

# Liquid Metal Embrittlement

An introduction

Véronique Ghetta, Dominique Gorse

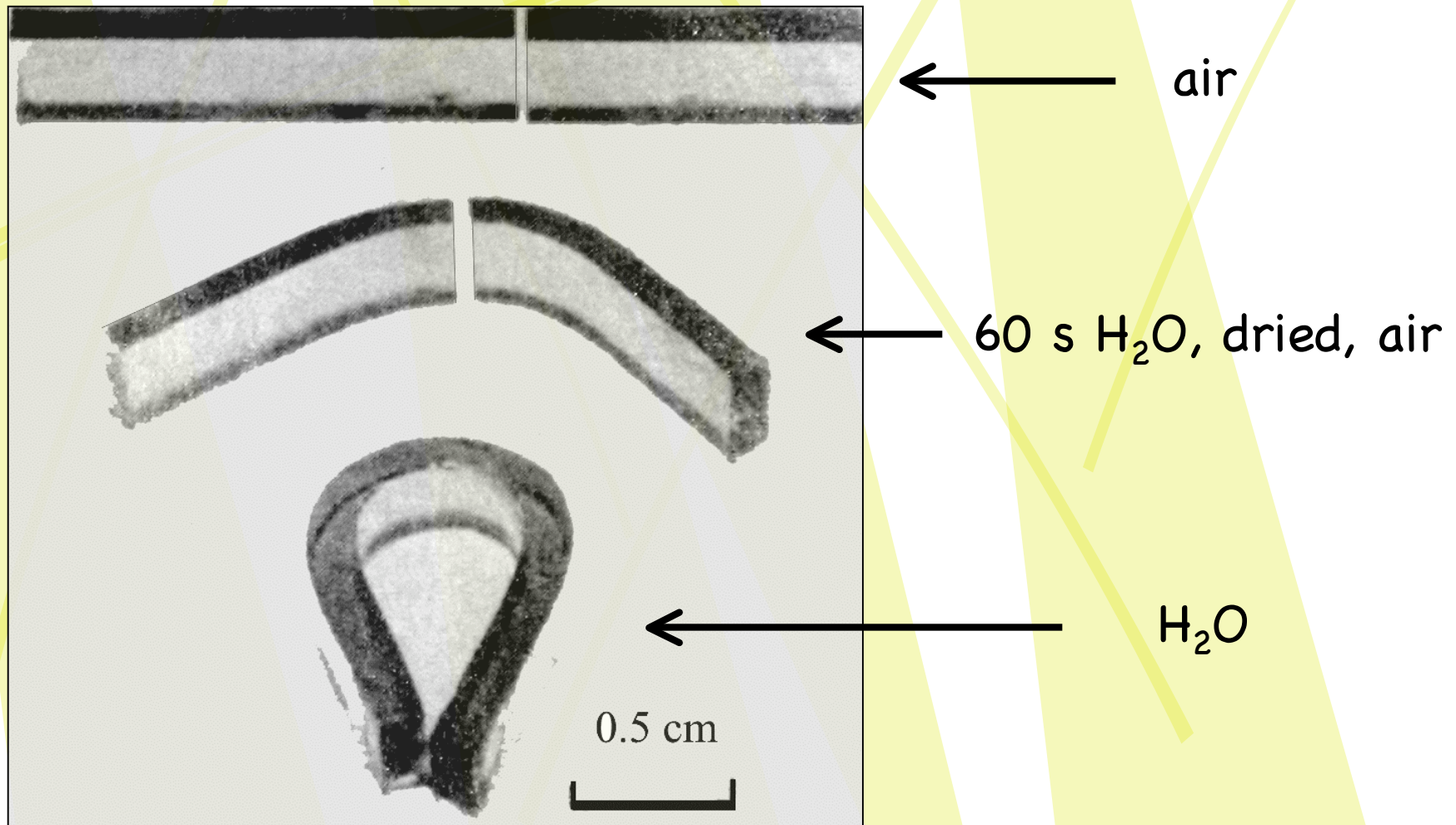
&

Vassilis Pontikis

# Outline

- Environment & Mechanical behavior
- What is LME ?
- Fundamentals of mechanical failure
- Experimental facts
- Empirical criteria
- Modeling
- Conclusive remarks

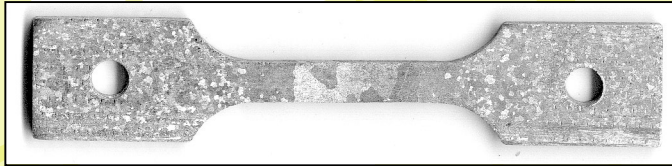
# Joffe effect, irradiated KCl, Rebinder et al., 1944



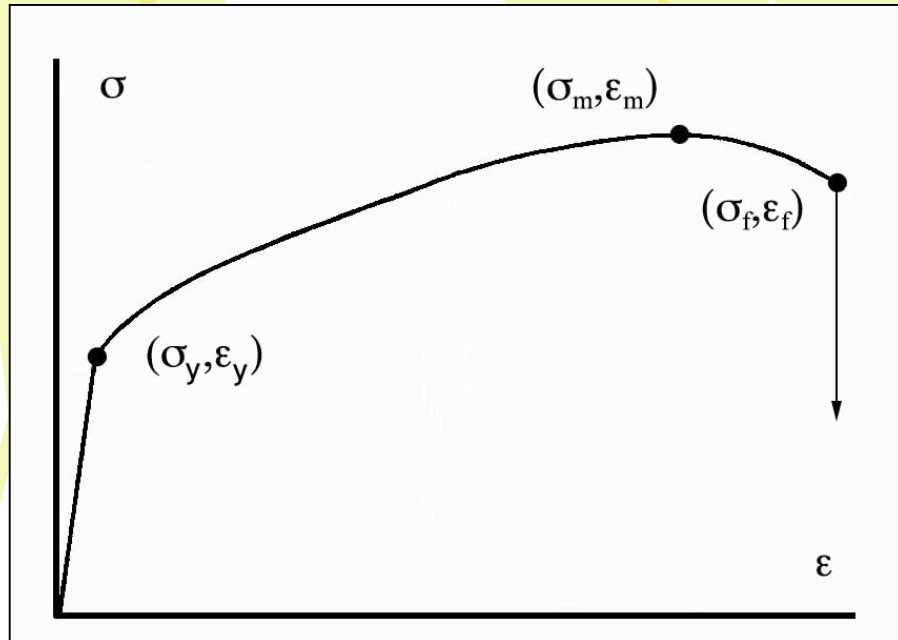
Steel 316L + Hg, Medina-Almazan et al. (2005)

