Interdisciplinary Research for
Sustainable Energy and Process Technologies

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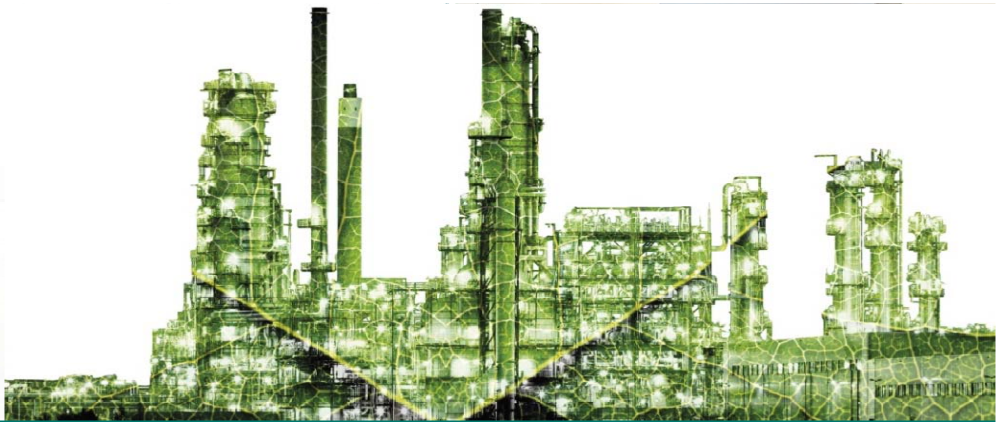


Michael Schütze

Mechanical Limits to the Protective Effect of Oxide Scales on High Temperature Materials

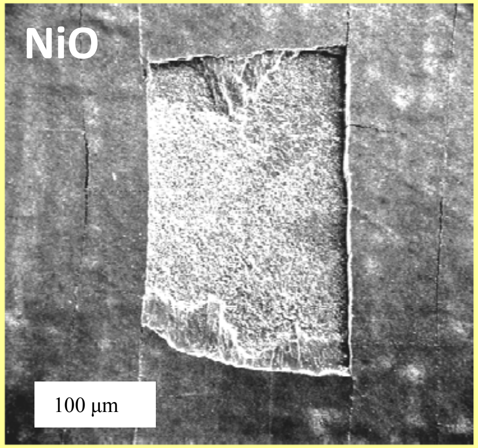
Materials
Chemical Engineering
Biotechnology

www.dechema-dfi.de

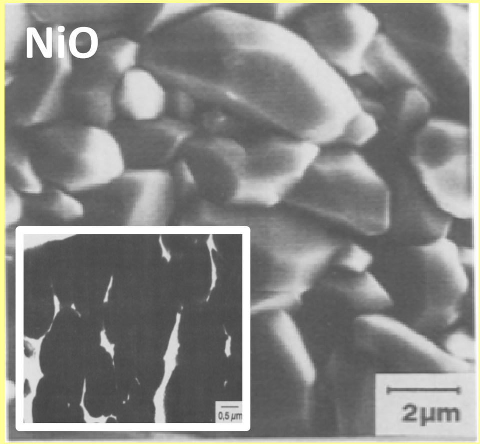
Frankfurt am Main, Germany

Stresses ➡ “Mechanical“ Oxide Scale Failure

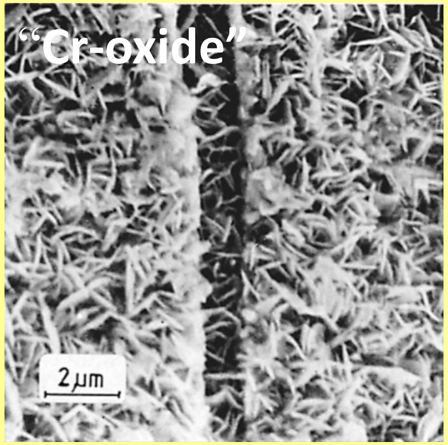
Spalling

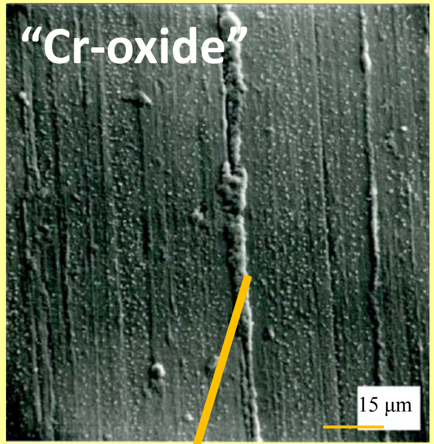


Micro Cracking

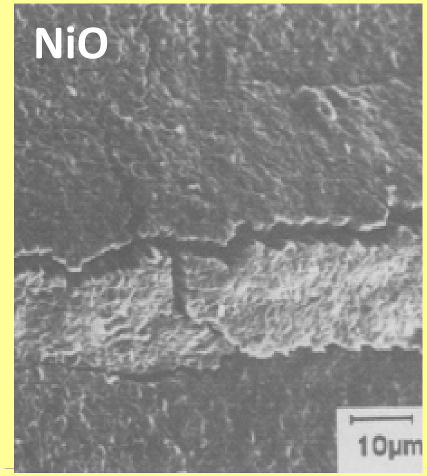


Through-Scale Cracking

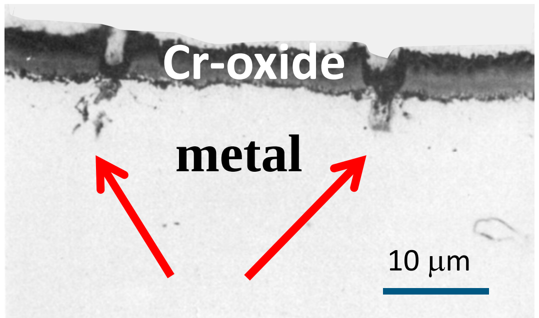




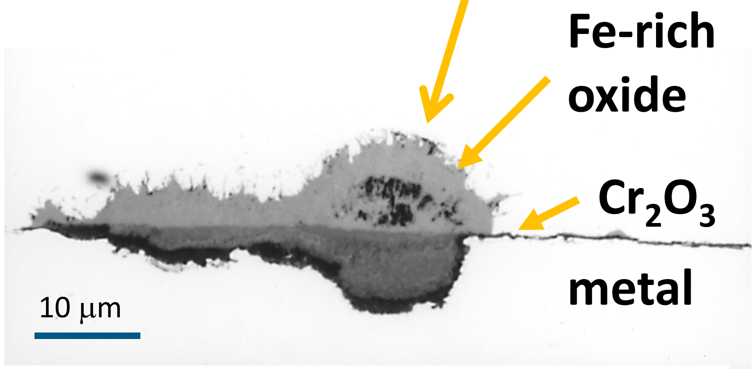
Delamination



Consequences ➡ **Increased Metal Consumption**
Loss of Protective Effect



Subsurface Attack

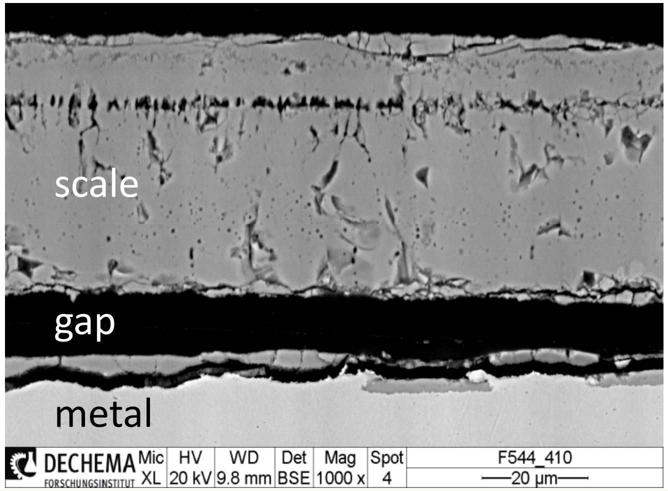


Breakaway Oxidation

Role of Scale Thickness

$$\boxed{\varepsilon_c \propto \frac{1}{d}}$$

d = scale thickness

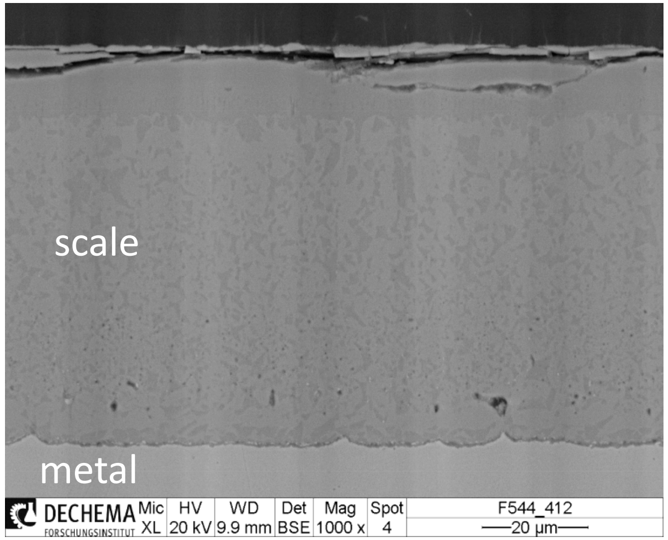


synth. air (dry)

scale thickness
$d \approx 52$ µm

physical defects
$c_\perp \approx 22$ µm

Cross-sections of Fe-Oxide scales on Fe (99.5%) after 16hr isothermal oxidation at 650°C in dry and humid atmosphere, respectively.



