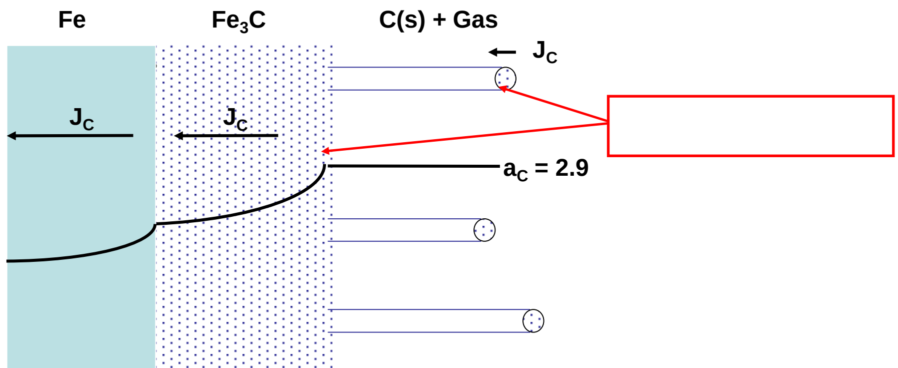
CONCLUSIONS: DUSTING OF Fe



- Gas in contact with Fe_3C surface layer and nanoparticles
- Carbon diffuses inward through Fe_3C
- C nucleation at favoured sites

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Gas Composition Effects

$$CO + H_2 = H_2O + C \qquad (1)$$

$$2CO = CO_2 + C \qquad (2)$$

$$CH_4 = 2H_2 + C \qquad (3)$$

Net carbon uptake: $Rate = k_1 p_{CO} p_{H_2} + k_2 p_{CO}^2 + k_3 p_{H_2}^2$

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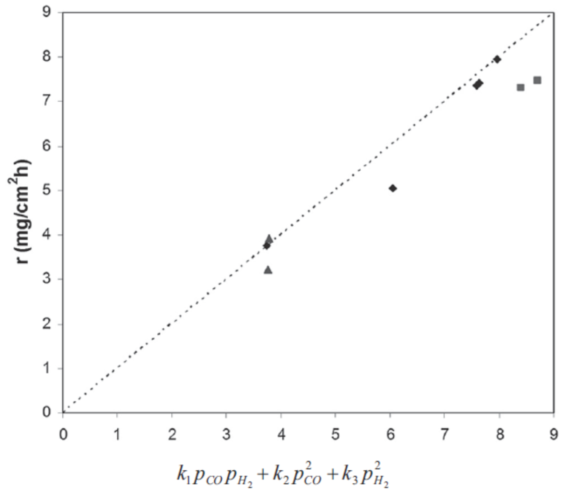
Gas Composition Effects

$$CO + H_2 = H_2O + C \quad (1)$$
$$2CO = CO_2 + C \quad (2)$$
$$CH_4 = 2H_2 + C \quad (3)$$



Dusting kinetics determined by parallel reaction paths

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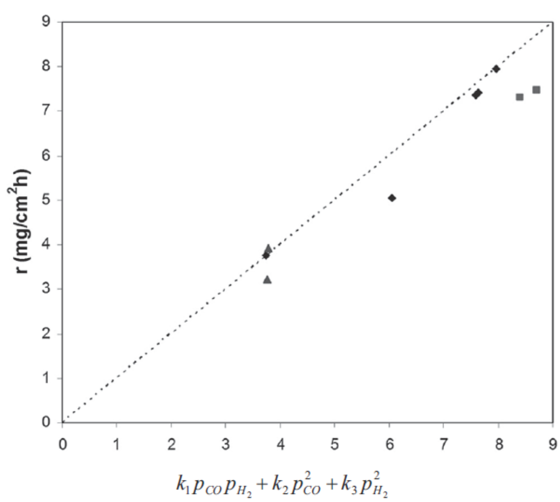
Gas Composition Effects



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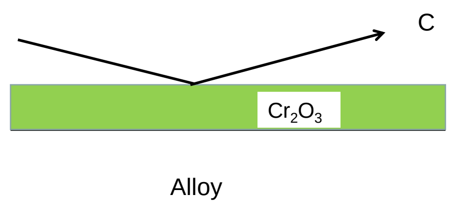
Ferritic Cr Steels, Isothermal



Syngas is oxidising to Cr
Ferritic alloys have fast D
Cold working surface before service…

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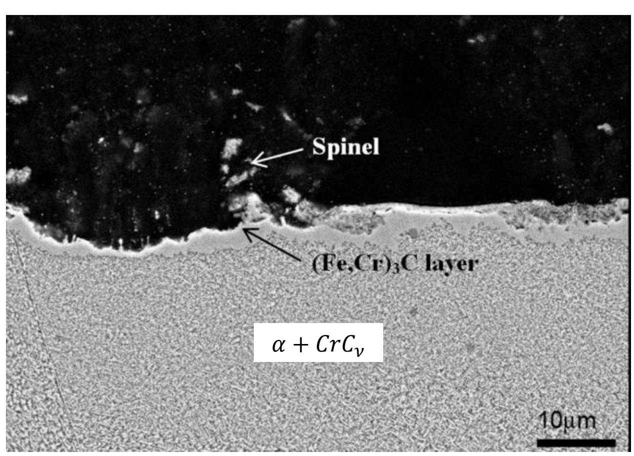
Ferritic Cr Steels, Thermal Cycling



Fe-25Cr, 680°C in $CO/H_2/H_2O$ (a_c =2.9, $p(O_2)$ = 10^{-23} atm)

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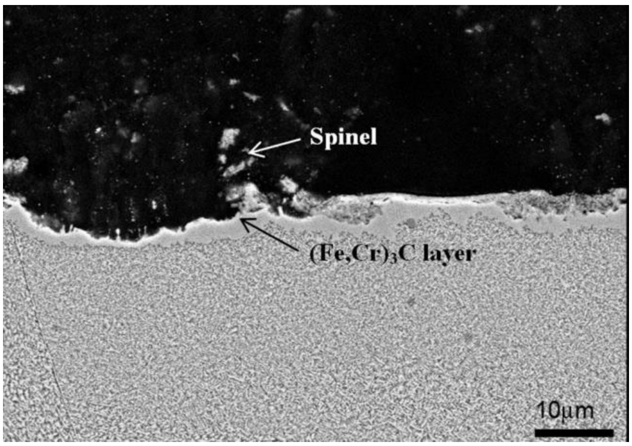
Ferritic Cr Steels, Thermal Cycling



Fe-25Cr, 680ºC in $CO/H_2/H_2O$ (a_c =2.9, $p(O_2)$ = 10^{-23} atm)

- Alloy protected by Cr_2O_3 scale at first
- Repeated T-cycles damage scales
- C enters Cr-depleted alloy
- Precipitates..
- Prevents scale…
- Continued C entry…
- Then

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SUMMARY

- C-supersaturated gas catalysed by Fe produces $\underline{C}$
- Fe_3C surface layer formed
- Fe_3C also catalyses release of C from gas
- C diffuses in (a) growing Fe_3C layer
  (b) precipitates within layer, causes disintegration
- Fe_3C particles catalyse C deposition, cause C nanotube growth
- Chromia scale can protect alloy against dusting

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