*316L-Hg*

# Tensile deformation & failure-I



$$\sigma_E^{th} \approx \frac{\mu}{10}$$



## Dislocations

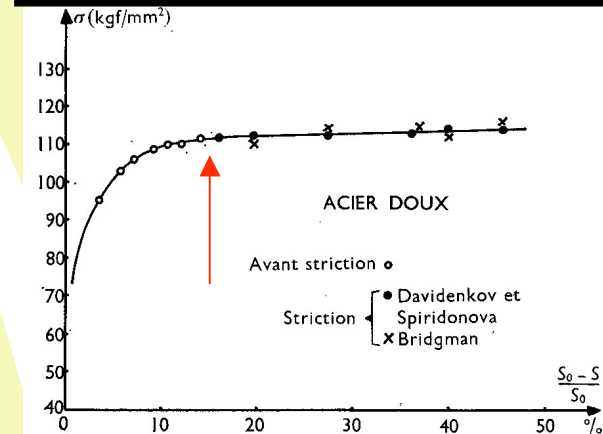
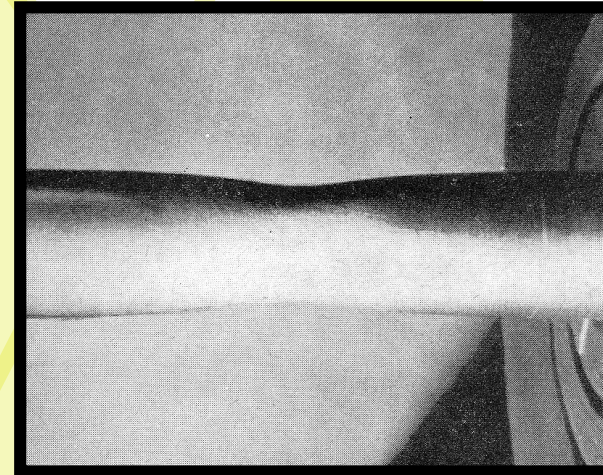
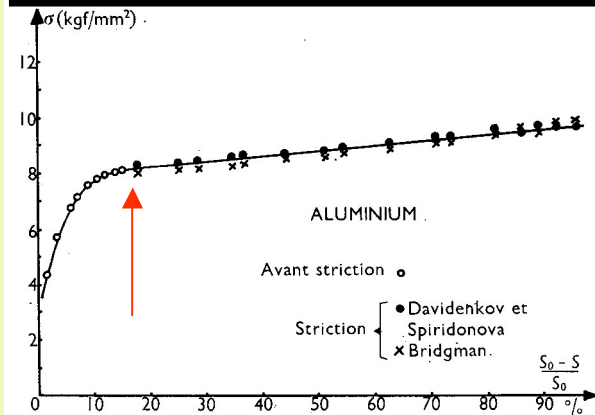
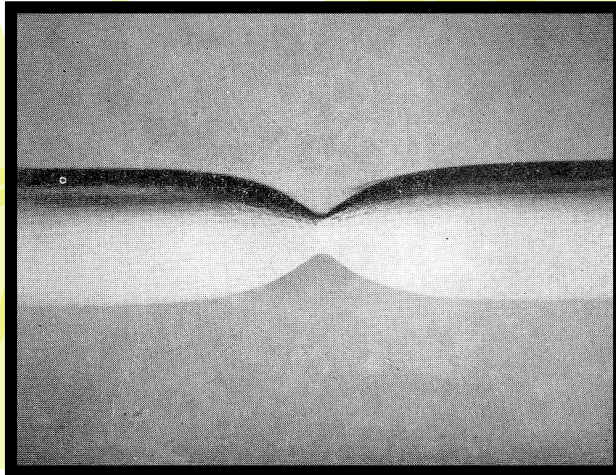
$$\begin{cases} \sigma_E^{\text{exp-fcc}} \approx 10^{-5} \mu \\ \sigma_E^{\text{exp-bcc}} \approx 10^{-3} \mu \text{ (} T \text{-dependent)} \end{cases}$$