Synth. air & 10Vol. % H_2O

scale thickness
$d = 73$ µm

physical defects
$c_\perp \approx 5$ µm

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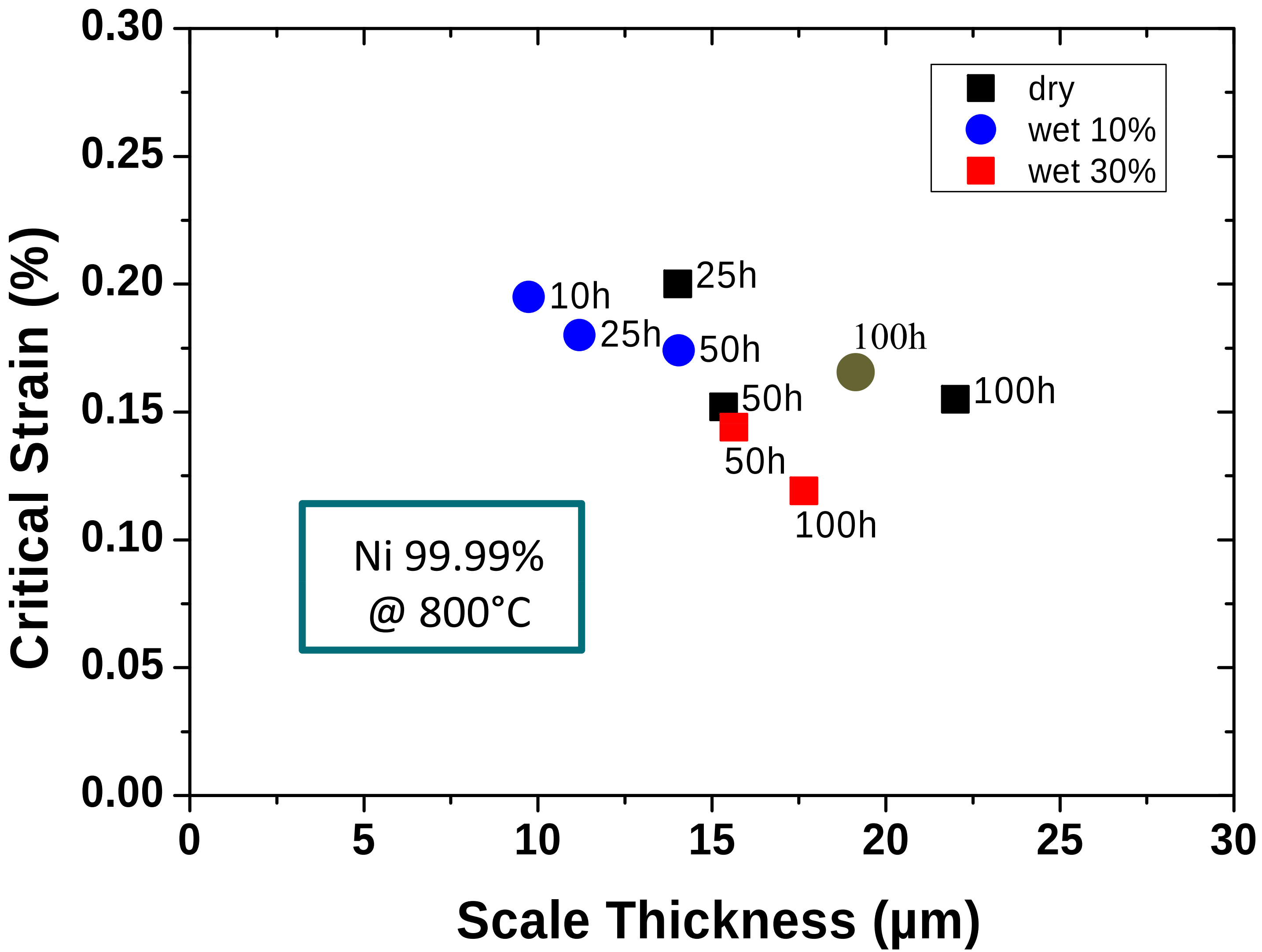
RT Critical Strain (Tension) vs. Scale Thickness



Models for Scale Failure

parameters influencing mechanical properties of scales

Promote scale failure

a) Through scale cracking (tensile)

$$\varepsilon_c^t = \frac{K_{Ic}}{f \cdot E_{ox}\sqrt{\Pi c}}$$

$K_{Ic}\downarrow$

$E_{ox}\uparrow\ c\uparrow$

b) Interfacial crack growth (compressive)

$$\varepsilon_c^i = \frac{K_{Ic}}{f\sqrt{\Pi c}} \cdot \frac{(1 + r/d)\cdot(1+\upsilon)}{2E_{ox}}$$

$K_{Ic}\downarrow\ r\downarrow\ \upsilon\downarrow$

$E_{ox}\uparrow\ c\uparrow\ d\uparrow$

c) Spalling (compressive)

i)

$$\varepsilon_c^t = \frac{\sqrt{3}\,K_{Ic}}{f \cdot E_{ox}\sqrt{\Pi c}}$$

$K_{Ic}\downarrow$

$E_{ox}\uparrow\ c\uparrow$

ii)

$$\varepsilon_c^s = \sqrt{\frac{2\gamma_0}{dE_{ox}(1-\nu)}}$$

$$\gamma_0 = \gamma_i\left(1 + \frac{0.1E_{ox}}{2\gamma_i}\cdot\frac{r^2}{\lambda}\right)\left(\frac{A_0 - A_{sep}}{A_0}\right)$$

$E_{ox}\uparrow\ d\uparrow$

$\gamma_i\downarrow\ r\downarrow\ \gamma_0\downarrow$

$\lambda\uparrow\ A_{sep}\uparrow$

$$\boxed{E = (1 - \rho)^n}$$

$$\boxed{K_{Ic} = \sqrt{2\cdot\gamma_i\cdot E}}$$

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physical defect dimensions(c)

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$E_{ox}\uparrow$ $c\uparrow$ $d\uparrow$

c = f(d) A_{sep} = f(c)

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$\gamma_i\downarrow$ $r\downarrow$ $\gamma_0\downarrow$

$\lambda\uparrow$ $A_{sep}\uparrow$

$$E = (1-\rho)^n$$

$$K_{Ic} = \sqrt{2\cdot\gamma_i\cdot E}$$

geometrical dimensions

Models for Scale Failure

parameters influencing mechanical properties of scales

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$$\boxed{E = (1 - \rho)^n}$$

$$\boxed{K_{Ic} = \sqrt{2 \cdot \gamma_i \cdot E}}$$

mechanical properties
→ material constants

material properties constants ➡ η^i

	tension	compression
interfacial cracking / beginning of exfoliation	$\eta^{\mathrm{if}} = \frac{K_{Ic}(1+\nu)}{2fE\sqrt{\pi c_0}}$	$\eta^{\mathrm{if-}} = -\frac{K_{Ic}(1+\nu)}{2fE\sqrt{\pi c_0}}$
through cracking / spalling	$\eta^{t} = \frac{K_{Ic}}{fE\sqrt{\pi c_0}}$	$\eta^{sh} = -\frac{K_{Ic}\sqrt{3}}{fE\sqrt{\pi c_0}}$

c – defect size, c_0 – 1µm for normalizing, E – scale Young´s modulus, f – defect geometry factor,
r – interface roughness, ν – Poisson ratio, K_{Ic} – scale fracture toughness

➡ η^i **as a materials constant for the mechanical oxide properties (E , K_c , ν)**

