DUSTING OF Ni AND AUSTENITICS

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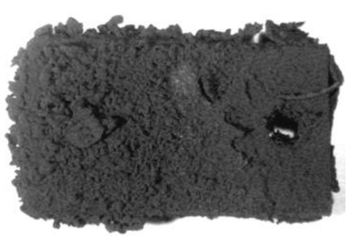
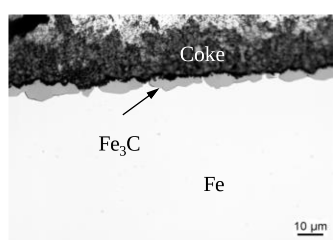
DUSTING REACTIONS



Fe



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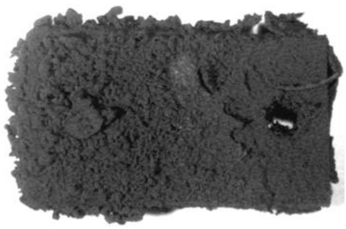
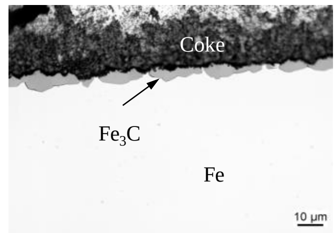
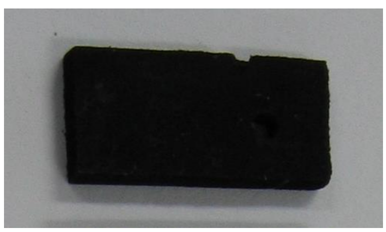
DUSTING REACTIONS

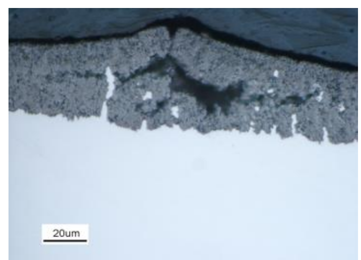


Fe





Ni



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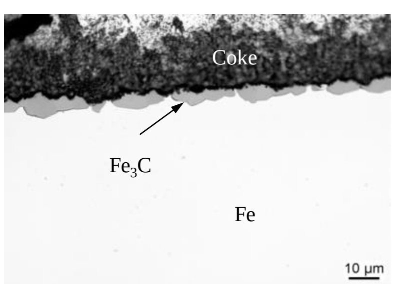
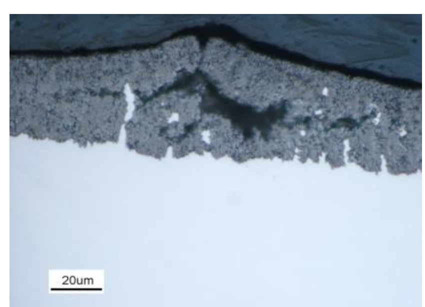
Fe or Ni





Fe
Lots of coke
Coke in contact with Fe_3C
Fe_3C in contact with Fe

Ni
Less coke
No Ni carbide
Coke in contact with Ni

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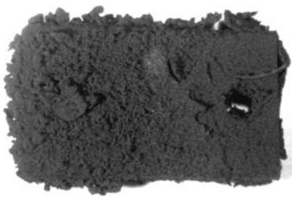
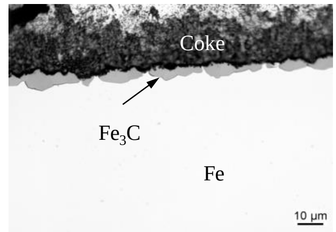
SOURCE OF CARBON





Supersaturated gas

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

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CARBON DEPOSITION **CATALYSED**