## Instability

$$\sigma_m = \frac{d\sigma}{d\varepsilon} \text{ (Considère)}$$

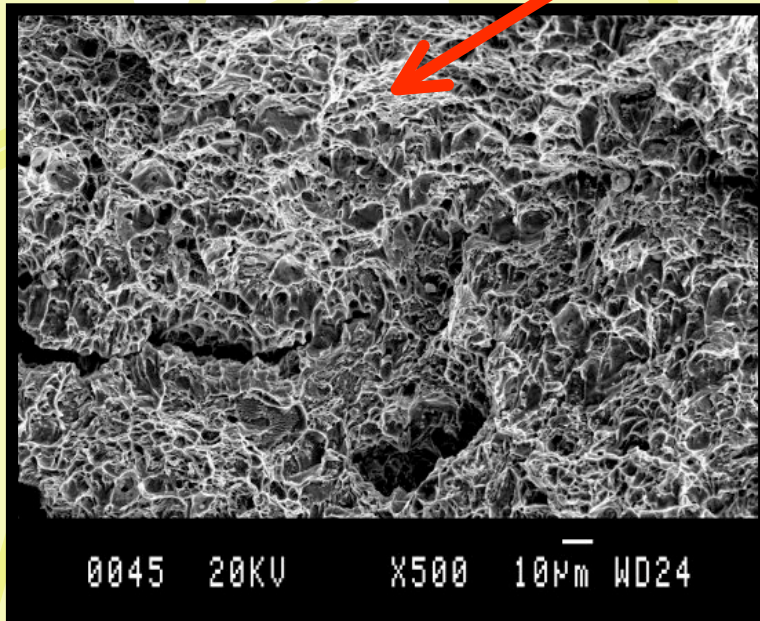


# Tensile deformation & failure-II



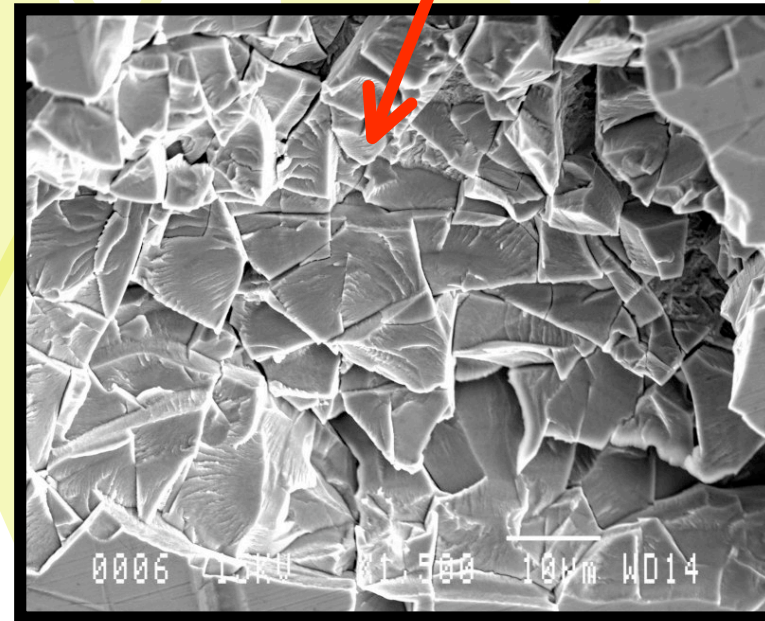
Creep :  $\dot{\epsilon} \approx \sigma^n$  ,  $n\dot{\epsilon}_i t_f = 1$  (Monkman - Grant, 1956)

# Microvoid coalescence & Cleavage



$$T > T_{BDT}$$

Mechanism of ductile transgranular fracture (1040 carbon steel [1])

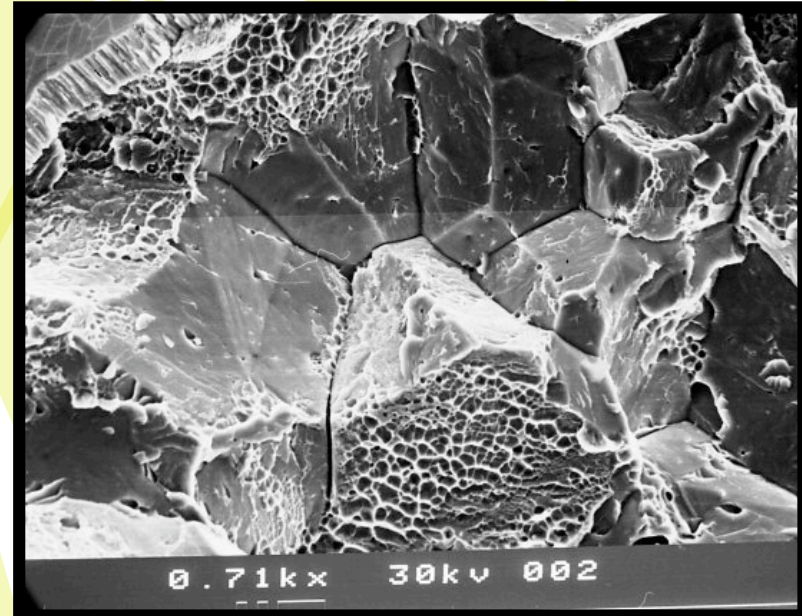
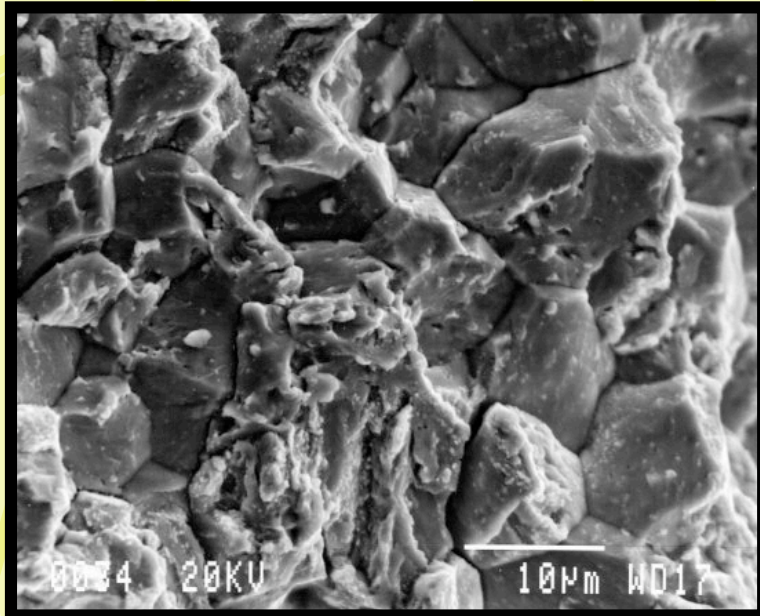


$$T < T_{BDT}$$

Mechanism of brittle transgranular fracture: cleaving of the crystals along crystallographic planes (bcc Cr [1]).