Further reading in M. Schütze , P. Tortorelli , I. Wright , Oxid. Met. 2010

Failure Strain as a Function of Geometrical Dimensions and Mechanical Oxide Properties

$$\varepsilon_c = \frac{\eta}{\omega} \qquad \omega \approx \sqrt{\frac{c}{c_0}} \qquad \Rightarrow \qquad \boxed{\varepsilon_c \approx \frac{\eta}{\sqrt{c/c_0}}}$$

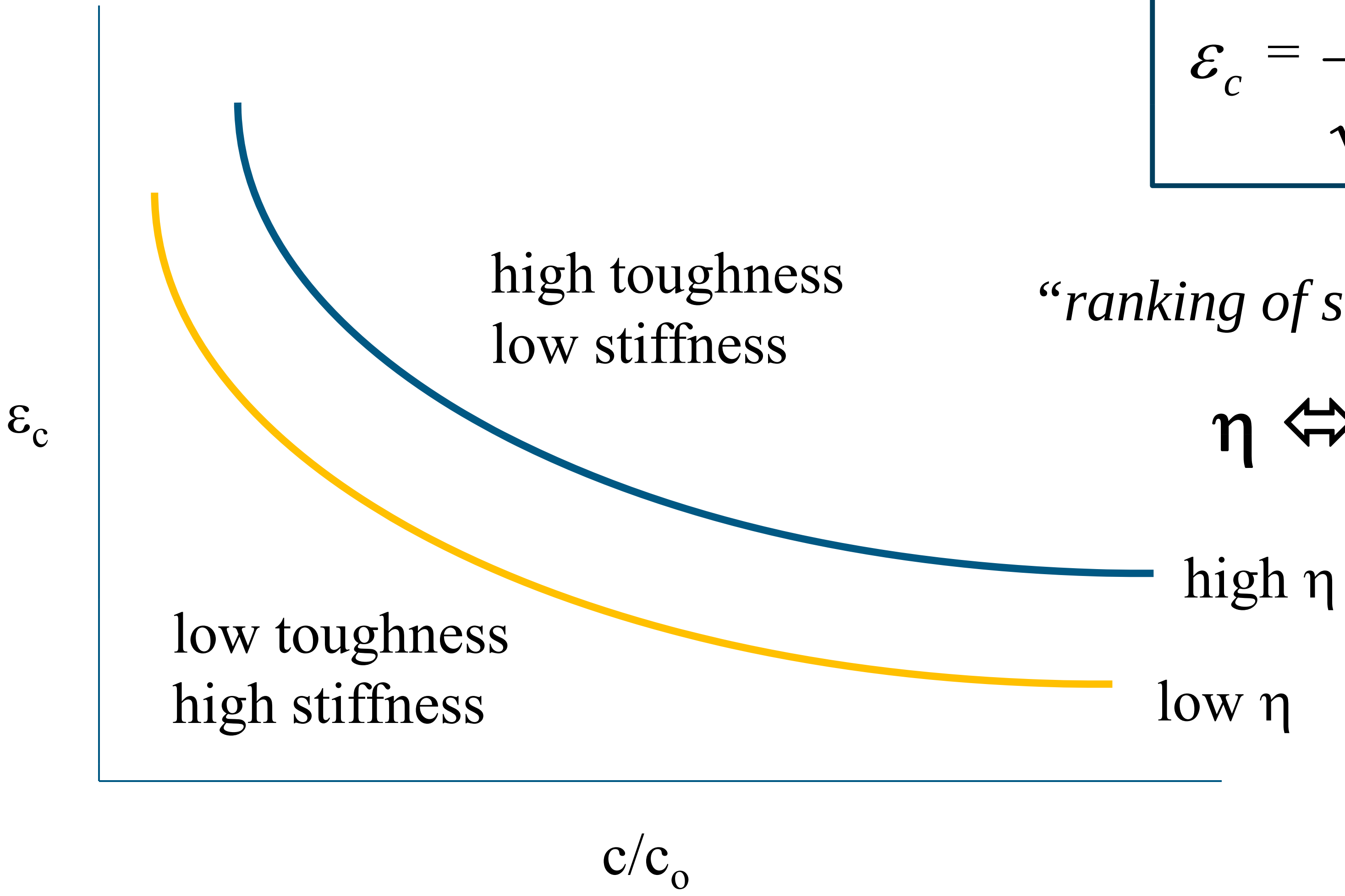
Mechanical properties parameters summarized in η

Geometrical dimension parameters summarized in ω

Highest variable impact from defect size c

η as a combined factor for the mechanical properties

$$\varepsilon_c = \frac{\eta}{\sqrt{c/c_0}}$$

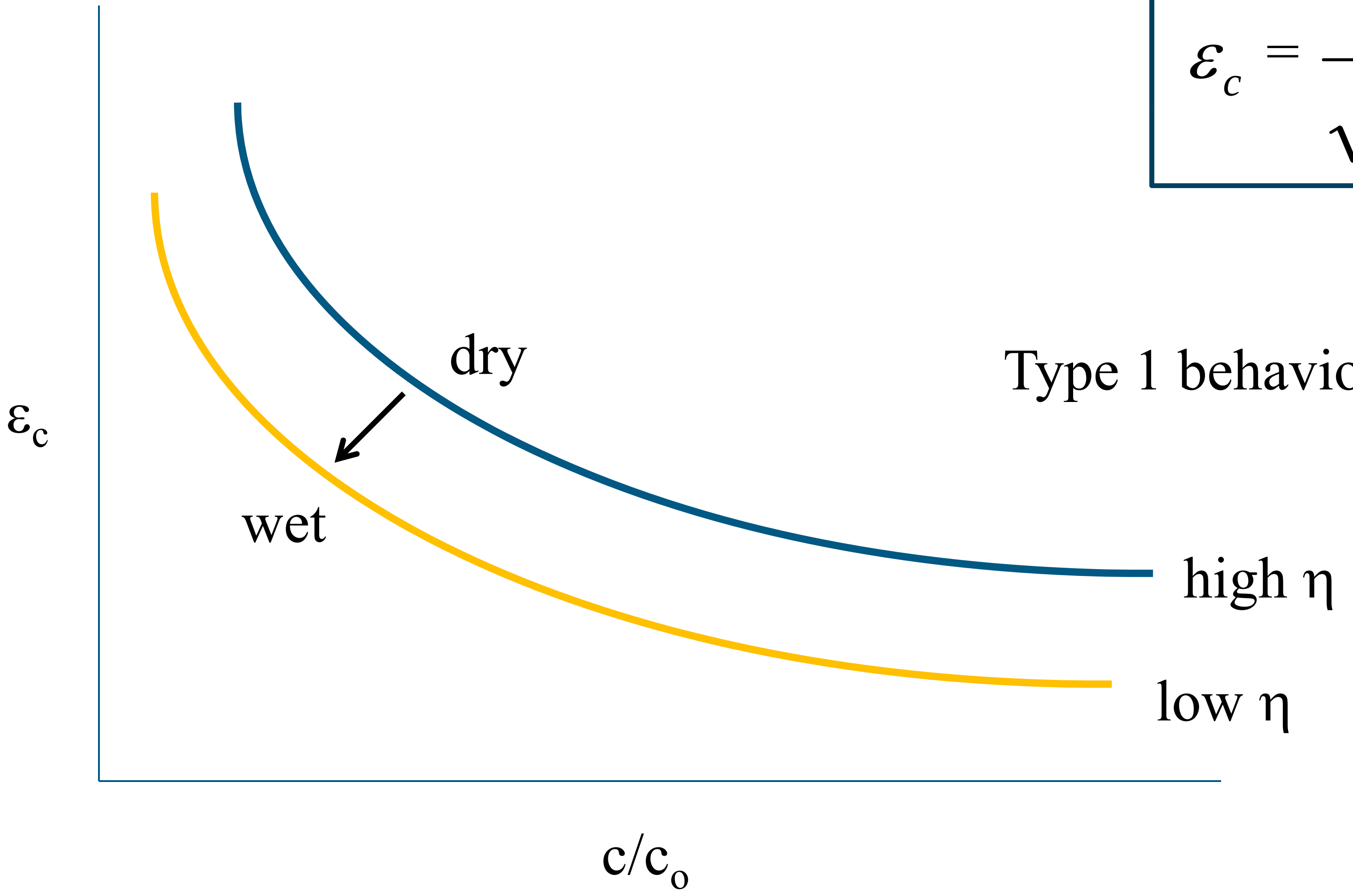


“ranking of scale phases”

