University
of Siegen
Germany

Coupling diffusion and local equilibrium in modelling oxidation, nitridation and carburisation

B. Gorr, U. Krupp, H.-J. Christ
Institut für Werkstofftechnik

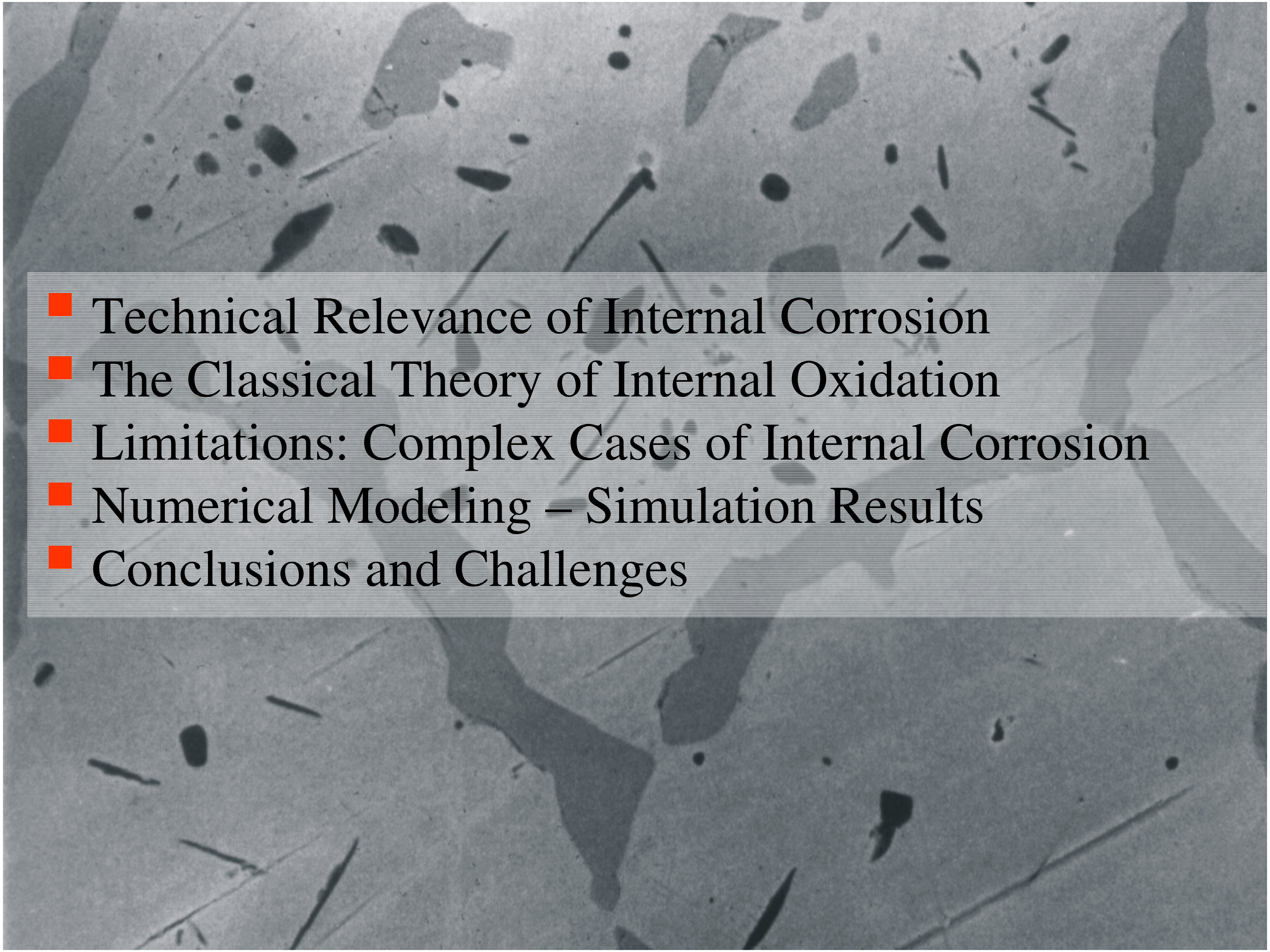
GTT-Technologies Annual Workshop, Herzogenrath, Germany,
May 17-19, 2006

People Involved

- Bronislava Gorr
- Vicente Braz da Trindade Filho
- Robert Orosz
- Udo Buschmann
- Dr. Shih Ying Chang
- Prof. Wolfgang Wiechert
- Prof. Hans-Jürgen Christ
- Dr. Klaus Hack
- and others

Financial Support

- DFG
- EU project OPTICORR

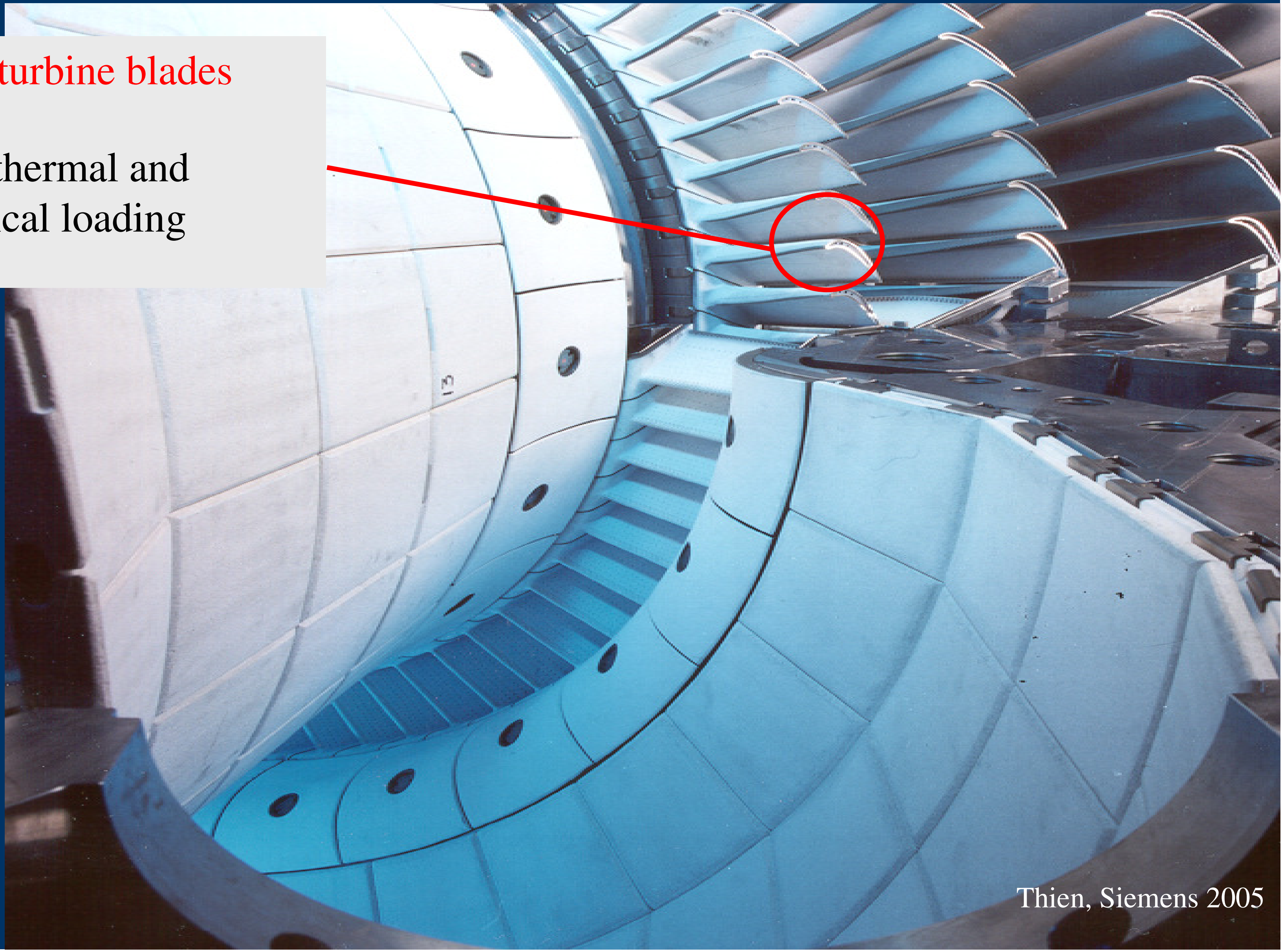


- Technical Relevance of Internal Corrosion
- The Classical Theory of Internal Oxidation
- Limitations: Complex Cases of Internal Corrosion
- Numerical Modeling – Simulation Results
- Conclusions and Challenges