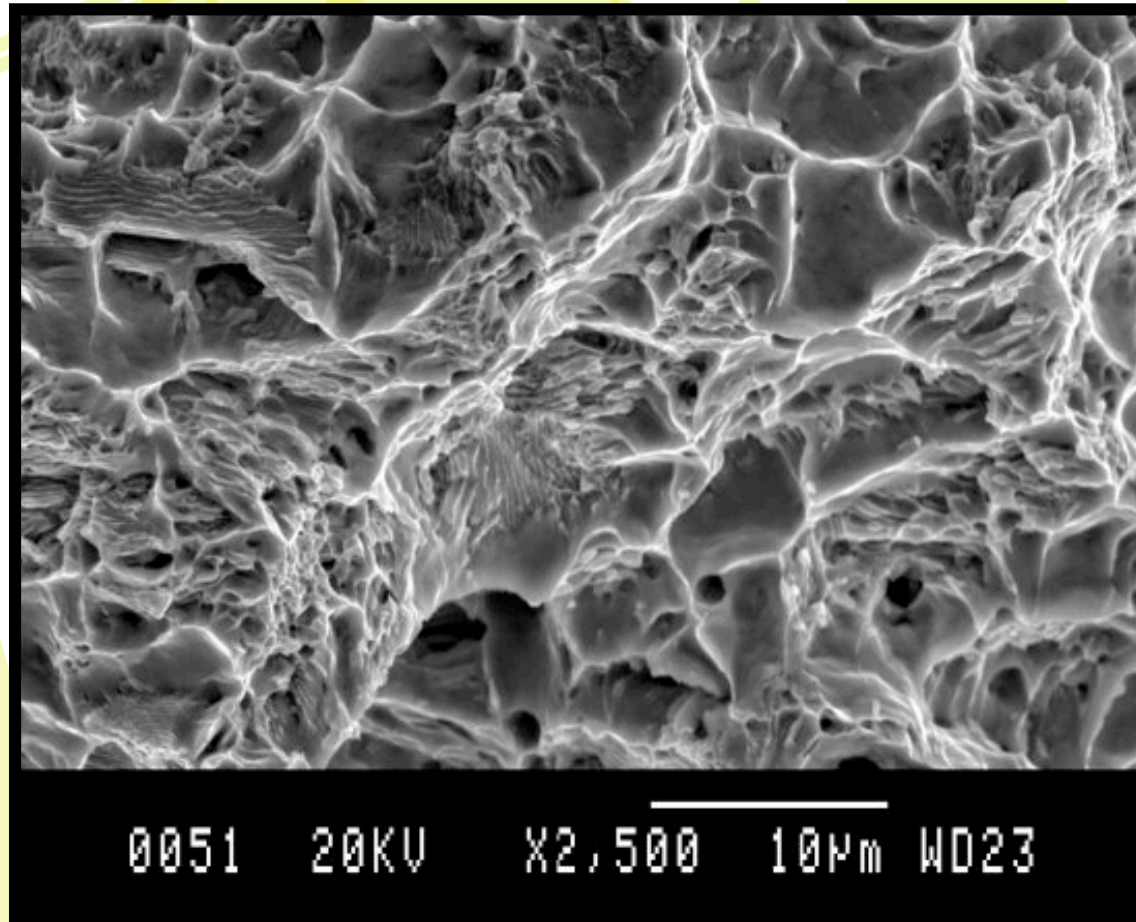
# Intergranular fracture



*Steel, from ref. [1]*

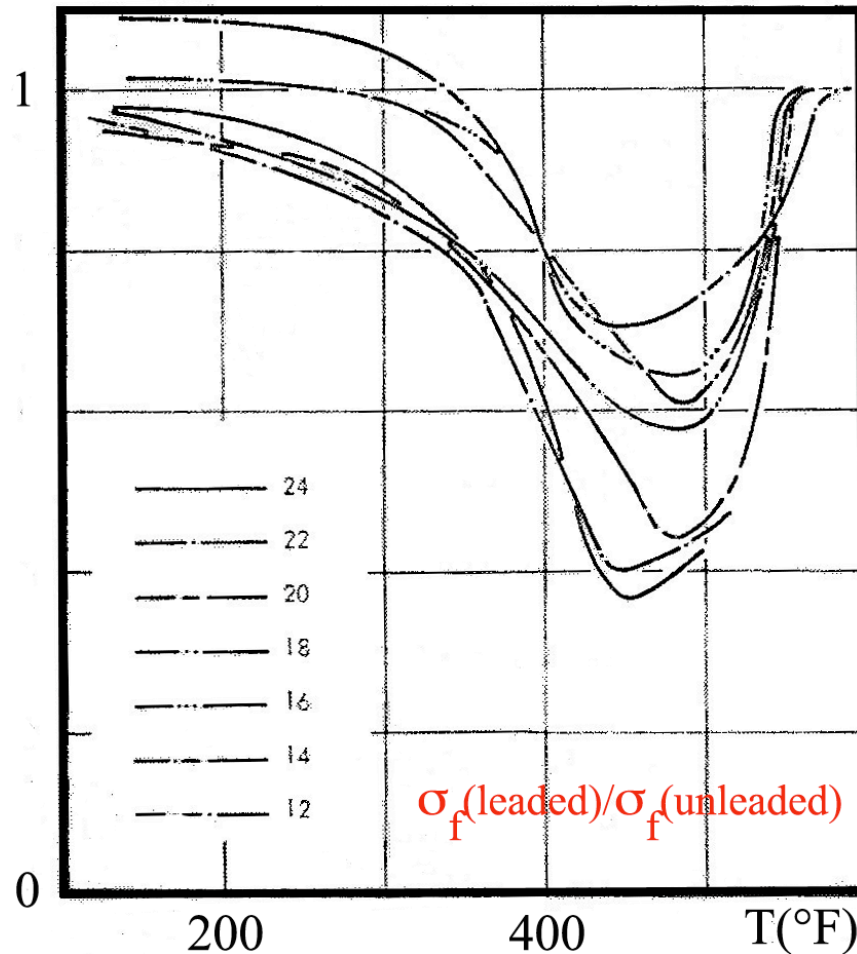


# Mixed fracture: cleavage + MVC



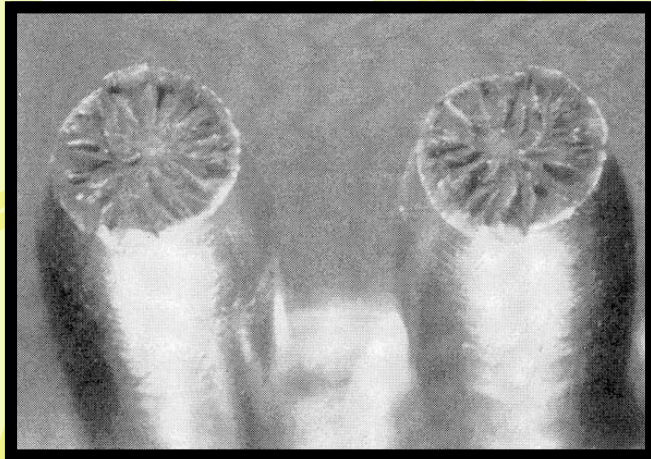
Steel [1]

# Macroscopic features - I

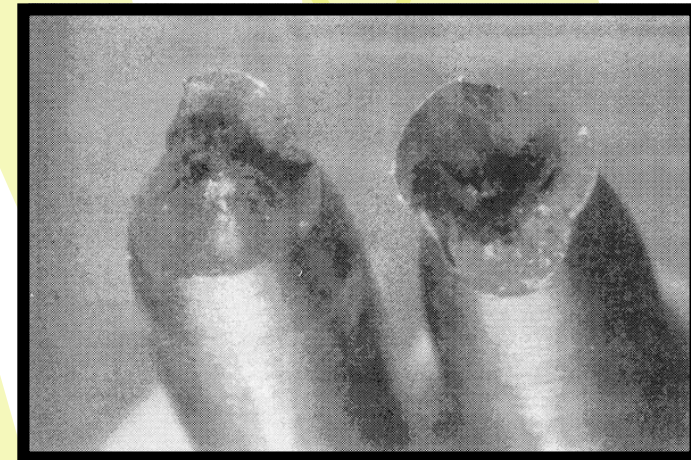
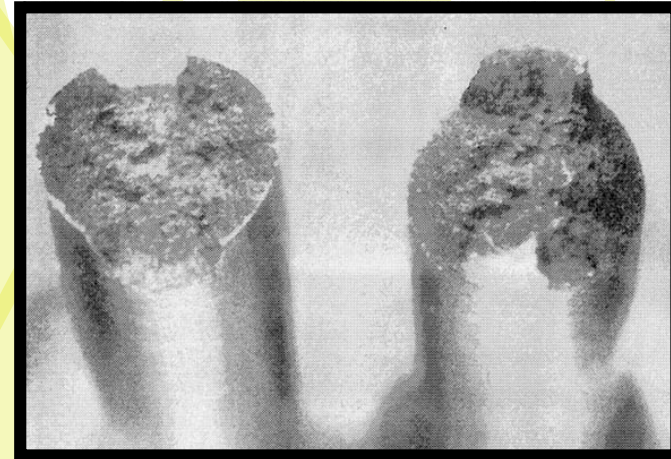