$$\boldsymbol{\eta \Leftrightarrow k_p}$$

Influence of the environment on the mechanical properties

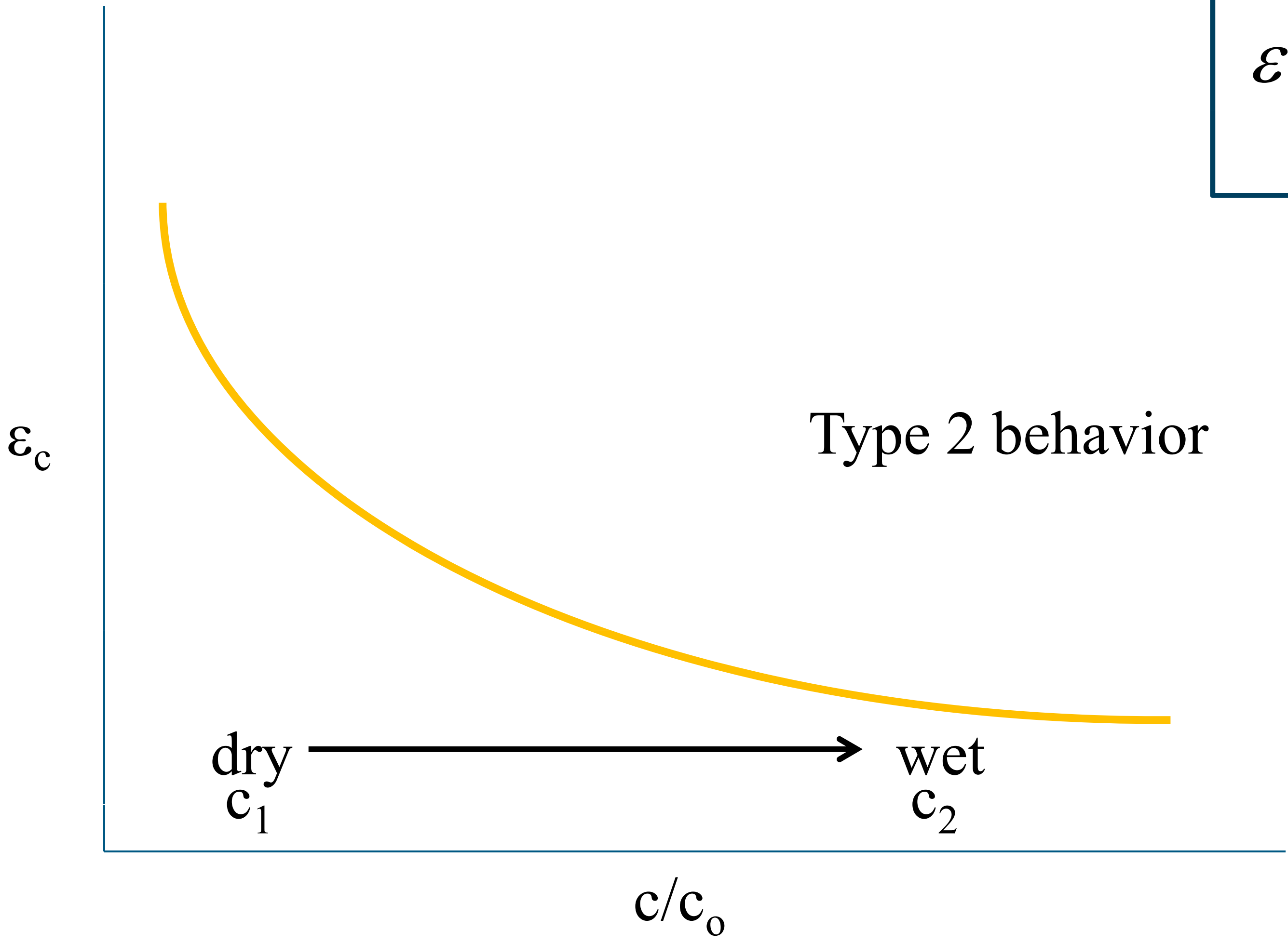
$$\varepsilon_c = \frac{\eta}{\sqrt{c/c_0}}$$



Type 1 behavior

Influence of the environment on the mechanical properties

$$\varepsilon_c = \frac{\eta}{\sqrt{c/c_0}}$$

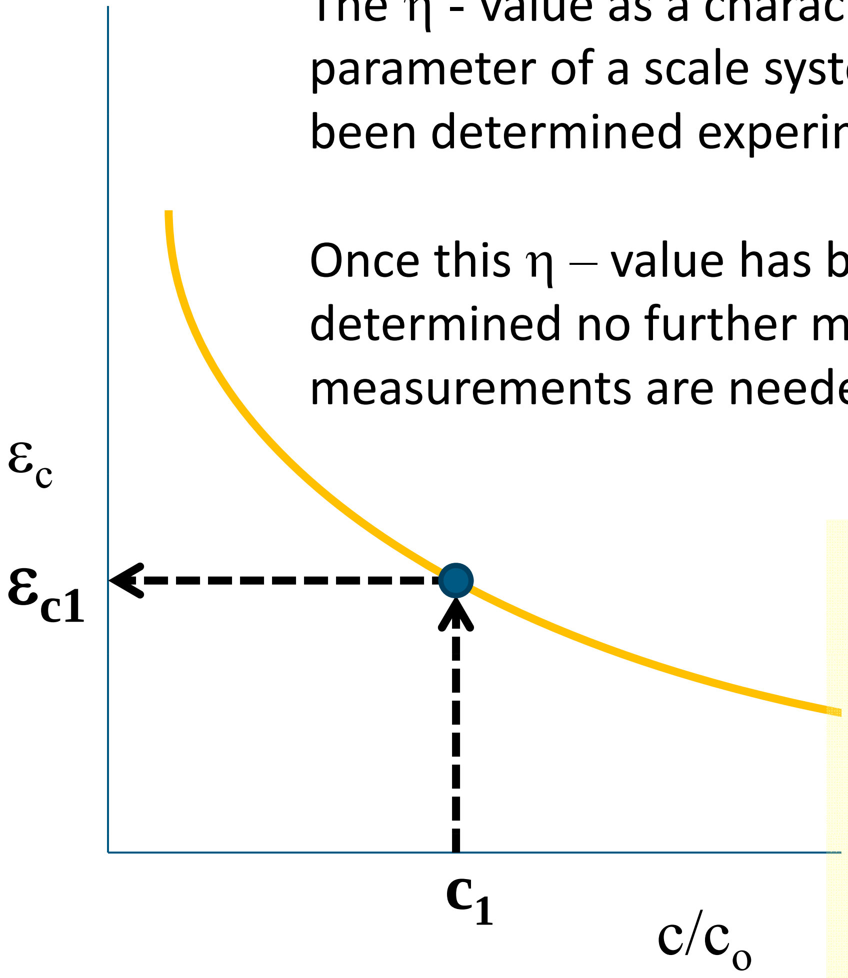


Quantitative assessment of failure strain without mechanical test

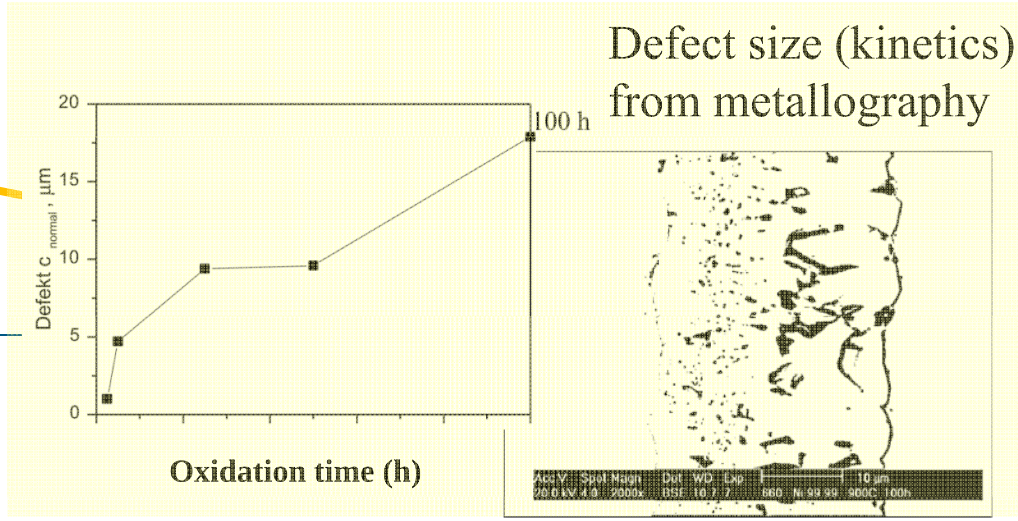
The η - value as a characteristic parameter of a scale system has been determined experimentally