Internal Corrosion of Gas Turbine Blades

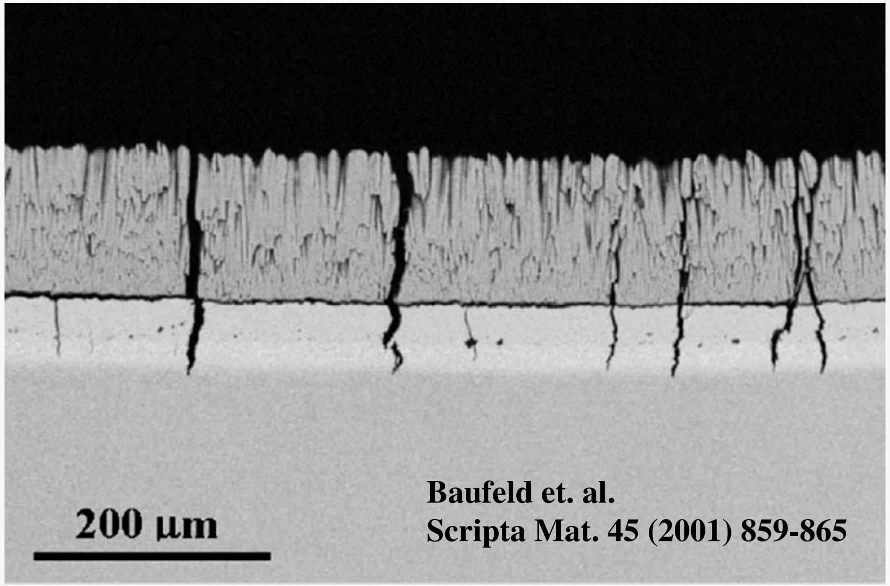
1st stage turbine blades

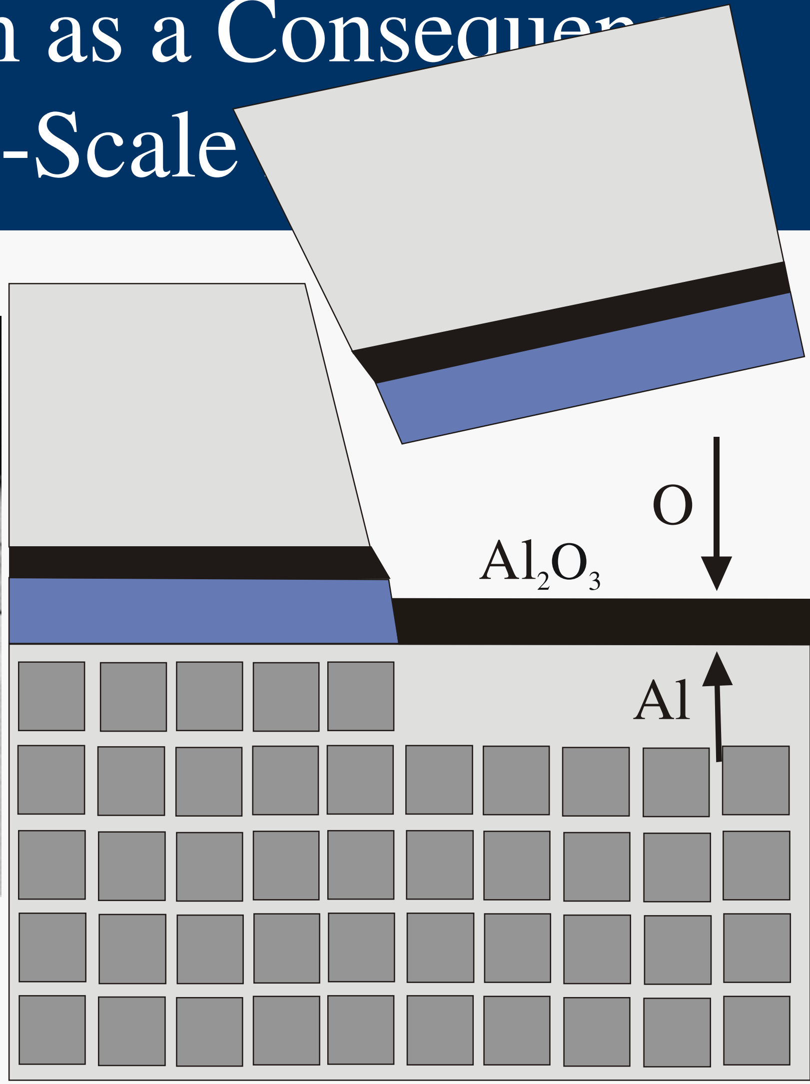
highest thermal and mechanical loading



Thien, Siemens 2005

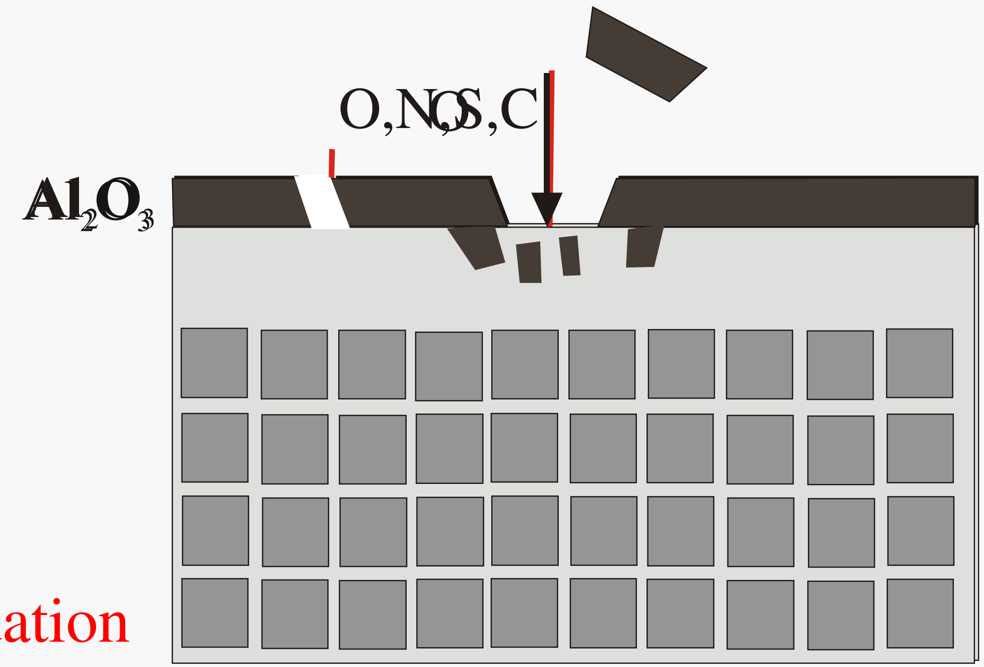
Internal Corrosion as a Consequen
of Protective-Scale





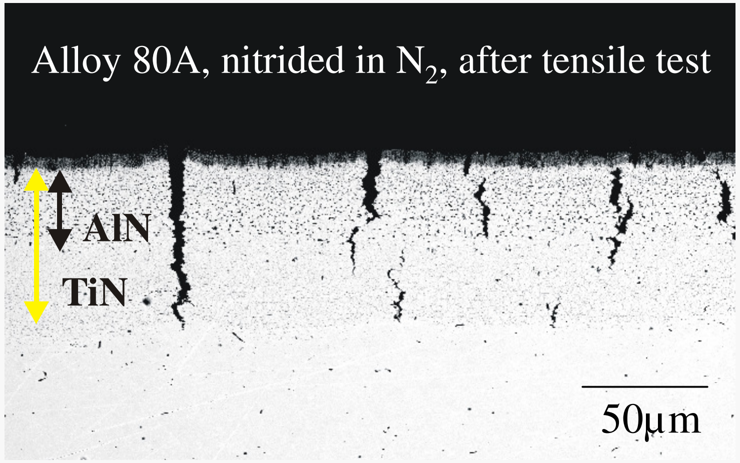
scale spalling/cracking
oxidation of the substrate