Ratio of fracture stresses of 4145 steel with & without Pb(0.3%)

# Macroscopic features - II



Room T



$400 < T < 620 \text{ } ^\circ\text{F}$

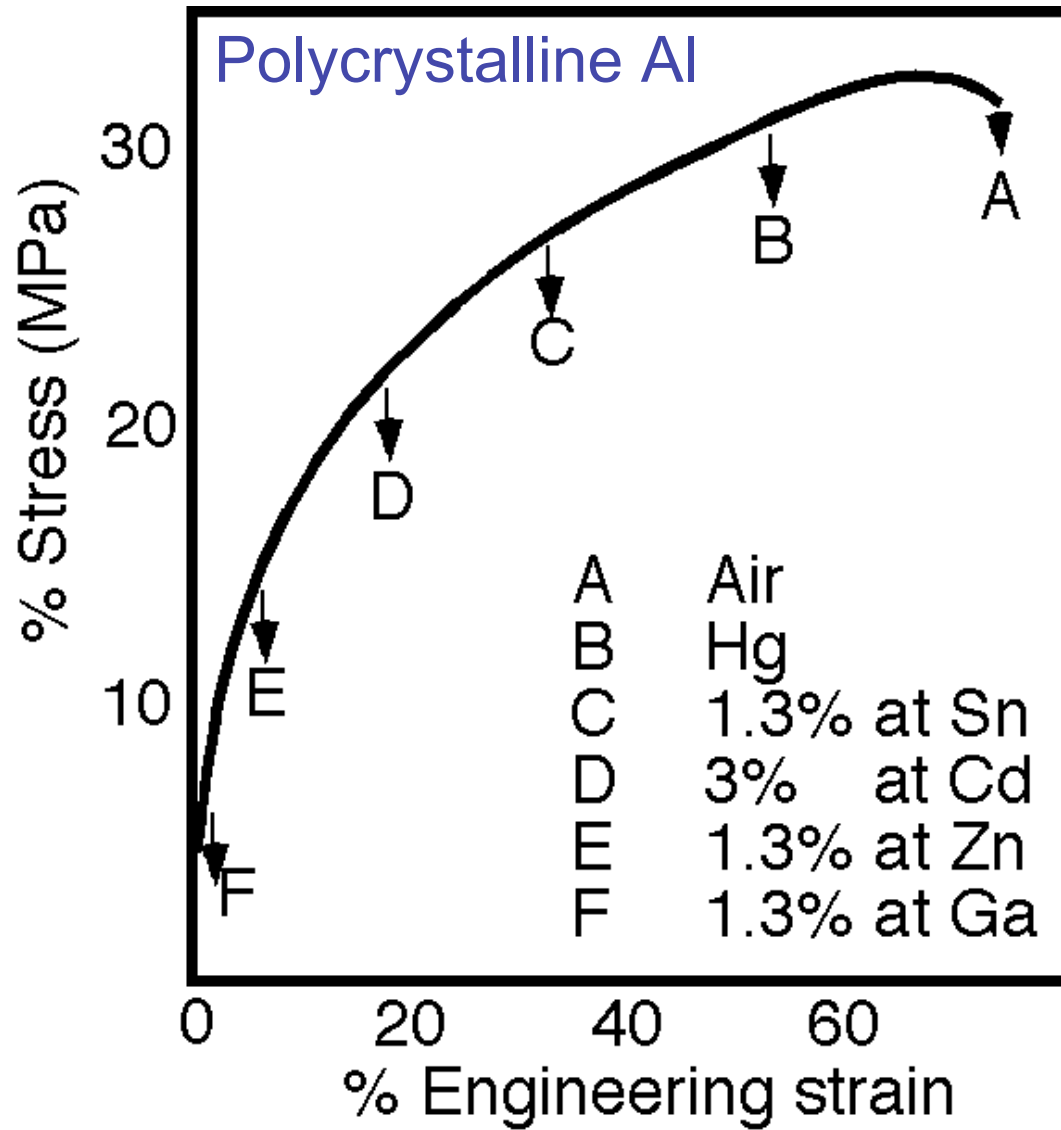
Steel 4145

*Mostovoy & Breyer, (1968)*

# LME&Chemistry

The effect of impurities