I. Gas + Fe, Ni → Fe, Ni + <u>C</u>

II. Supersaturation relaxed by precipitation

(a) $\underline{C} + 3Fe \rightarrow Fe_3C(s)$

(b) $\underline{C} + Ni \rightarrow C(s) + Ni$

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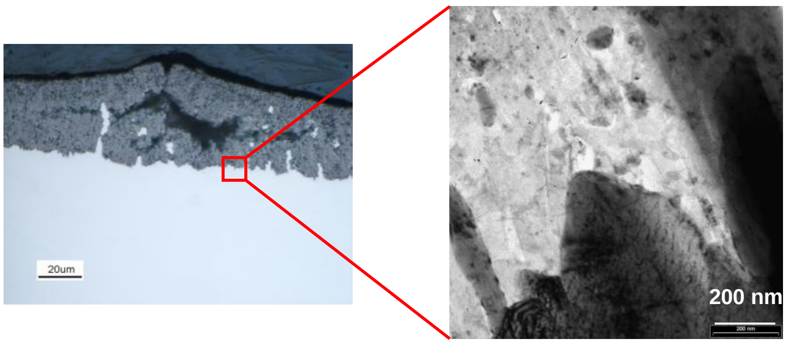
Metal Dusting of Nickel

$CO + H_2 = H_2O + C \quad a_C > 1$

Reaction catalysed by Ni



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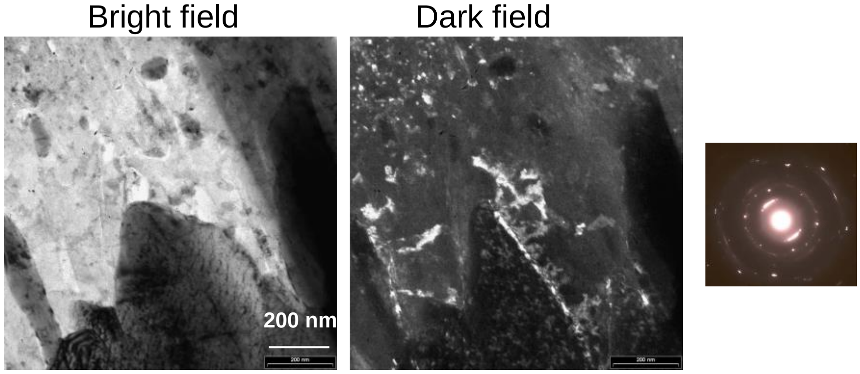
Metal Dusting of Nickel

$CO + H_2 = H_2O + C \quad a_C > 1$

Reaction catalysed by Ni

Bright field

Dark field



Ni disintegrates into nanoparticles dispersed in coke

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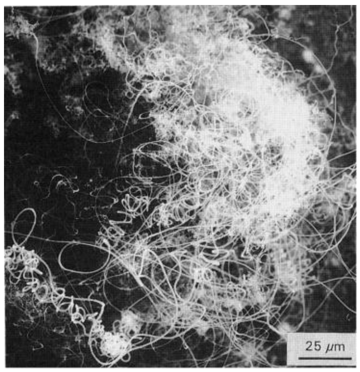
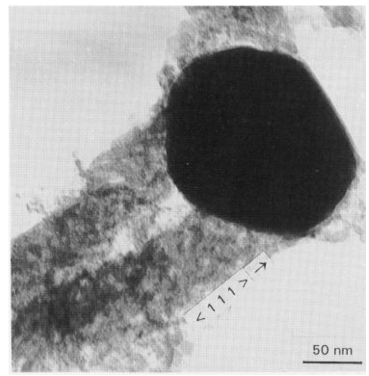
GAS–METAL INTERACTIONS: Austenite

Gas + γ-Ni = C(nanotubes) + Ni(particles)





Mitchell & Young, J.Mater.Sci.,**29**,4357(1994)

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RATE CONTROL?

- Metal consumption
- Coke accumulation

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RATE CONTROL?

- Metal consumption
- Coke accumulation

NOTE: Concentration of Ni in coke approximately constant

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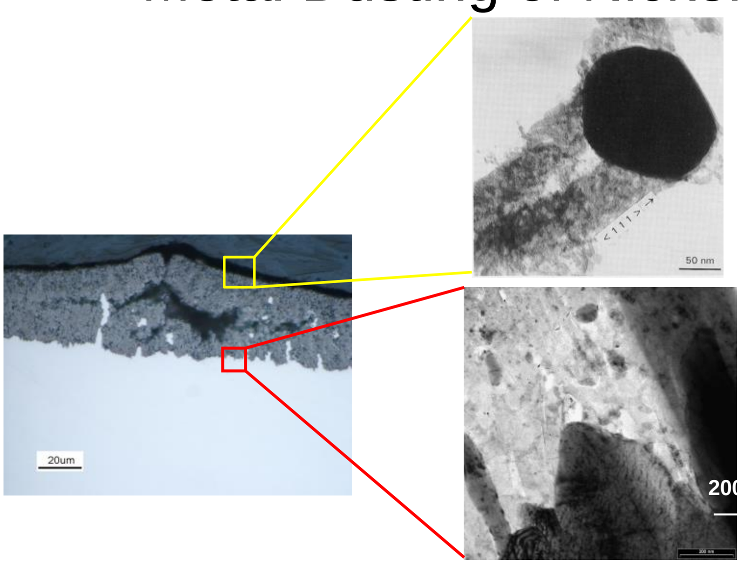
Metal Dusting of Nickel