Once this η – value has been determined no further mechanical measurements are needed

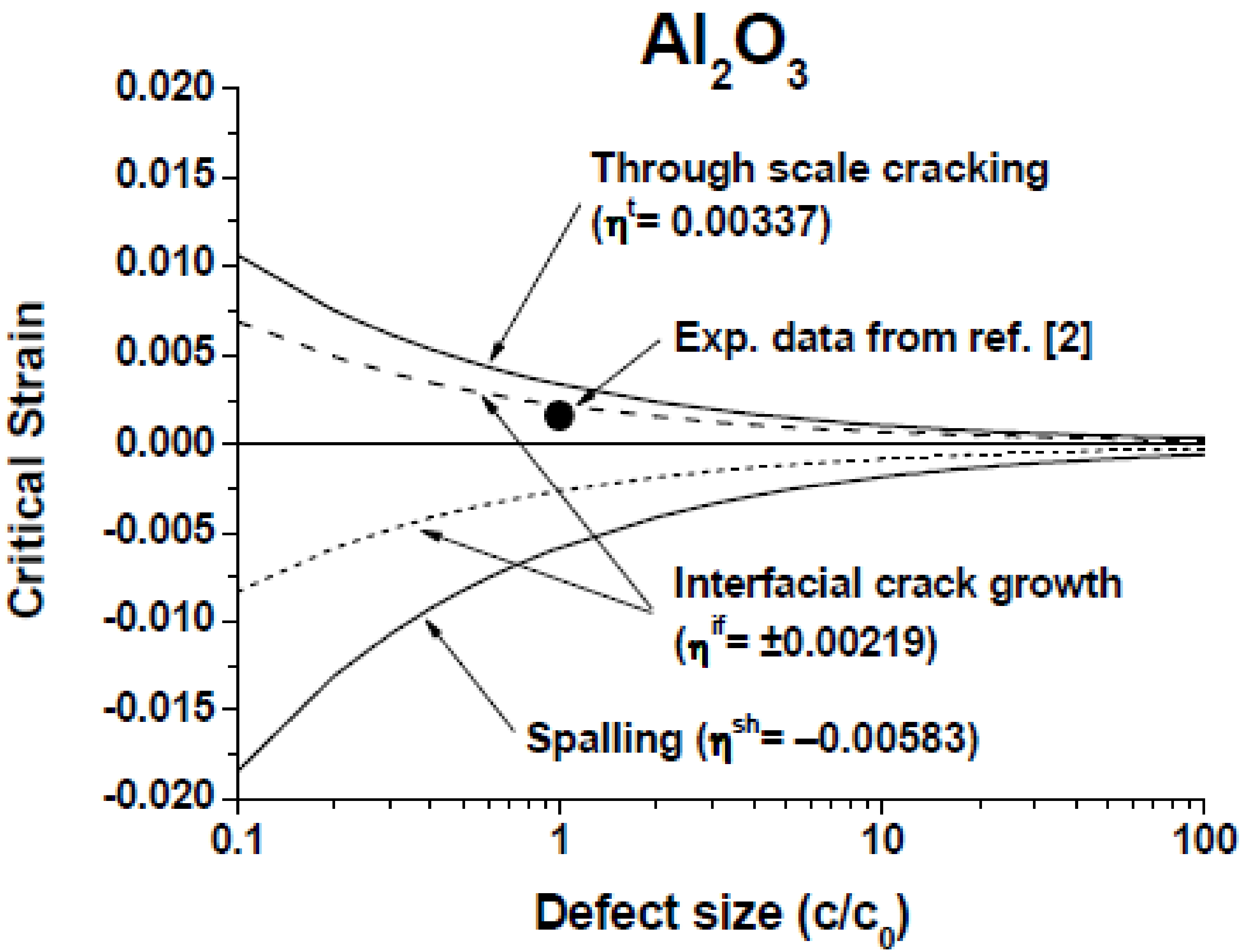
$$\varepsilon_c = \frac{\eta}{\sqrt{c/c_0}}$$



C_1 from metallography



Results from Model Calculations



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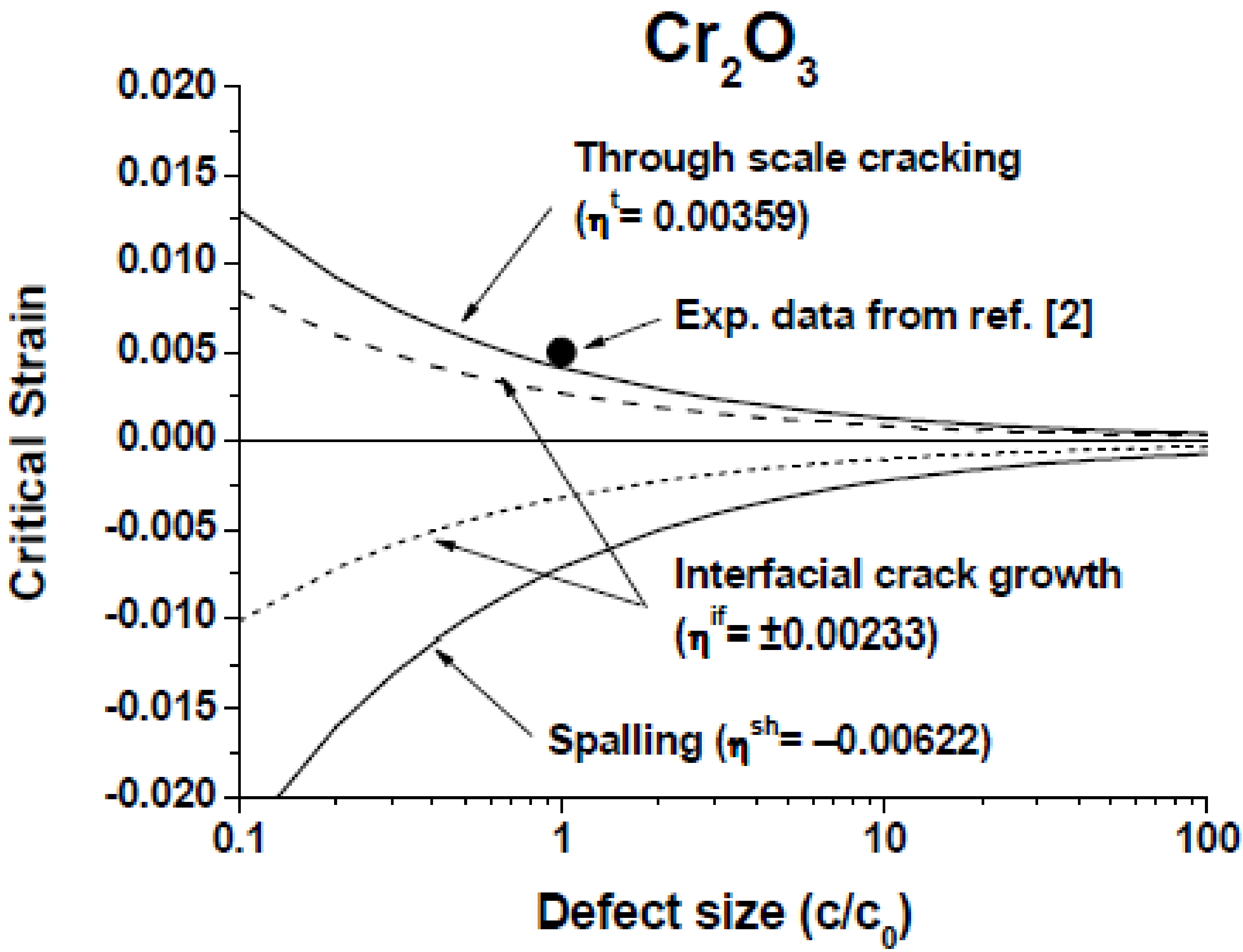