*Westwood et al., (1971)*

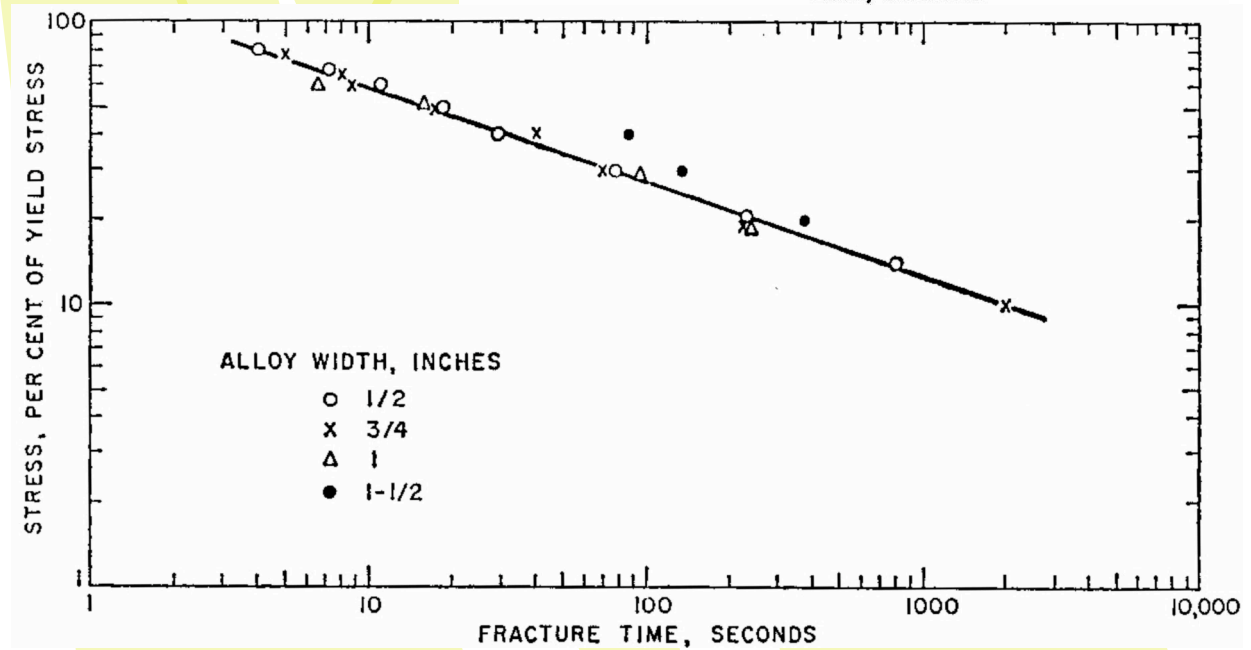
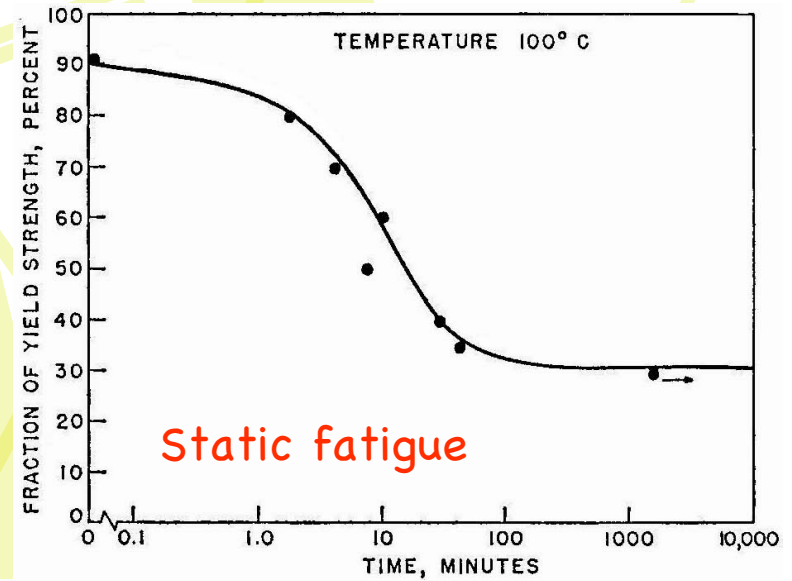




# LME

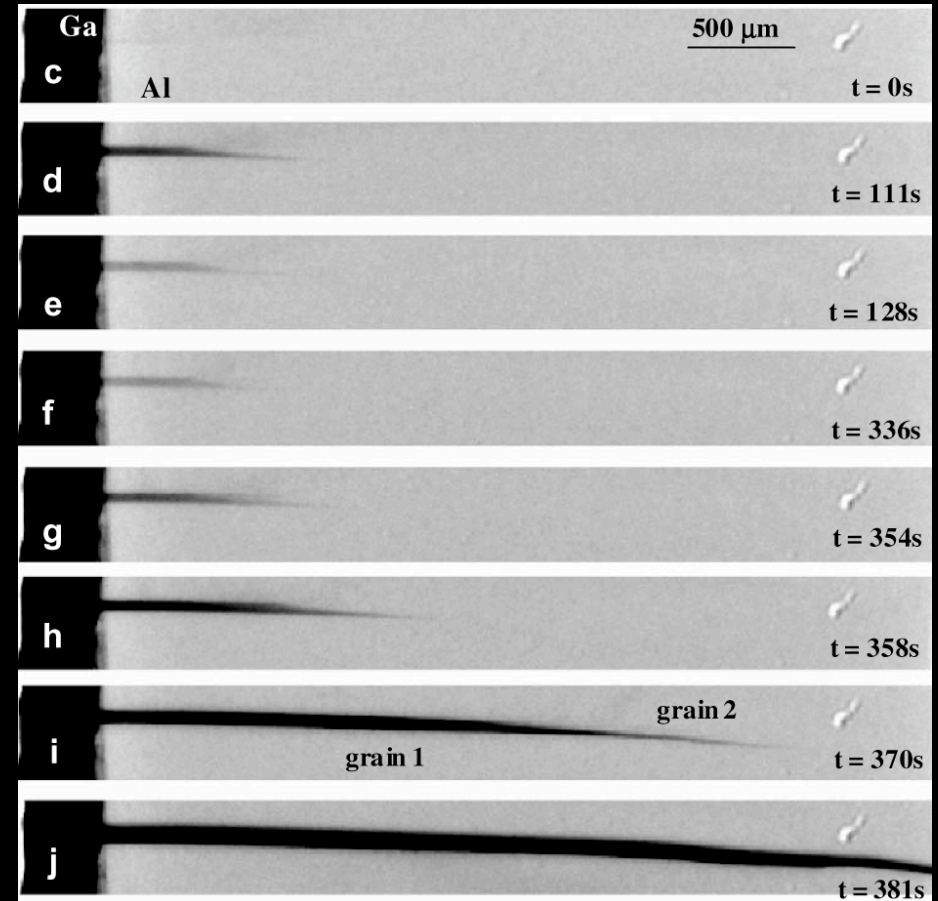
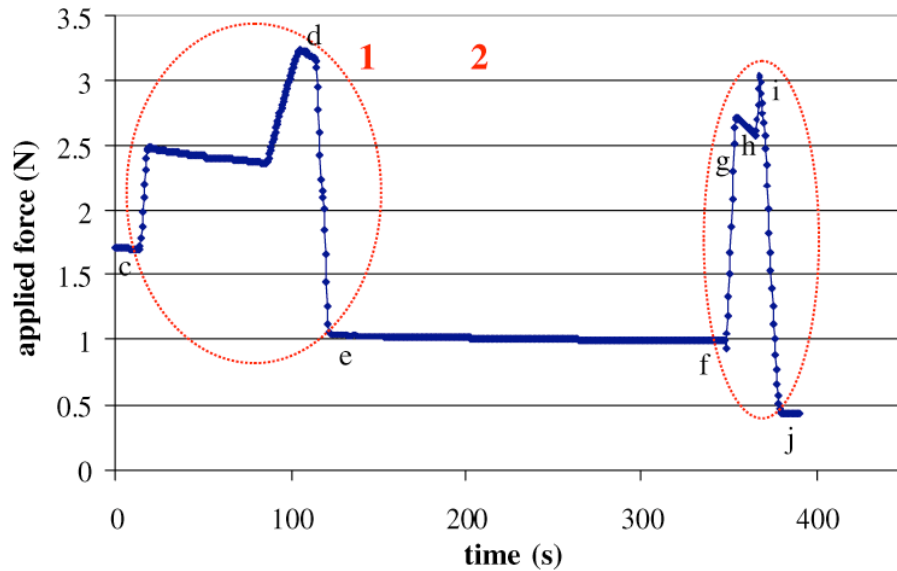
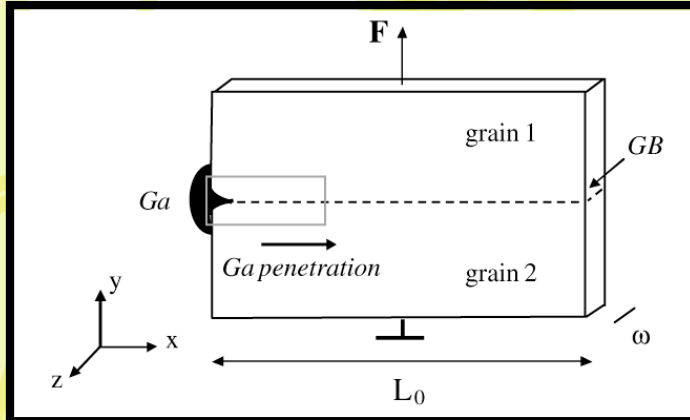
Delayed failure