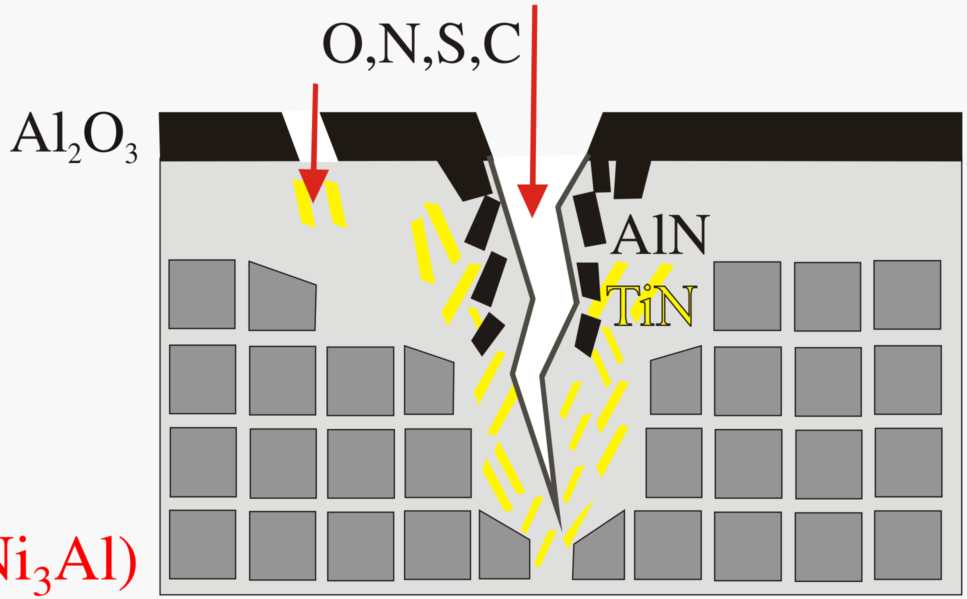
Internal Corrosion as a Consequence of Protective-Scale Failure



Al depletion
=>transition to internal oxidation
and internal corrosion, e.g., nitridation

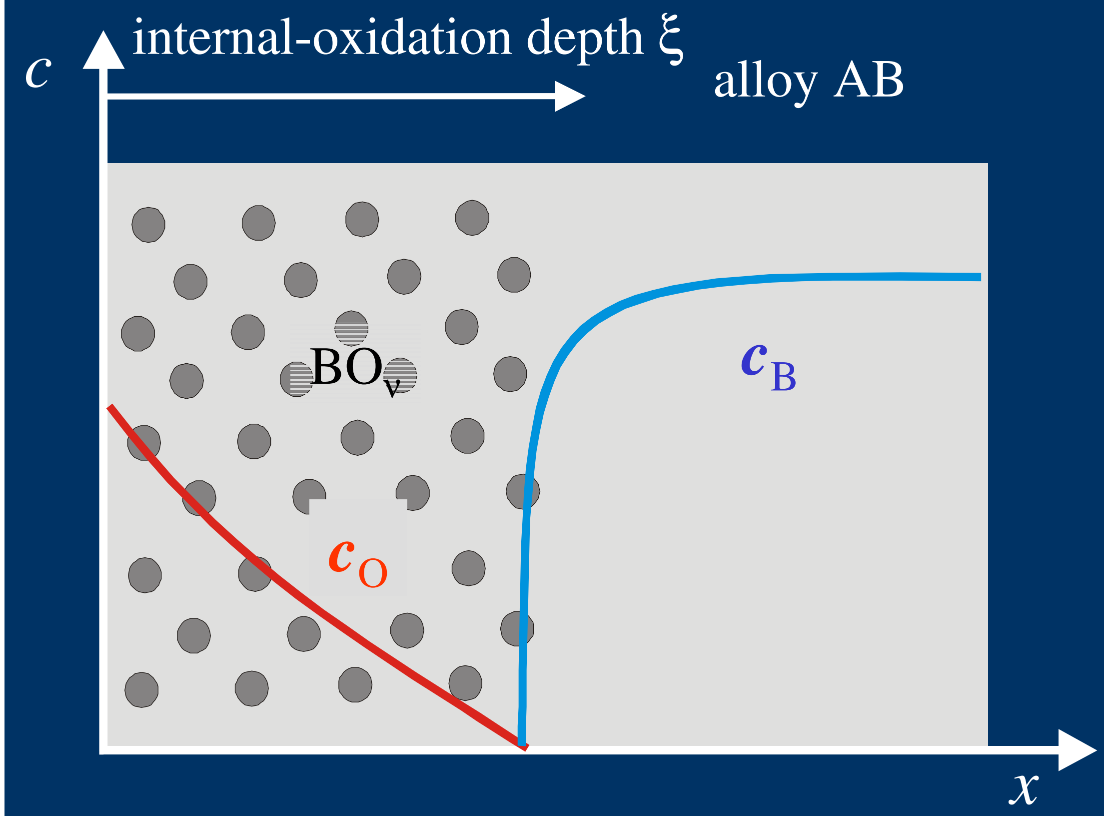
Internal Corrosion as a Consequence of Protective-Scale Failure





dissolution of the γ´ phase (Ni_3Al)
embrittlement + crack formation

Carl Wagner's Theory of Internal Oxidation



C. Wagner, Z. Elektrochemie, 21 (1959) 773
G. Böhm, M. Kahlweit, Acta Met., 12 (1964) 641

parabolic progress:

$$\xi(t) = 2\gamma\sqrt{D_O t}$$

diffusion PDEs:

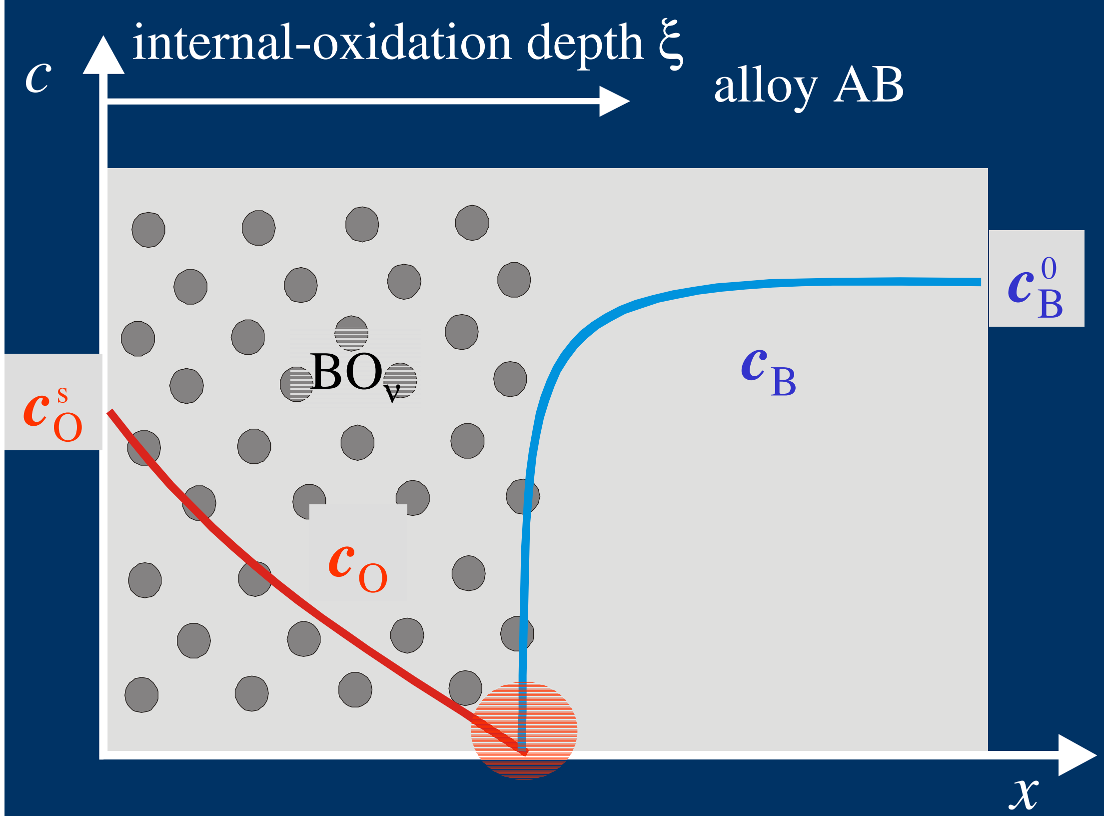
$$\frac{\partial c_{O/B}}{\partial t} = D_{O/B}\frac{\partial^2 c_{O/B}}{\partial x^2}$$

solution ($c_{O/B}(x=\xi) = 0$)

$$c_O = c_0^s\left(1 - \frac{\operatorname{erf}\left(x/2\sqrt{D_O t}\right)}{\operatorname{erf}\gamma}\right)$$

$$c_B = c_B^0\left(1 - \frac{\operatorname{erfc}\left(x/2\sqrt{D_B t}\right)}{\operatorname{erfc}\left(\gamma\sqrt{D_O/D_B}\right)}\right)$$