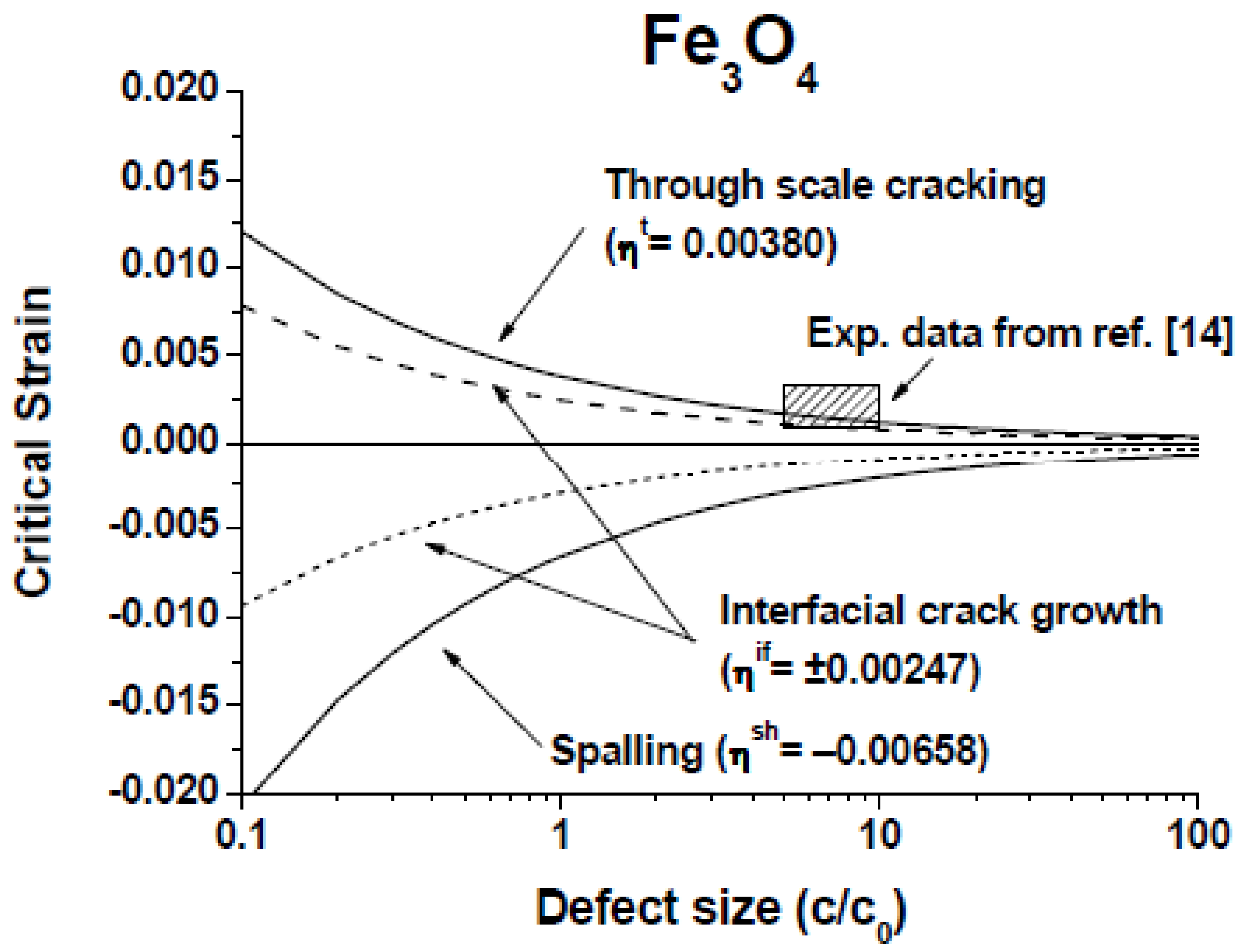

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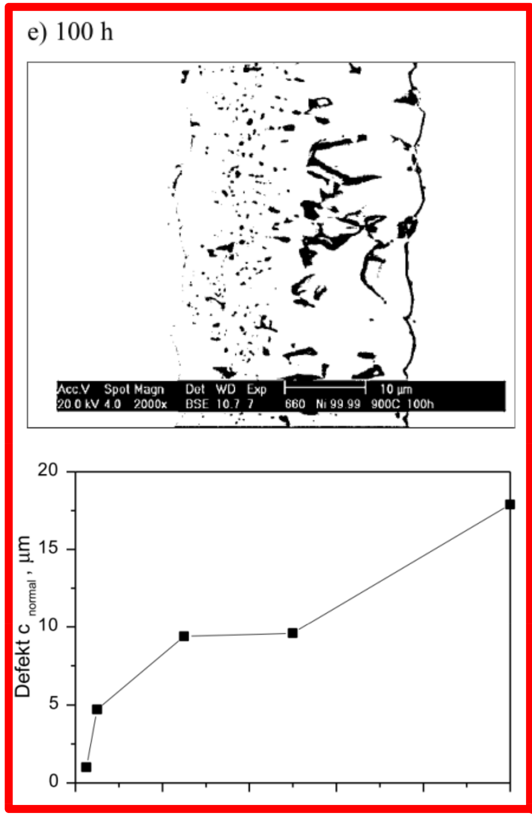
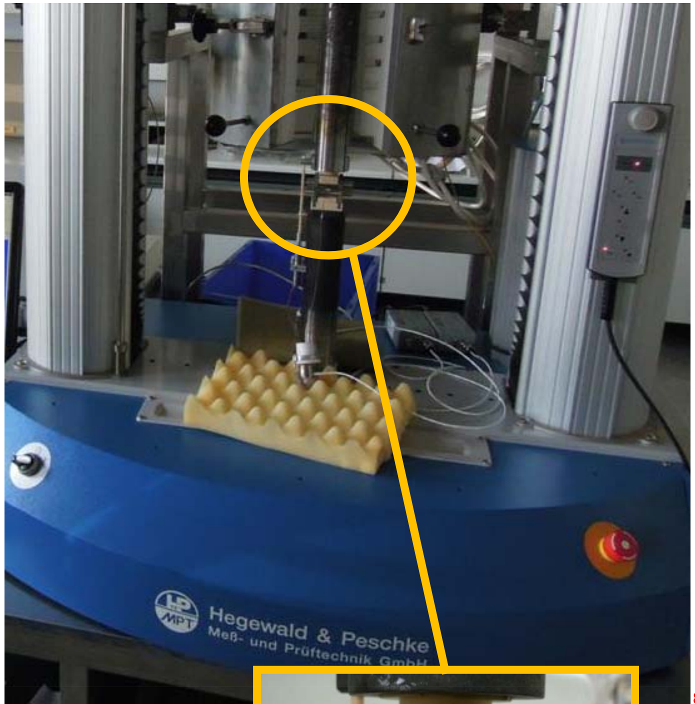
Experimental Data

Experimental Determination of η from ε_c vs. c

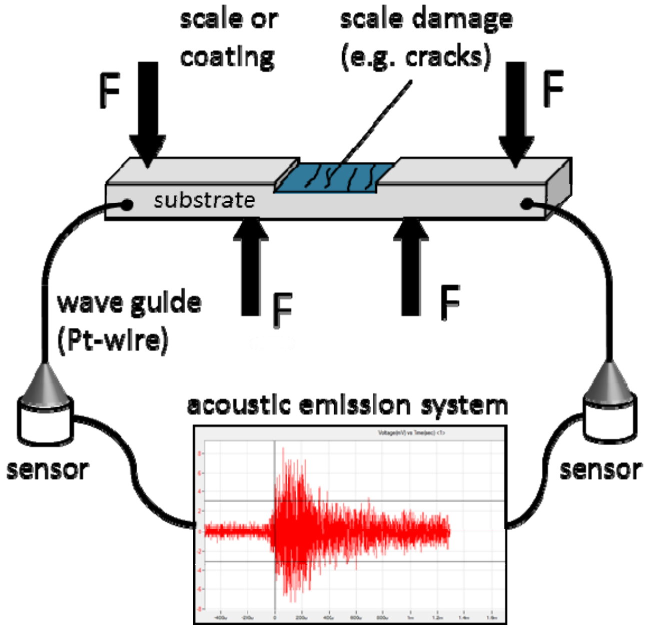
ε_c from 4 PB + acoustic emission

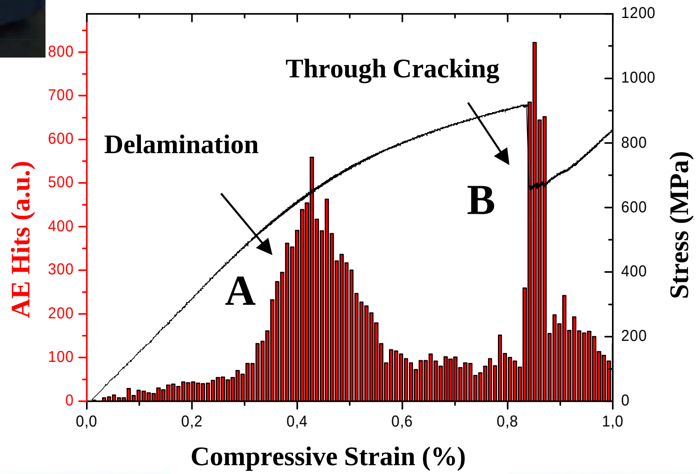
Defect size c (kinetics) from metallography