2024-T4 Al alloy + Hg amalgam



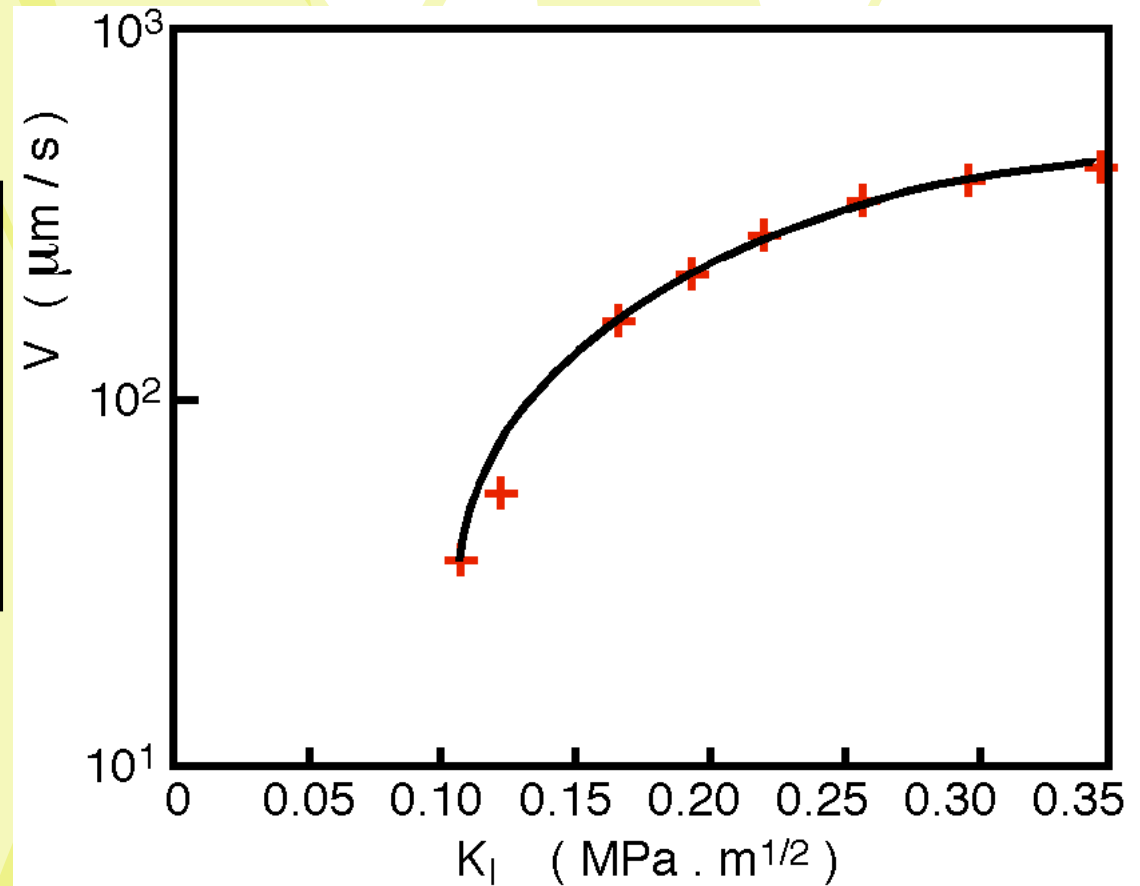
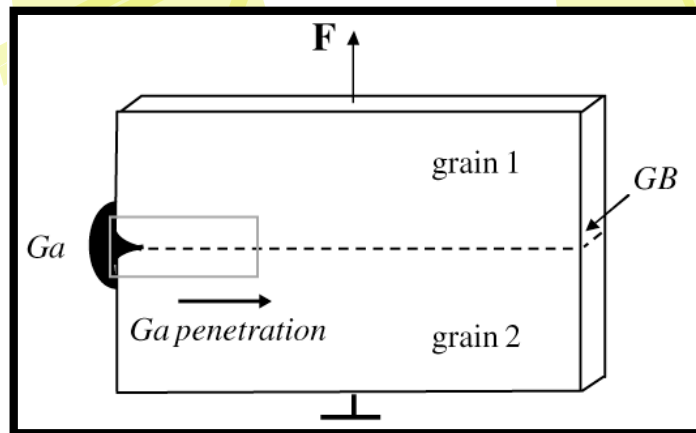
*Rostoker et al. (1960)*

# LME and Grain Boundaries: Al/Ga



*Ludwig et al. (2006)*

# LME and Grain Boundaries



# LME: consensus about facts

- **Instantaneous** failure under applied or residual stresses
- **Delayed** failure at a static stress level below the tensile strength
- Microstructure is important BUT LM's embrittle amorphous alloys too ! Ashok et al. (1981)
- Plasticity is often present
- **Stress independent (?)** grain boundary penetration
- High temperature "corrosion"