Carl Wagner's Theory of Internal Oxidation



diffusional flux at ξ

$$\lim_{\varepsilon \to 0} \left[-D_O \left(\frac{\partial c_O}{\partial x} \right)_{x=\xi-\varepsilon} = \nu D_B \left(\frac{\partial c_B}{\partial x} \right)_{x=\xi+\varepsilon} \right]$$

precipitation depth ξ:

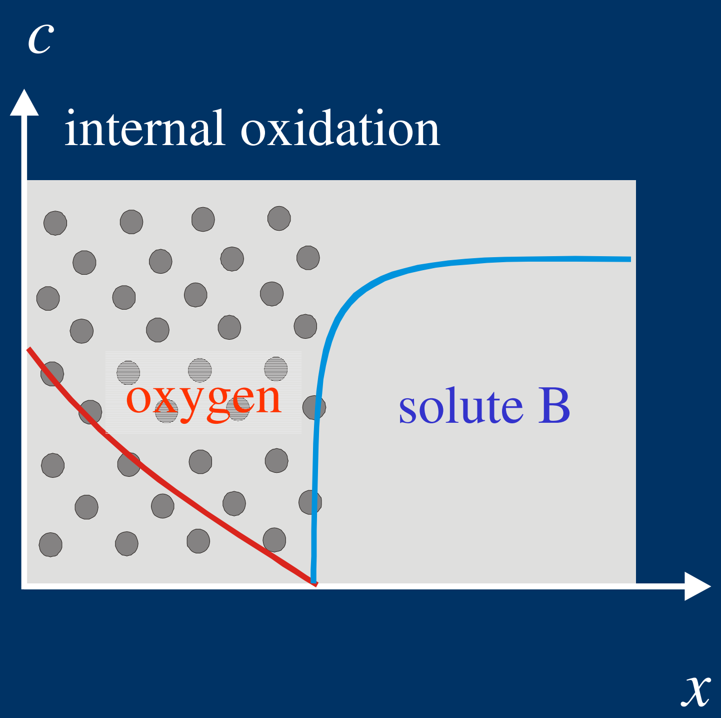
$$\xi^2 = \frac{\varepsilon 2 c_O^s D_O}{\nu c_B^0} t$$

for:

$$D_B / D_O << c_O^s / c_B^0 << 1$$

ε: labyrinth factor

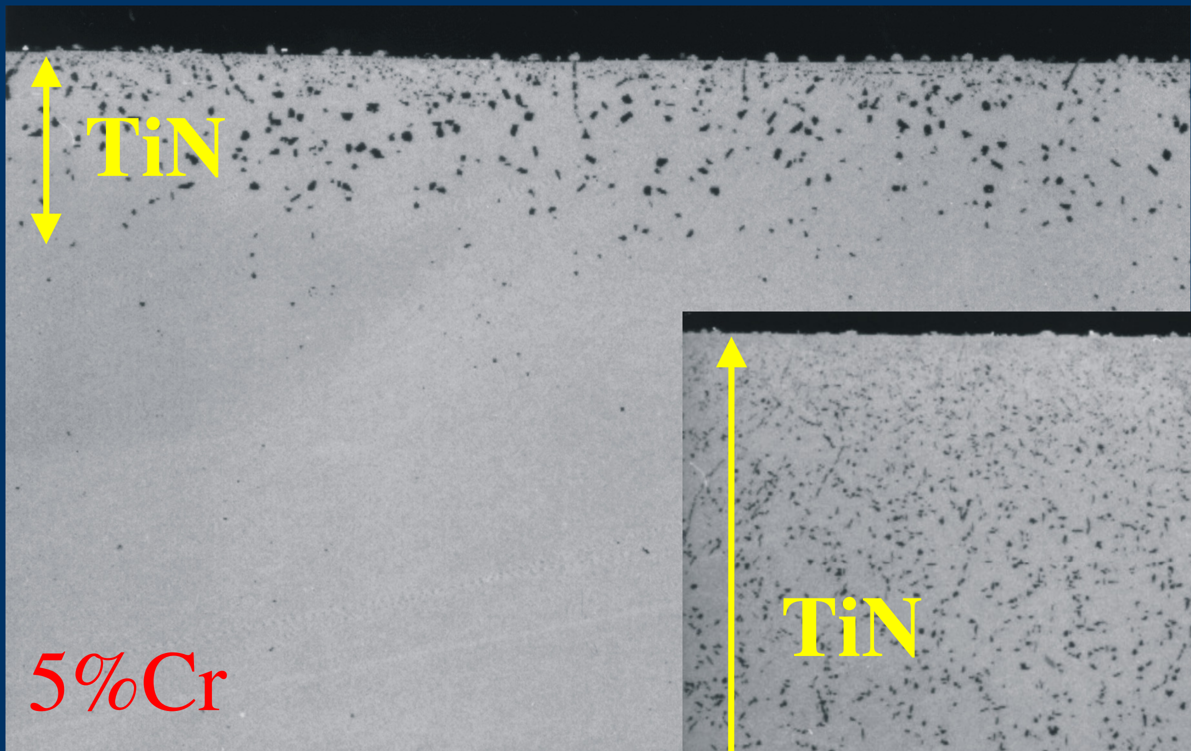
Carl Wagner's Theory of Internal Oxidation
Limitations:

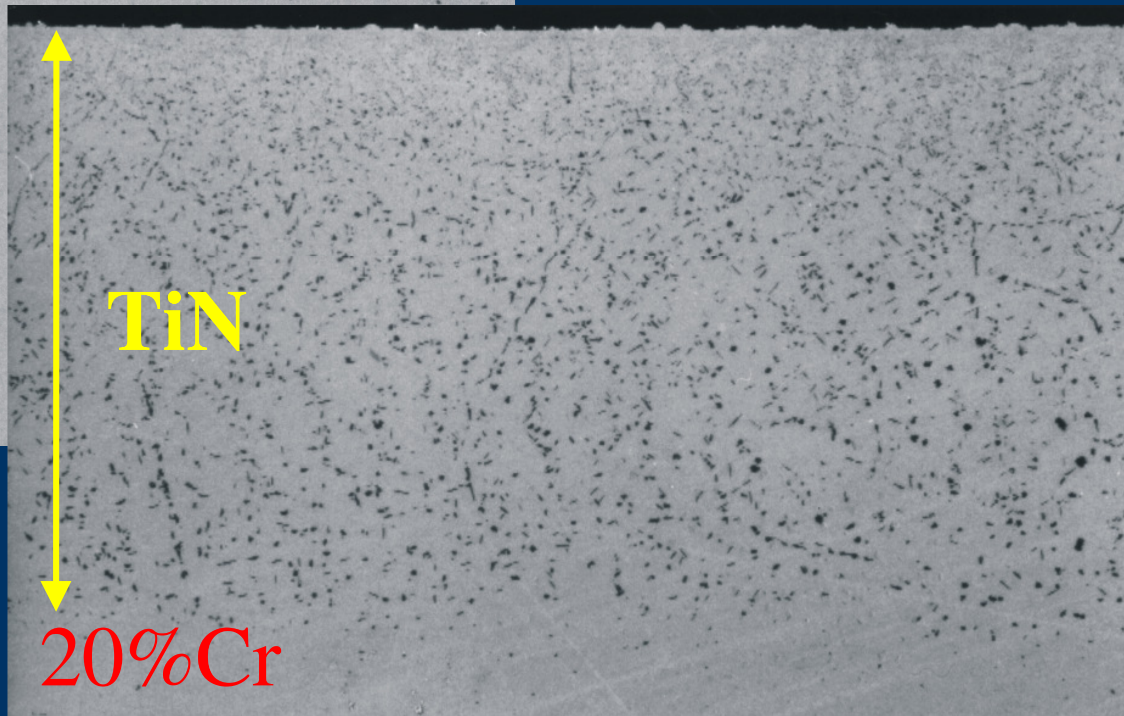


- only one type of precipitating compound
- of high thermodynamic stability (solubility product ≈ 0)
- constant surface concentration of corrosive species (no change in atmosphere or temperature)
- constant diffusivities of the reacting species

compare
J.L. Meijering, Adv. Met. Res., Vol. 5,. Wiley 1971, and D. L. Douglass, Ox. Met., 44 (1994) 81