$$\varepsilon_c \approx \frac{\eta}{\sqrt{c/c_0}}$$

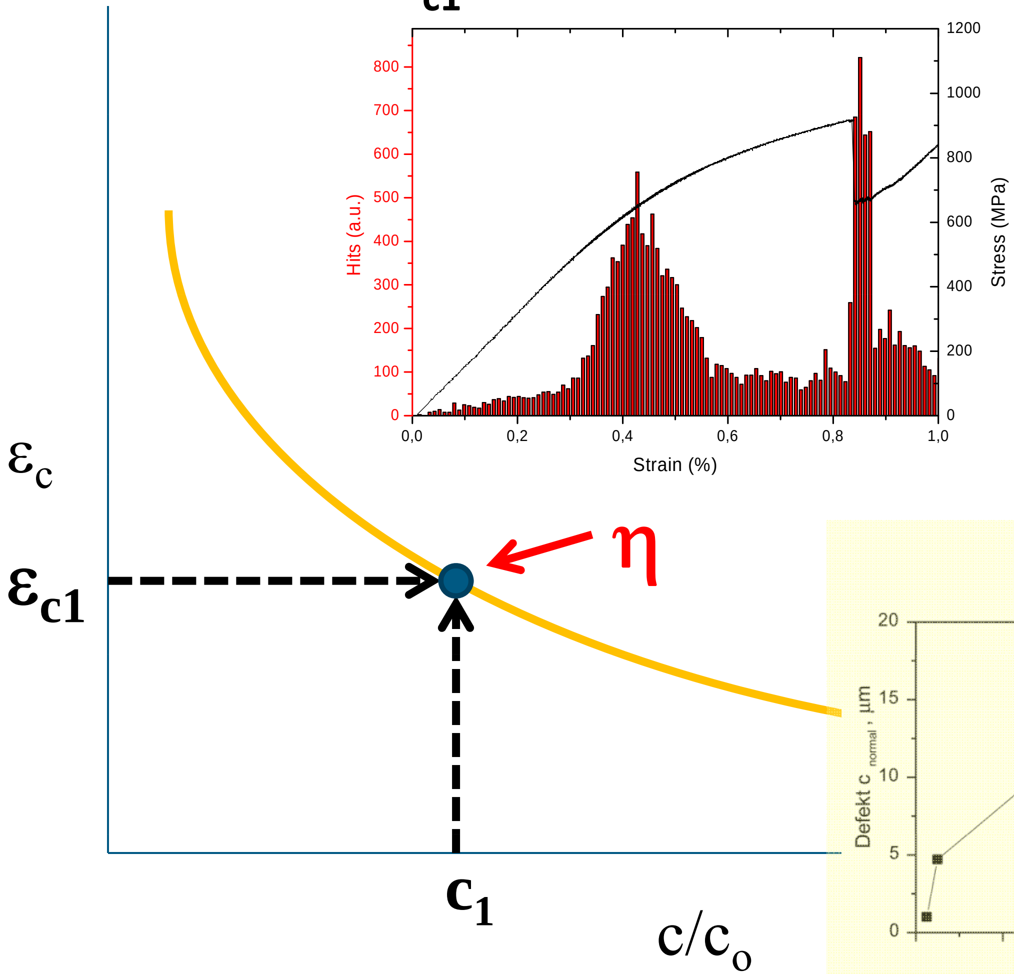




Experimental determination of η

$$\varepsilon_c = \frac{\eta}{\sqrt{c/c_0}}$$

ε_{c1} from 4 PB-test + AE



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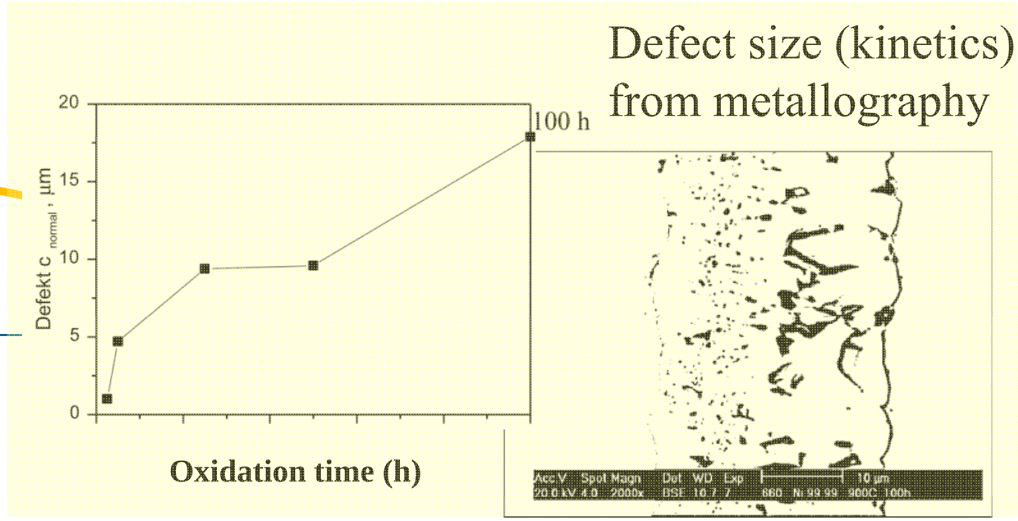
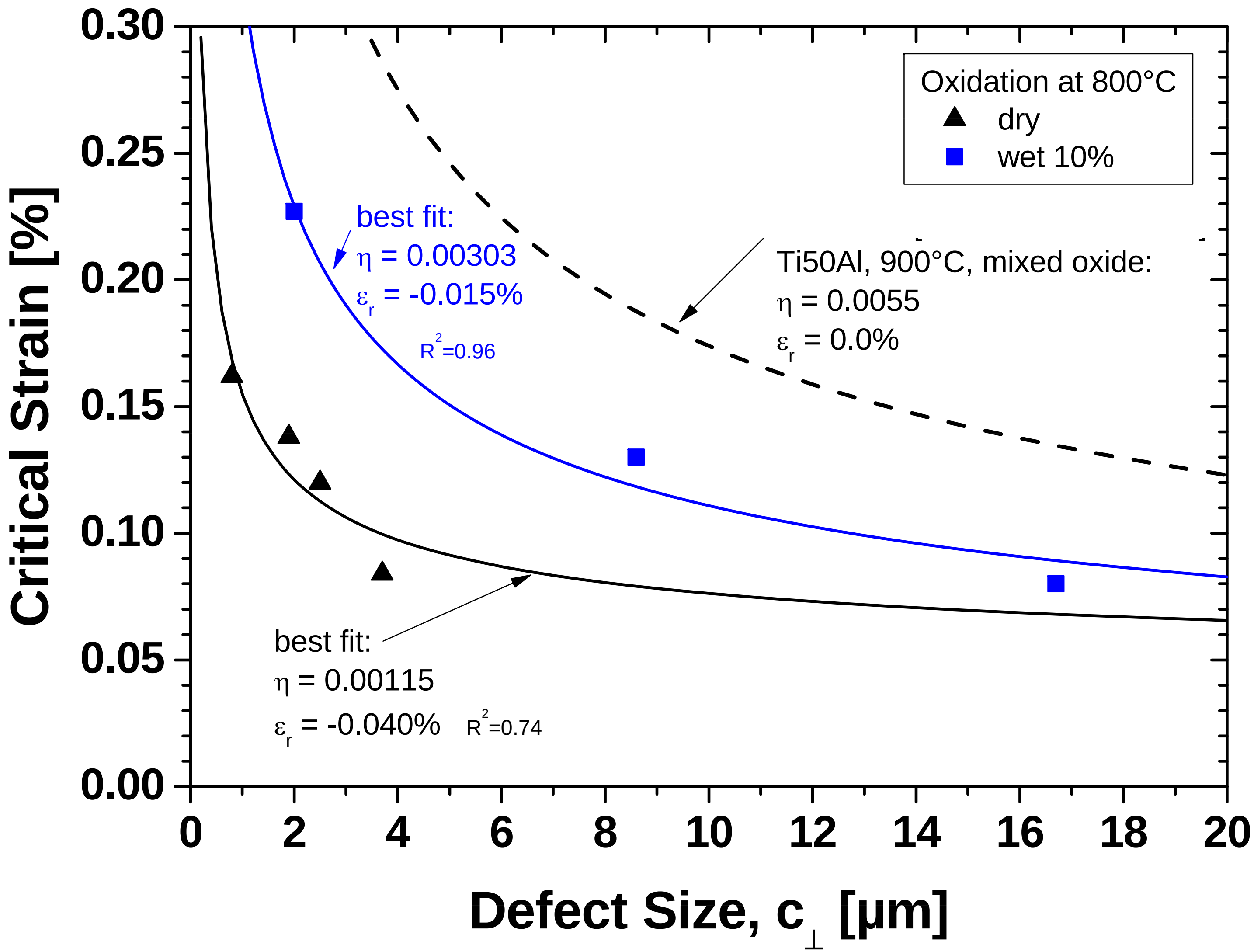
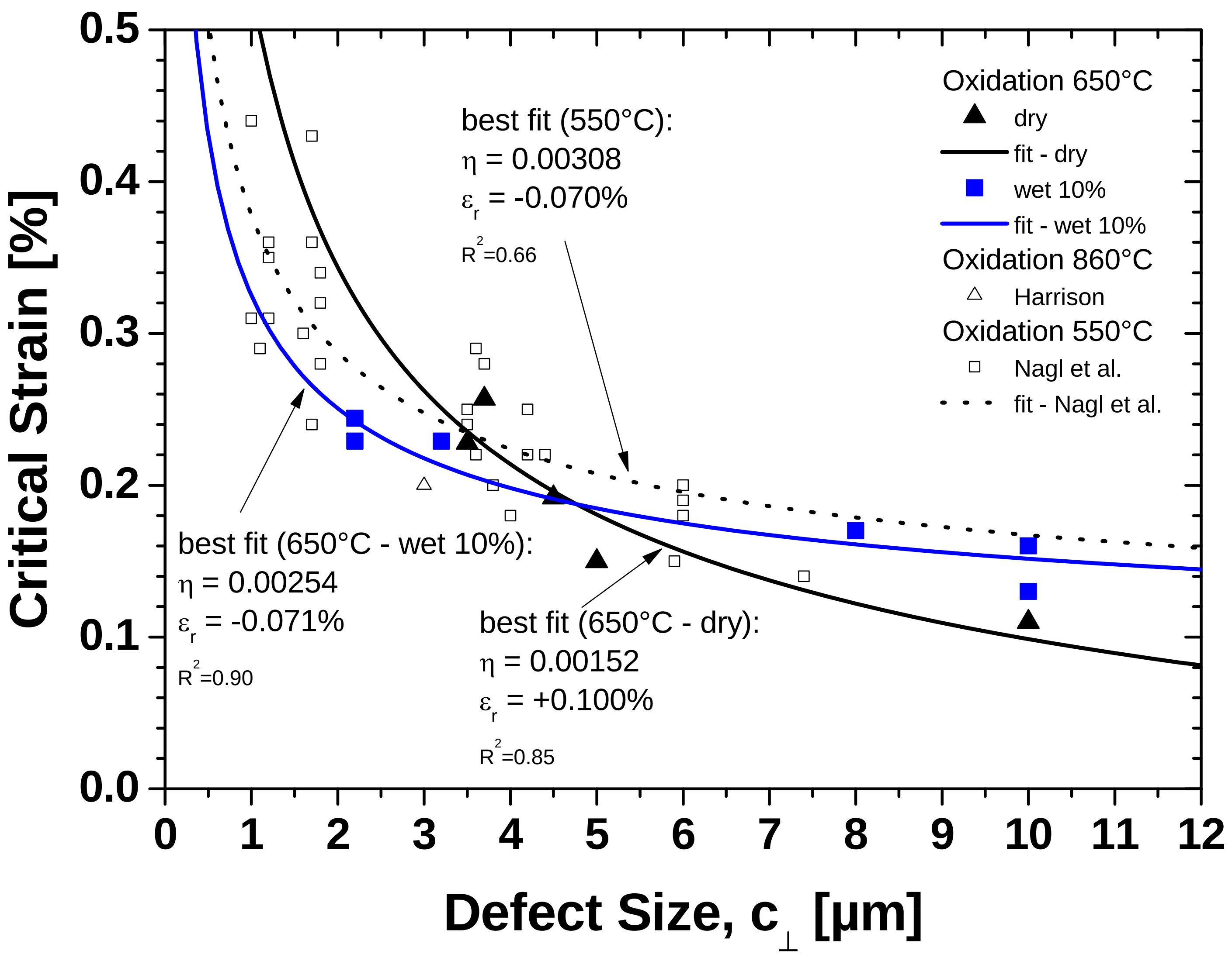