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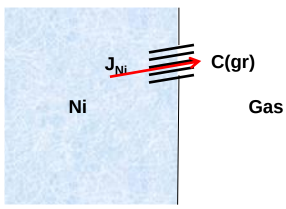
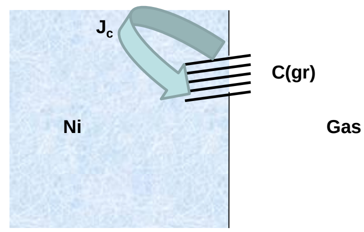
Dusting Mechanism Theories





Intercalation

- **Ni dissolves in C(gr)**
- **Diffuses out**
- **Reprecipitates as particles**

Carbon Supersaturation

- **C dissolves in Ni**
- **Supersaturates metal**
- **Precipitates as graphite**
- **Volume expansion disrupts metal**

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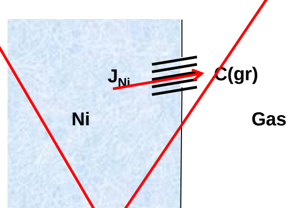
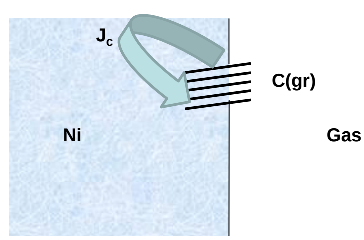
Dusting Mechanism





~~**Intercalation**~~

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Carbon Supersaturation

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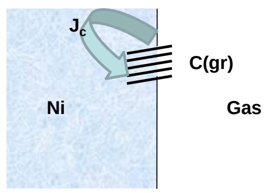
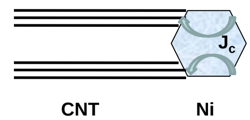
Single Mechanism





- C dissolves in Ni
- Diffuses to favoured site
- Precipitates as graphite

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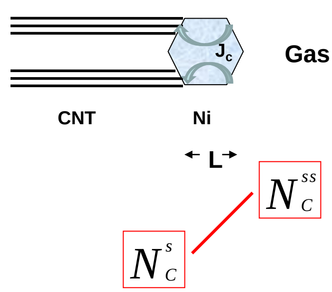
Nanotube Growth Rate



$$J_C = \frac{D_C^{\gamma}(N_C^{ss} - N_C^{s})}{L}$$

PREDICTION: v = 2 nm s^{-1}

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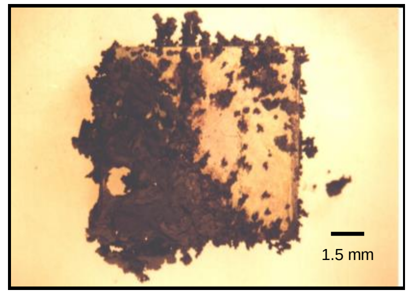
NANOTUBE GROWTH RATES

Cementite Catalysed
(Fe-25Cr)

Coking onset	1 cycle
Experiment end	81 cycle
Duration	80h

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

Austenite Catalysed
Alloy 601



Coking onset	81 cycle
Experiment end	234 cycle
Duration	153h

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

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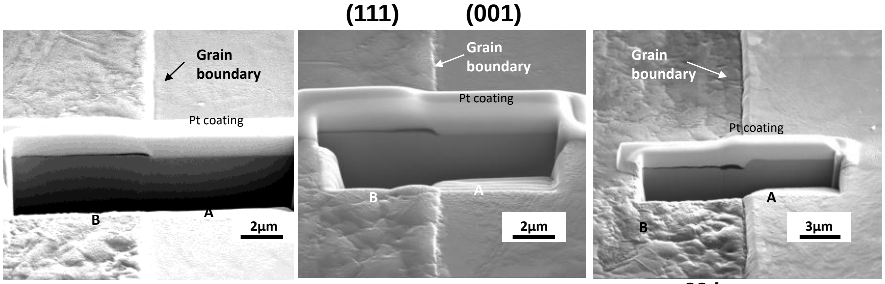
Carbon Uptake