Internal Nitridation of Ni-*x*Cr-2Ti Alloys



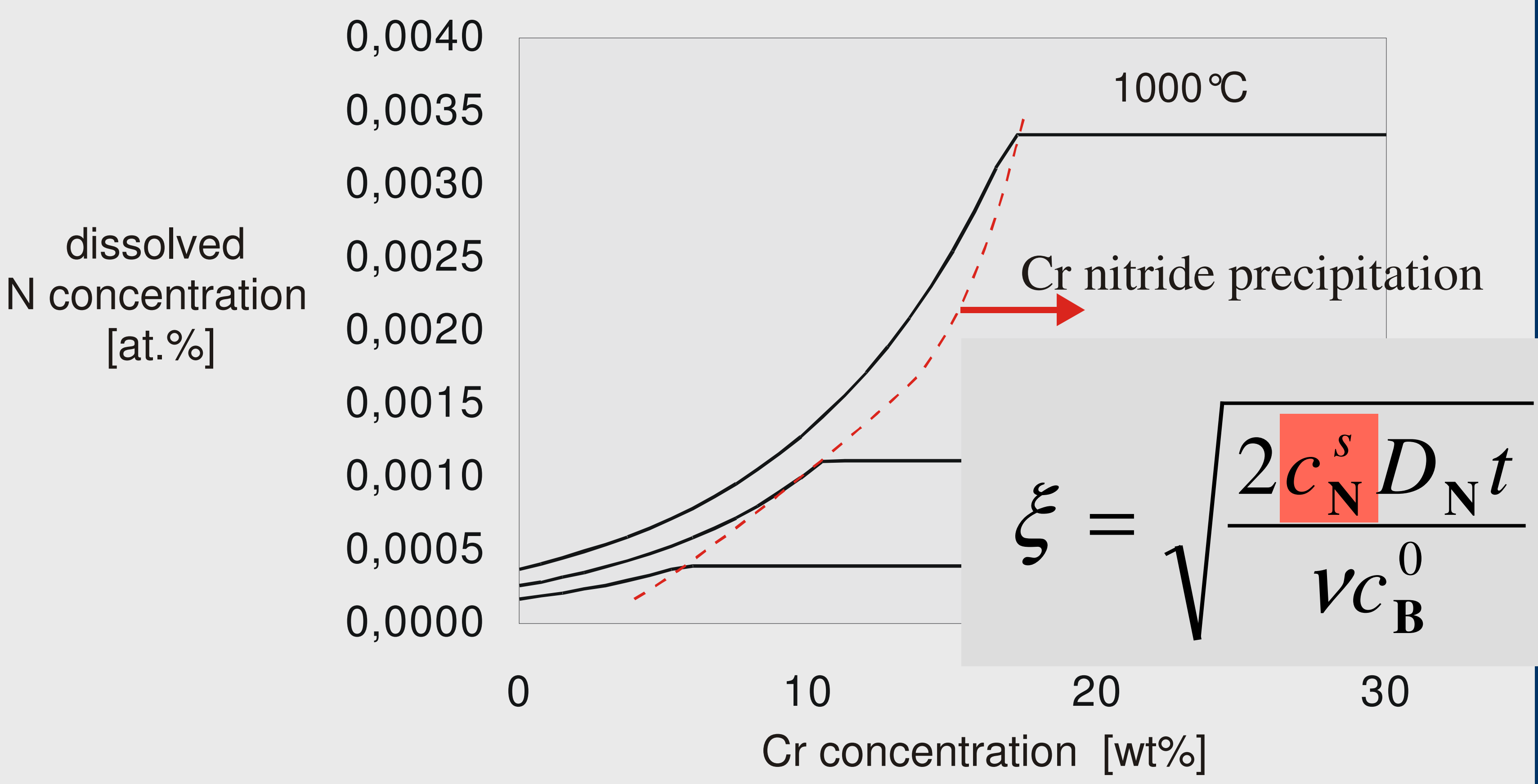


100μm

100h, 1100°C, N_2 atmosphere

Nitrogen Solubility in Ni-Cr Alloys

calculated by ChemApp + Ni-Cr-Al-Ti-N data set

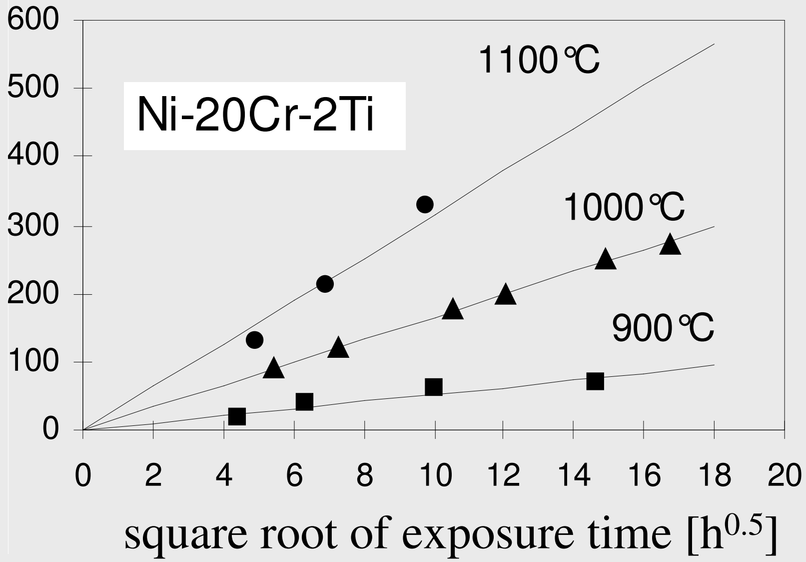


$$\xi = \sqrt{\frac{2 c_{\mathbf{N}}^{s} D_{\mathbf{N}} t}{\nu c_{\mathbf{B}}^{0}}}$$

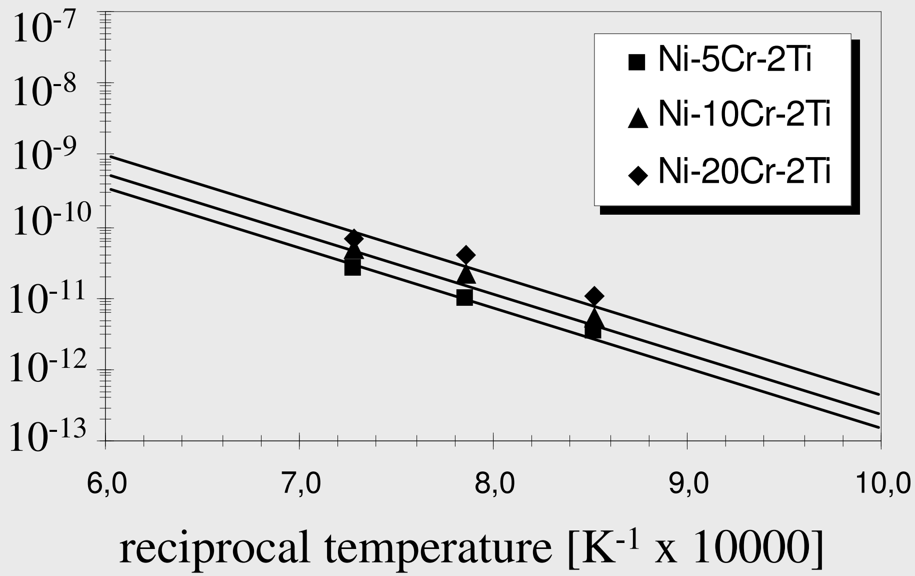
Cr enhances N solubility in Ni base alloys

Nitrogen Diffusion in Ni-Cr Alloys

precipitation depth ξ [μm]