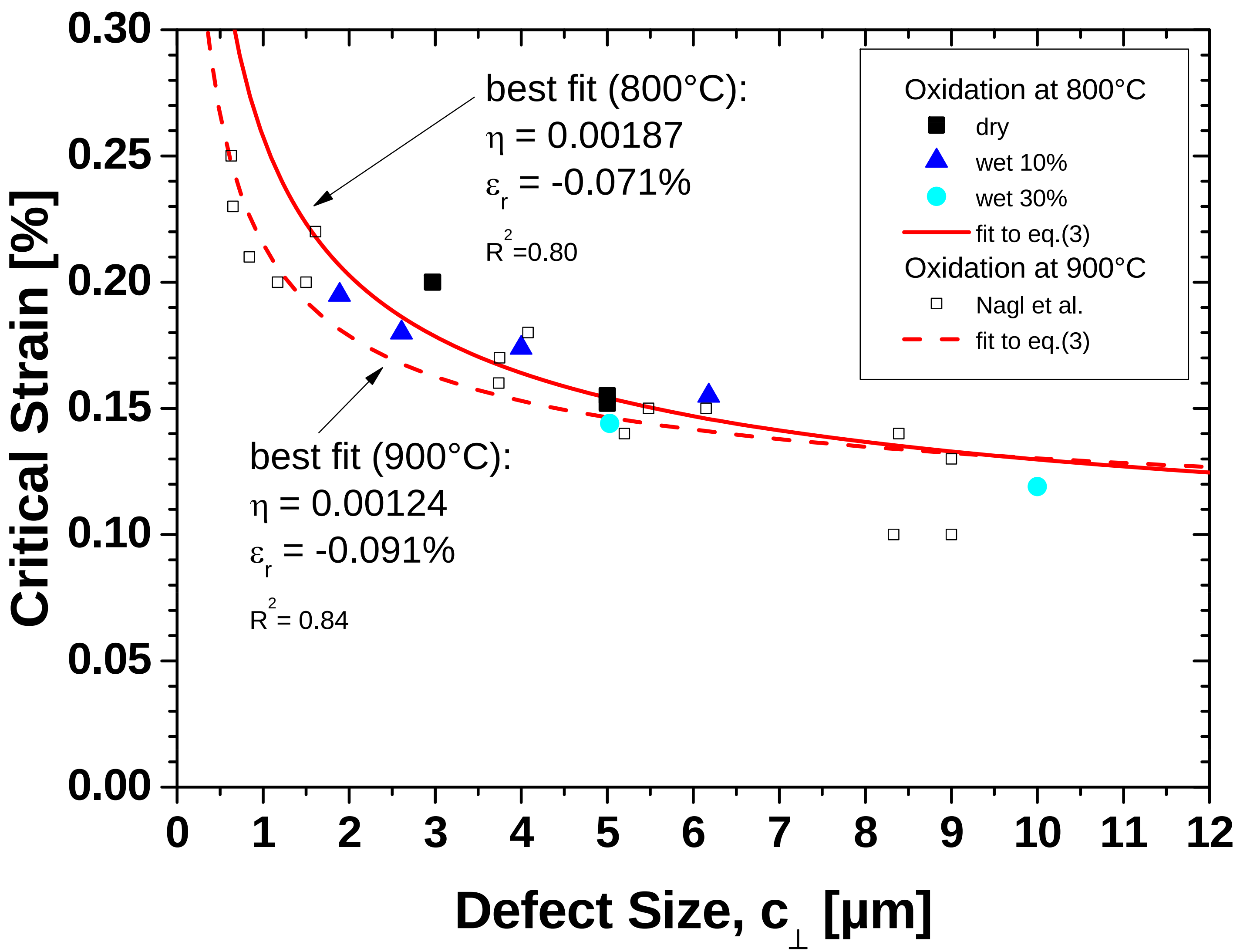
Ti-Oxide, 800°C and 900°C



Fe-Oxide, 550°C, 650°C and 860°C



Ni-Oxide, 800°C and 900°C



Still under Work:

Al_2O_3

Cr_2O_3

Summary

Characteristics of the η – c – approach :

- Mechanical properties of oxide scales can be summarized quantitatively by the parameter η

- Geometrical situation dominated by the parameter c

- Prediction of ε_c without mechanical testing once η is known

- Interesting potential for quantitative characterisation of the mechanical properties of surface oxide scales on high temperature materials and their mechanical limits

Thank you for your attention