(111) (001)



40 min 2 h 22 h

OBSERVE: Coke thickens on (111)
C-free (001) surface rises

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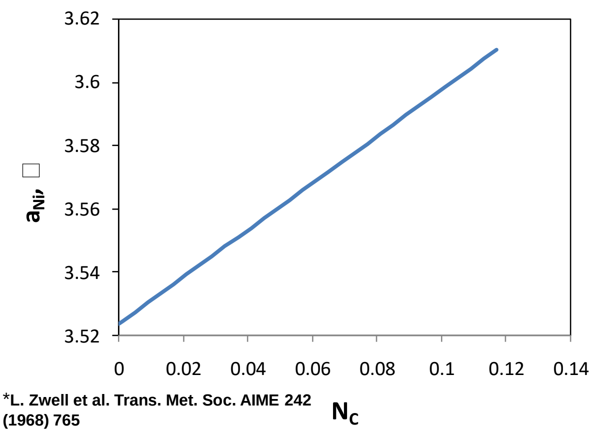
Lattice Dilation



*L. Zwell et al. Trans. Met. Soc. AIME 242 (1968) 765

CONCLUSION: Dissolved carbon dilates Ni
Dissolution precedes dusting

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Effect of Alloying on Carbon Diffusion

$$J_C = \frac{D_C^{\gamma}(N_C^{ss} - N_C^{s})}{L} \longrightarrow J_C = \frac{D_C^{\gamma}}{\gamma L}(a_C - 1)$$

Assume constant L, γ, a_C:

$$\gamma = \frac{1}{N_C^{s}}$$

$$J = const.\, D_C\, N_C^{s}$$

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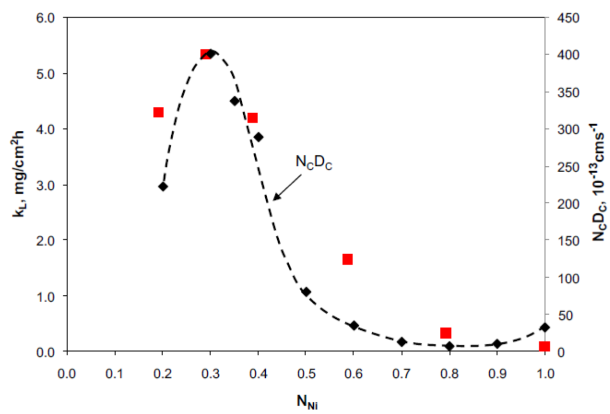
Coking Rates for Fe-Ni Alloys



CONCLUSION: Austenite dusting controlled by C diffusion

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Why Not Carbon Deposition on/at Surface

- Catalysis at surface produces C
- C diffuses to favourable site to nucleate C(gr)
- Nucleation process?

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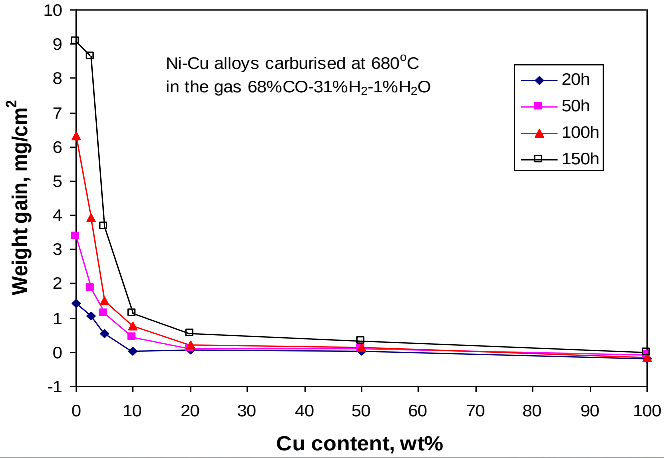
Carbon Uptake Kinetics on Ni-Cu



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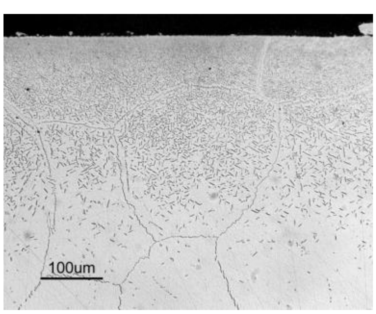
Does Cu Effect J_C?