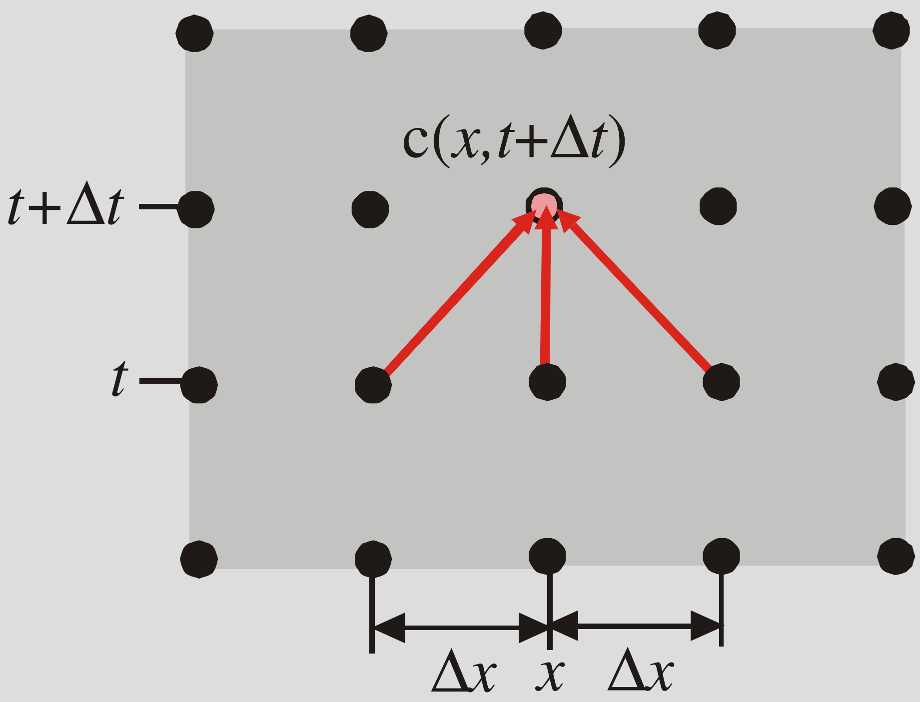


diffusion coefficient D_N [m²/s]



$$\xi = \sqrt{\frac{2 c_{\mathbf{N}}^{s} D_{\mathbf{N}} t}{\nu c_{\mathbf{B}}^{0}}}$$

Finite-Difference Simulation of Diffusion Processes



$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$

$$\left(\frac{\partial c}{\partial t}\right)_{x,t} \approx \frac{c(x,t+\Delta t)-c(x,t)}{\Delta t}$$

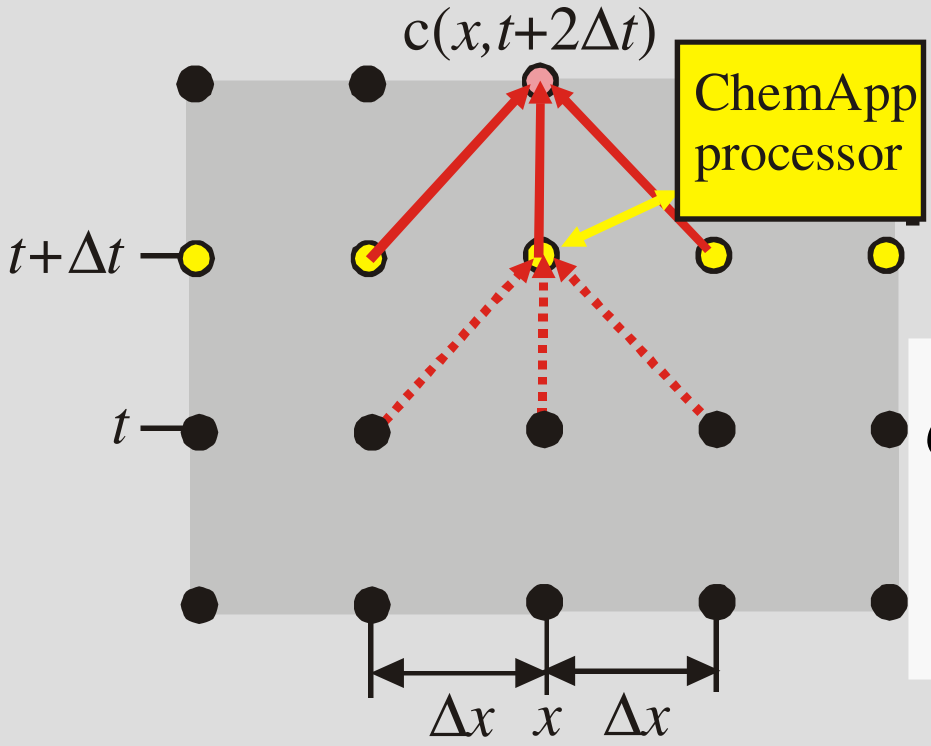
$$\left(\frac{\partial^2 c}{\partial t^2}\right)_{x,t} \approx$$

$$\approx D\frac{c(x+\Delta x,t)-2c(x,t)+c(x-\Delta x,t)}{\Delta x^2}$$

$$c_i(x,t+\Delta t) = c(x,t) + \frac{D\Delta t}{\Delta x^2}\left[c(x-\Delta x,t)-2c(x,t)+c(x+\Delta x,t)\right]$$

for all species i

Finite-Difference Simulation of Diffusion Processes + Precipitation



local thermodynamic equilibrium
ChemApp
+ tailored system data base

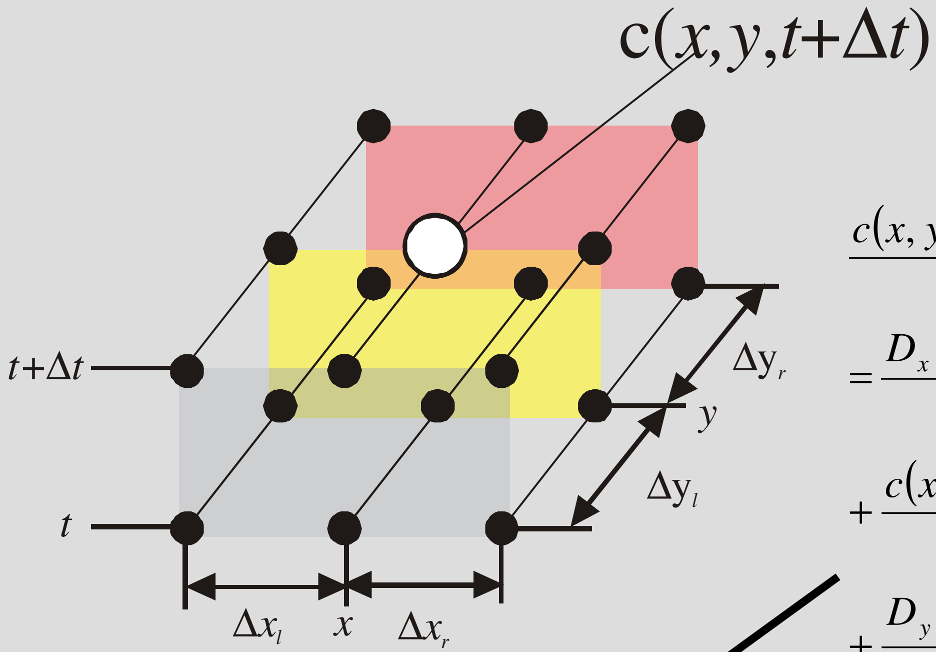
$$G = \sum_{j=1}^{m} c_j \left(G_{j,\text{pure}} + G_{j,\text{id}} + G_{j,\text{non-id}} \right)$$

= min !

$$c(x, t + \Delta t) = c(x,t) + \frac{D \Delta t}{\Delta x^2} \left[c(x - \Delta x, t) - 2c(x,t) + c(x + \Delta x, t) \right]$$

2D Finite-Difference Treatment of Diffusion

(Crank Nicolson implicit approach)



$$\frac{\partial c_{\mathrm{O/B}}}{\partial t} = D_{\mathrm{O/B}} \frac{\partial^2 c_{\mathrm{O/B}}}{\partial x^2}$$

$$\frac{c(x,y,t+\Delta t)-c(x,y,t)}{\Delta t}$$

$$= \frac{D_x(x,y)}{2}\left(\frac{c(x-\Delta x,y,t)-2c(x,y,t)+c(x+\Delta x,y,t)}{\Delta x_l(x,y)\cdot\Delta x_r(x,y)}\right.$$

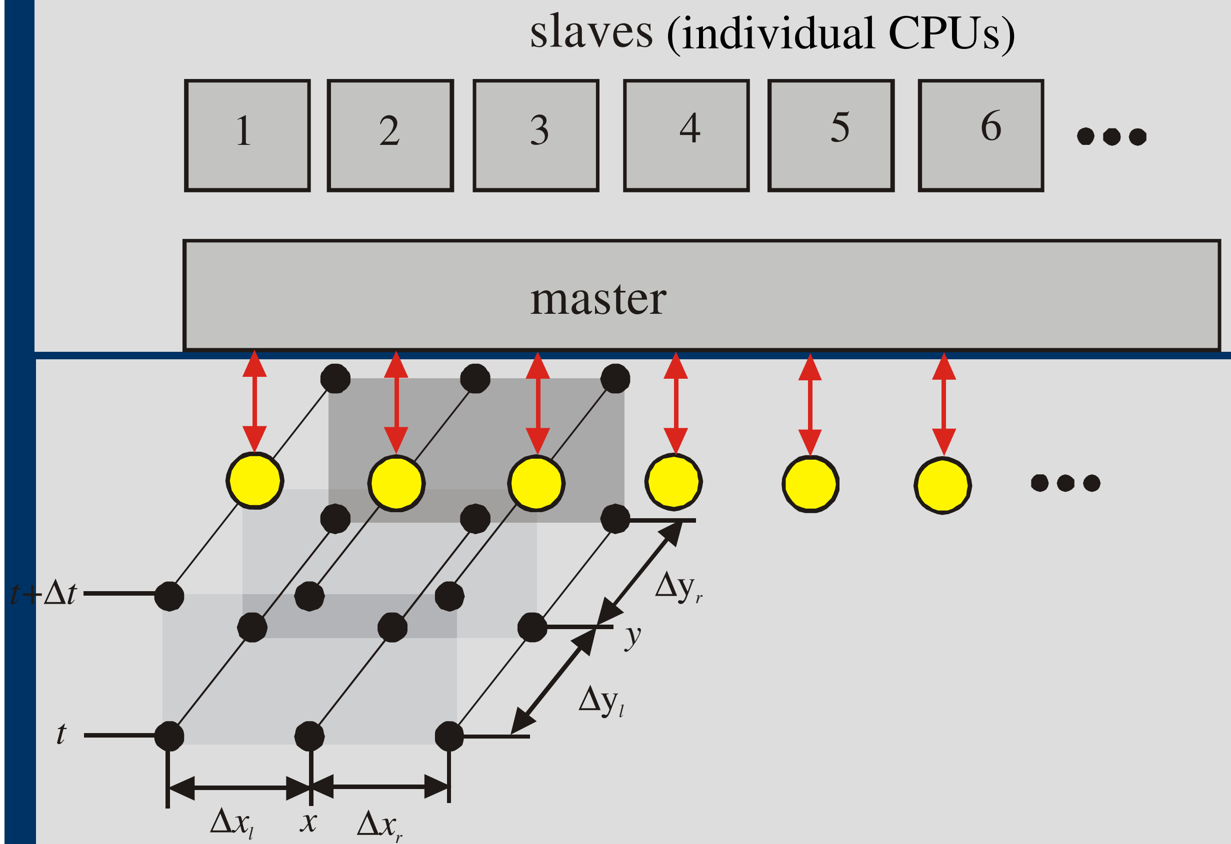
$$\left.+\frac{c(x-\Delta x,y,t+\Delta t)-2c(x,y,t+\Delta t)+c(x+\Delta x,y,t+\Delta t)}{\Delta x_l(x,y)\cdot\Delta x_r(x,y)}\right)$$

$$+ \frac{D_y(x,y)}{2}\left(\frac{c(x,y-\Delta y,t)-2c(x,y,t)+c(x,y+\Delta y,t)}{\Delta y_l(x,y)\cdot\Delta y_r(x,y)}\right.$$

$$\left.+\frac{c(x,y-\Delta y,t+\Delta t)-2c(x,y,t+\Delta t)+c(x,y+\Delta y,t+\Delta t)}{\Delta y_l(x,y)\cdot\Delta y_r(x,y)}\right)$$

variable diffusion coefficient
(e.g., location-dependent)

2D Finite-Difference Treatment of Diffusion
(Crank Nicolson implicit approach)



PVM + ChemApp
(parallel virtual machine)

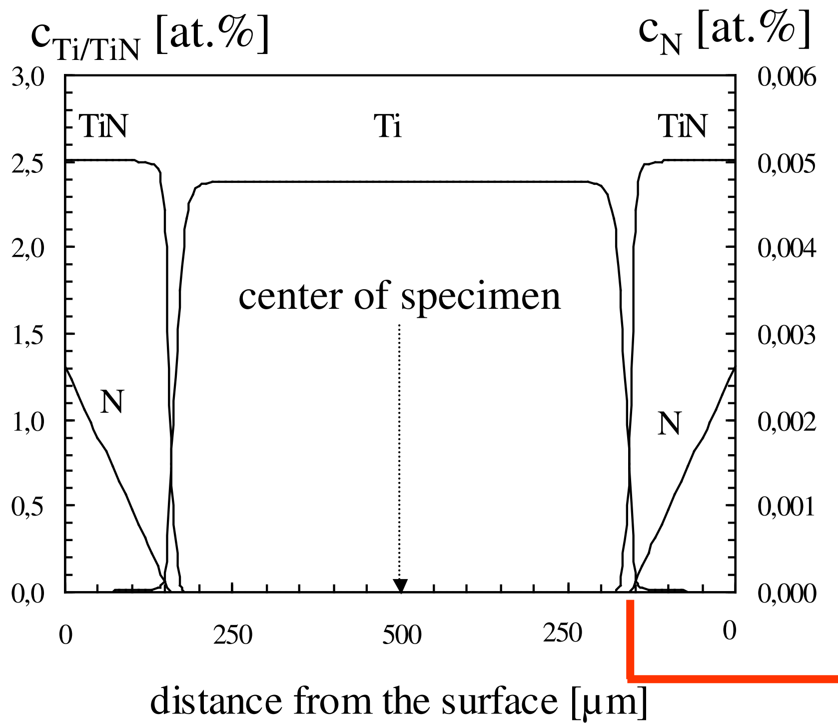
- ChemApp / system data base initialisation
- distributed equilibrium calculations

MatLab – main program

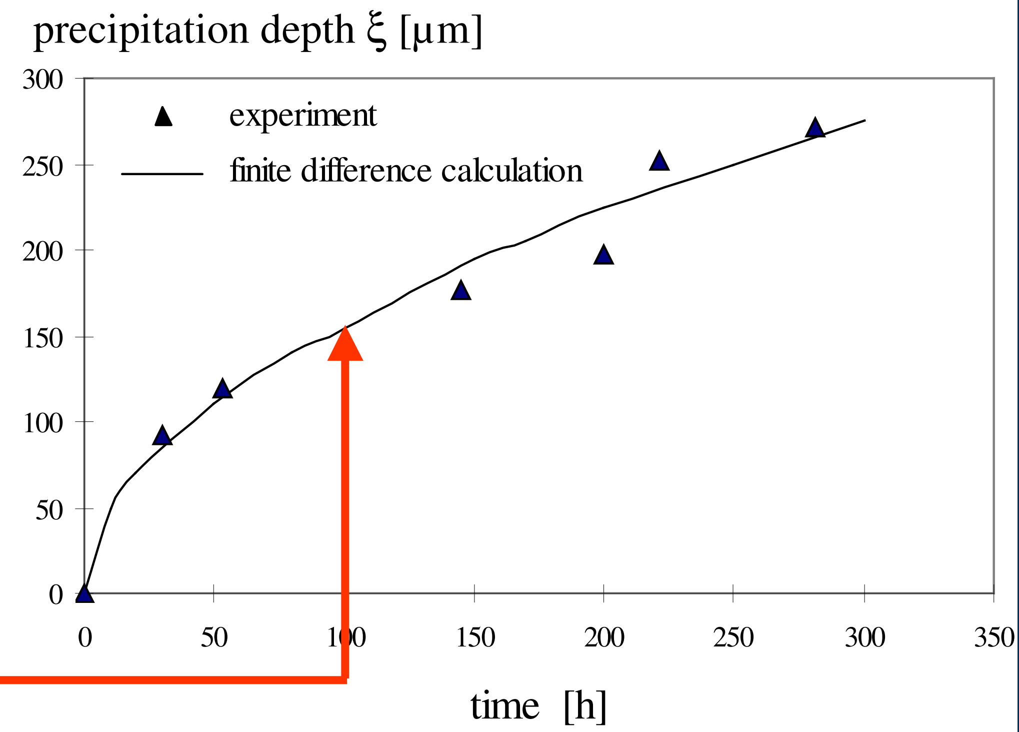
- FD diffusion calculation
- user interface