J_C

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

Carburised Ni-Cu-Cr alloy

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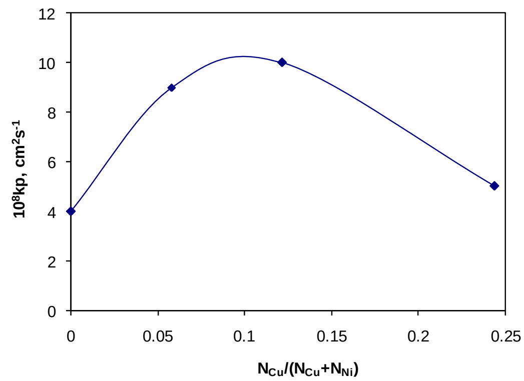
Effect of Cu on C Permeability



CONCLUSION: Cu does not affect C diffusion

Affects graphite nucleation/growth

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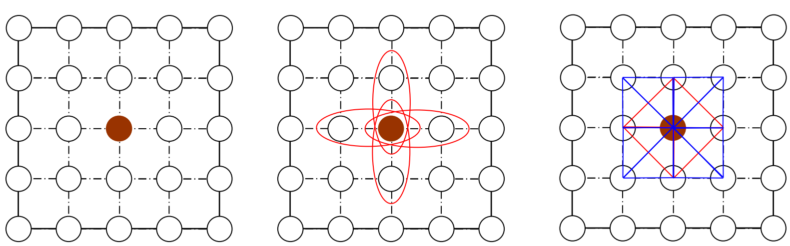
Effect of Copper on Coking Rate

If gas decomposed catalytically



Single atom site	Two-atom sites	Three-atom sites
Rate = $r_{Ni}(1-X_{Cu})$	Rate = $r_{Ni}(1-X_{Cu})^2$	Rate = $r_{Ni}(1-X_{Cu})^3$

For N-atom “ensemble”

Rate = $r_{Ni}(1-X_{Cu})^N$

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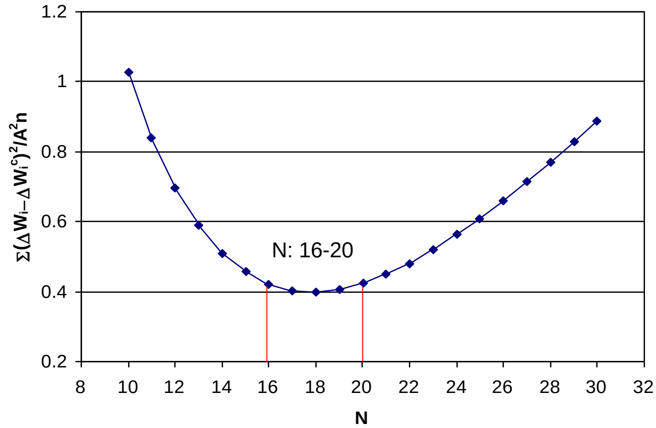
Effect of Cu on Rate of Carbon Deposition