Computer Simulation of Internal Nitridation (TiN in Ni-20Cr-2Ti)

concentration profiles:

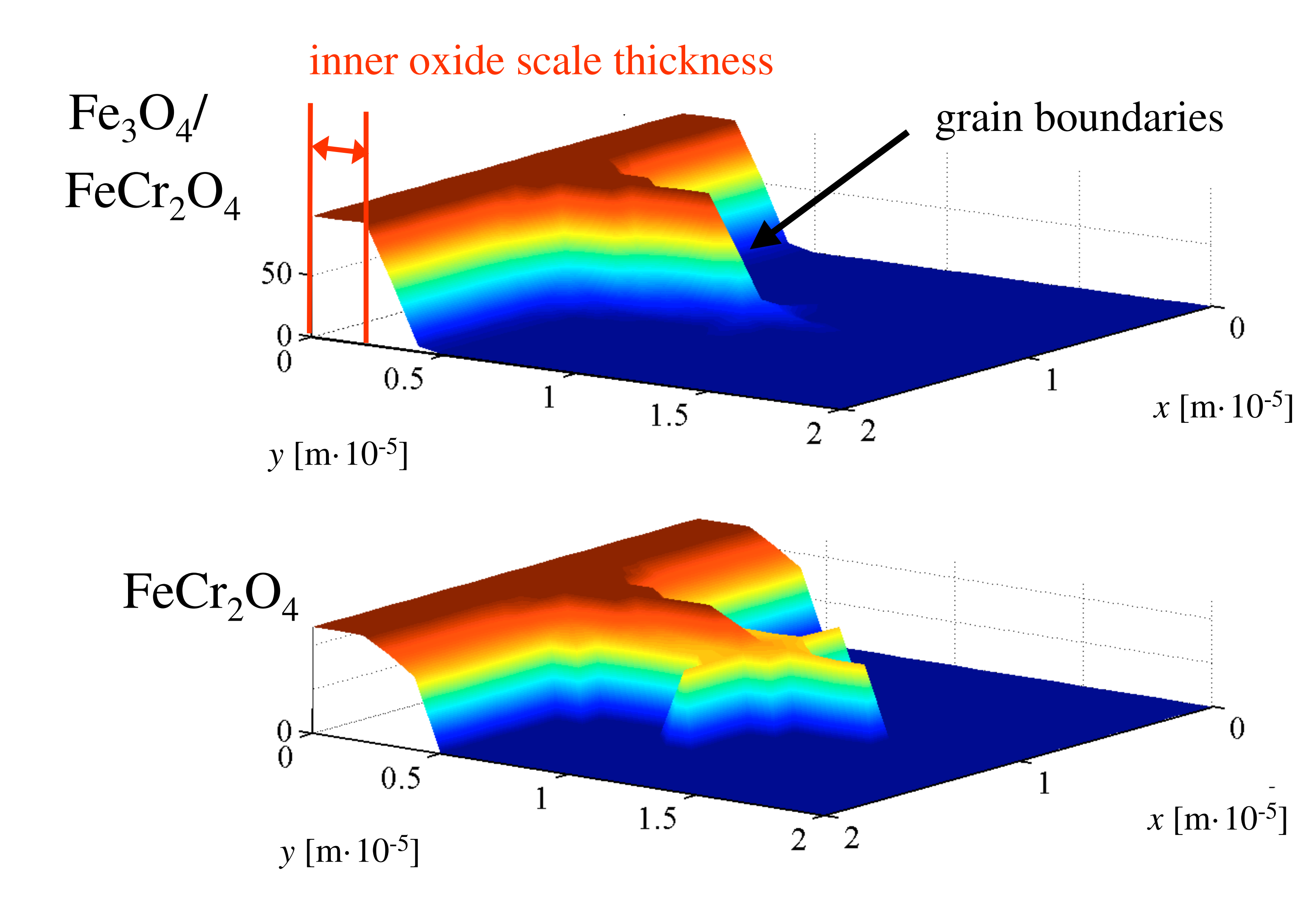


internal corrosion kinetics:

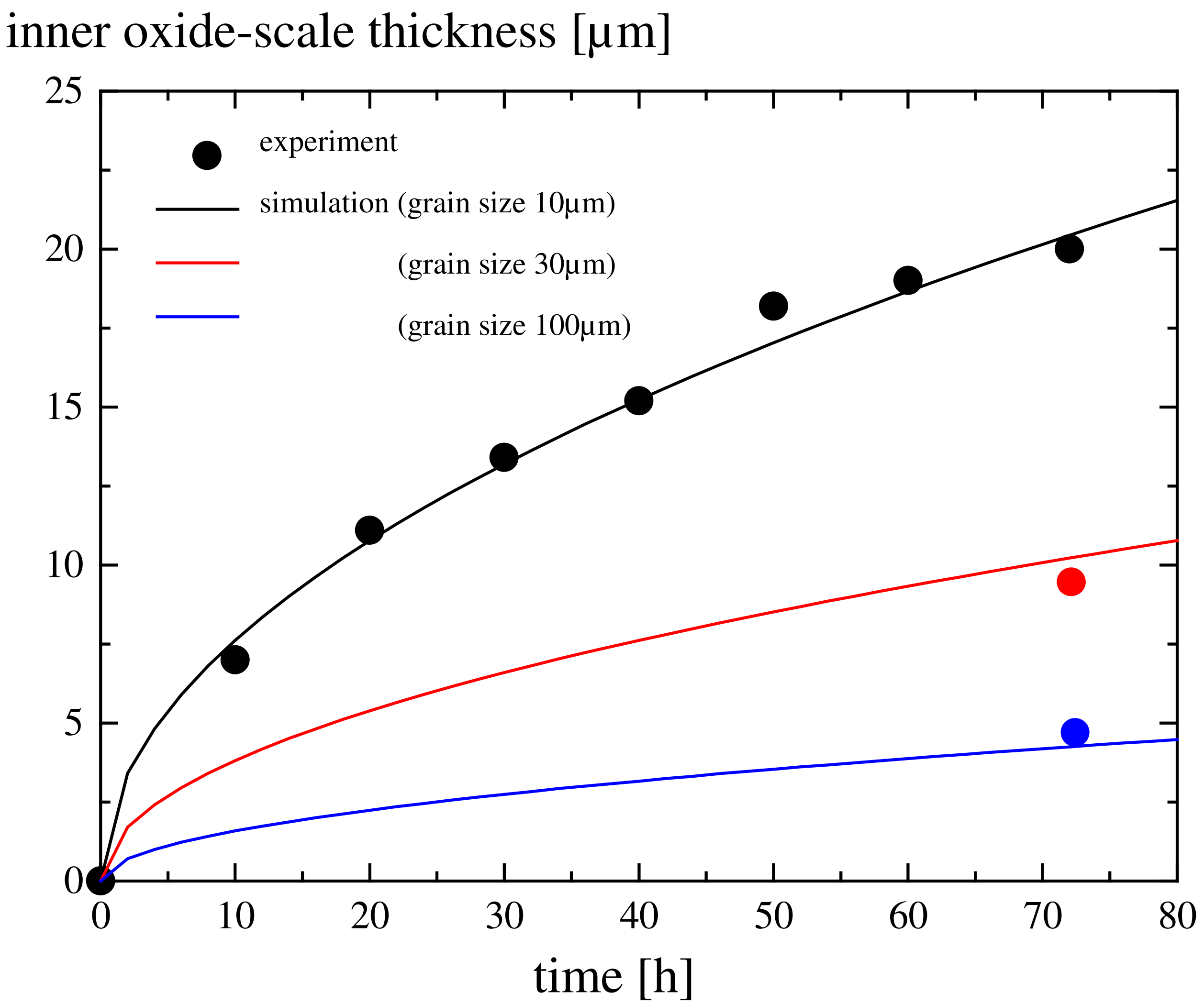


(1000°C, 100h, N_2 atmosphere)

2D Simulation of Internal Oxidation



Inner Oxide-Scale Growth (X60)



(1.43wt% Cr, 550°C, air)

Conclusions and Challenges

- internal corrosion may result in a strong deterioration of material properties (near-surface embrittlement, γ´dissolution)

- internal corrosion at lower temperatures governed by GB diffusion e.g. grain size effect of inner-oxide-scale growth on low-Cr steels

→

numerical model combining
-2D finite difference approach
-ChemApp + system data

flexible, sufficiently fast (parallel computation)