Minimise residuals in weight uptake

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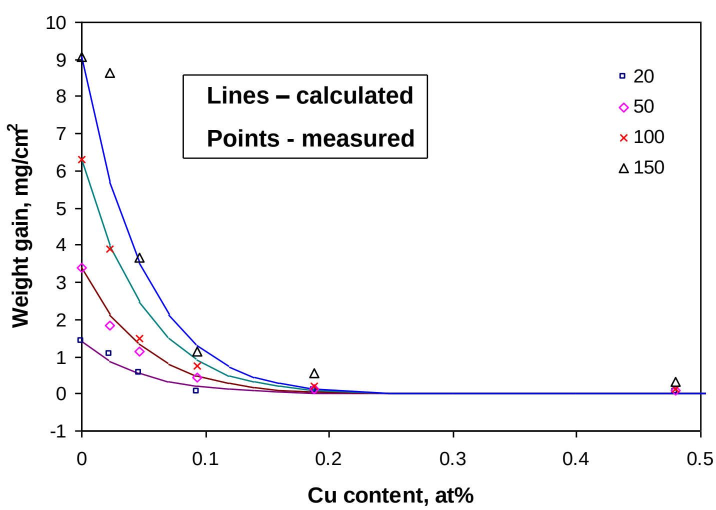
Effect of Cu in Ni on Rate of Carbon Deposition

Success of Model (N=18)



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PHYSICAL SIGNIFICANCE OF CATALYTIC "ENSEMBLE"

GAS INTERACTIONS

$CO + H_2 = C(ad) + H_2O$

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

CANNOT INVOLVE 18 METAL ATOMS

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PHYSICAL SIGNIFICANCE OF CATALYTIC "ENSEMBLE"

GAS INTERACTIONS

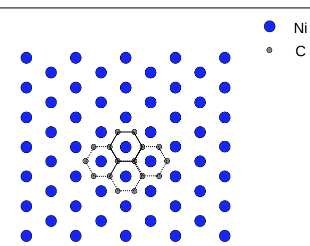
$CO + H_2 = C(ad) + H_2O$

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

CANNOT INVOLVE 18 METAL ATOMS

GRAPHITE NUCLEATION

$$x\mathrm{C}(atom) = \frac{x}{6}\mathrm{C}(gr)$$



The epitaxial relationship:
graphite (0002)/Ni (111)

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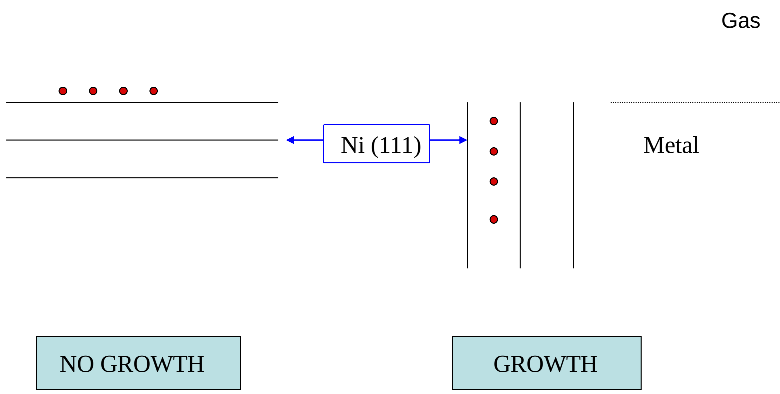
NICKEL ORIENTATION EFFECT ON GRAPHITE



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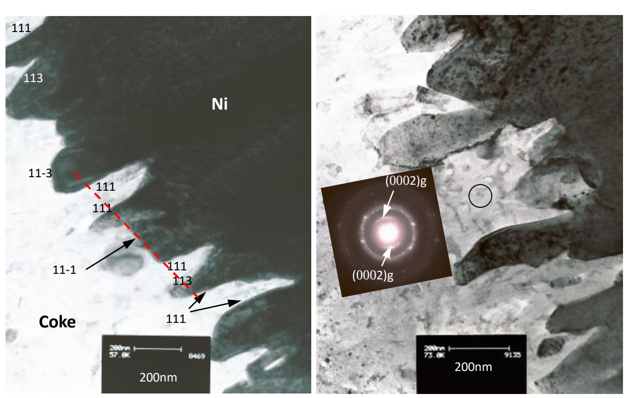
TEM Analysis C(gr) on Ni (111)



CONCLUSION: C grows along interior (111) planes

Reacted in 50%CO-48.9%H_2-1.1%H_2O gas at 680°C for 4.5 h

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Ni Dusting: Conclusions

- C diffusion in nanoparticles controls CNT growth
- C diffusion into bulk Ni precedes dusting
- Changing $D_C N_C$ changes rate
- Modifying nucleation sites changes rate
- Graphite grows along internal (111) Ni planes

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