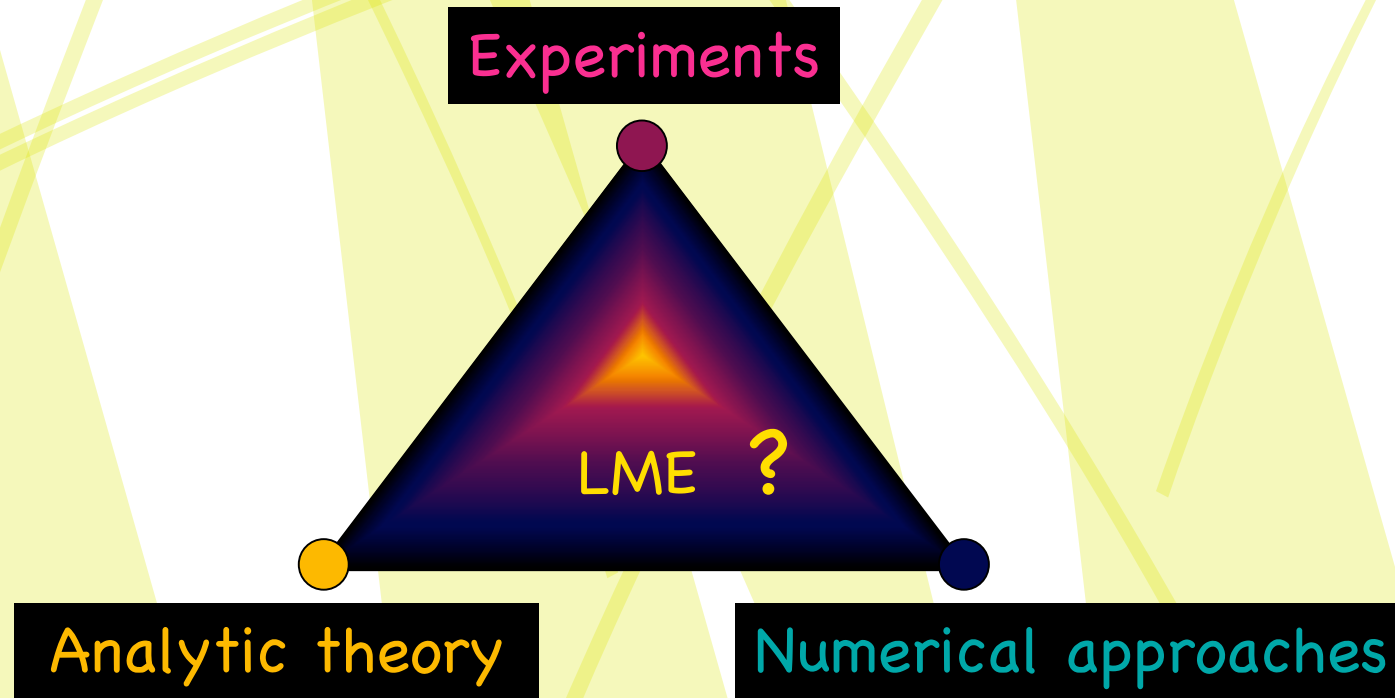


## From consensus: prerequisites & empirical criteria of occurrence

- Presence of an external stress
- A pre-existing crack or plasticity (at least limited) & presence of obstacles to dislocation motion e.g. grain boundaries, twins, precipitates
- Adsorption of the active species at the obstacles and at the tip(s) of propagating crack(s)
- Limited mutual solubility of the liquid and the solid
- Little or no tendency of stable high  $T_m$  compounds

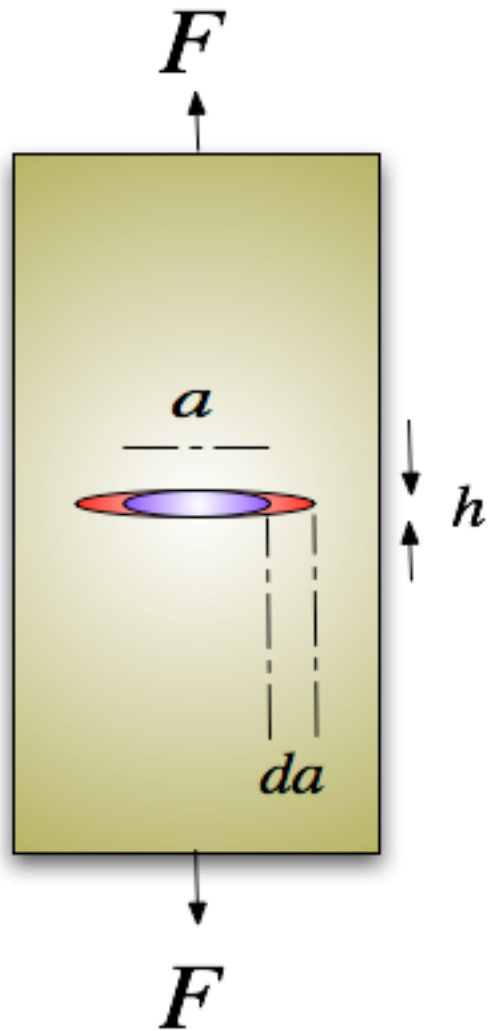
However factors determining which liquid metal will embrittle which solid metal still remain unclear !

# Is modeling understanding ?



An heuristic approach (sometimes a random walk)

# Modeling LME & Crack propagation: Elasticity



$$dU = \pi a da \frac{\sigma^2}{E}$$

$$G = \frac{dU}{da} = \pi a \frac{\sigma^2}{E}$$

$$G_c = 2\gamma_s$$

$$\sigma_c = \sqrt{\frac{2\gamma_s E}{\pi a}}$$

(Griffith-1921)

Adsorption of the liquid at the crack tip decreases  $\gamma_s$  and thus  $\sigma_c$

## LME & Crack propagation: ...adding plasticity

Griffith's model is elastic (Orowan, Stoloff & Johnson, ...)

$$\sigma_c = \sqrt{\frac{2\gamma_{eff}E}{\pi a}} \quad (Orowan-1950)$$

But...

$$\gamma_{eff} = \gamma_p + \gamma_s \quad (Al : \gamma_p \approx 4200\gamma_s, \text{Kargol } et \text{ al.}, 1977)$$

However...

$$\gamma_{eff} = A\gamma_s, \quad A \approx \sigma_0 / \sigma_y \approx 100 \text{ for steel} \quad (Gilman, 1960)$$

Small changes in  $\gamma_s$  large influence on  $\gamma_{eff}$



# “Thermodynamic” model: Successes & limitations

- Cu/Pb-melt *Eborall et al. (1956)*
- Al bicrystals/HgGa solution *Kargoll et al. (1977)*
- Al 6061/inclusions Bi, Cd, Pb *Roth et al. (1980, 1982)*

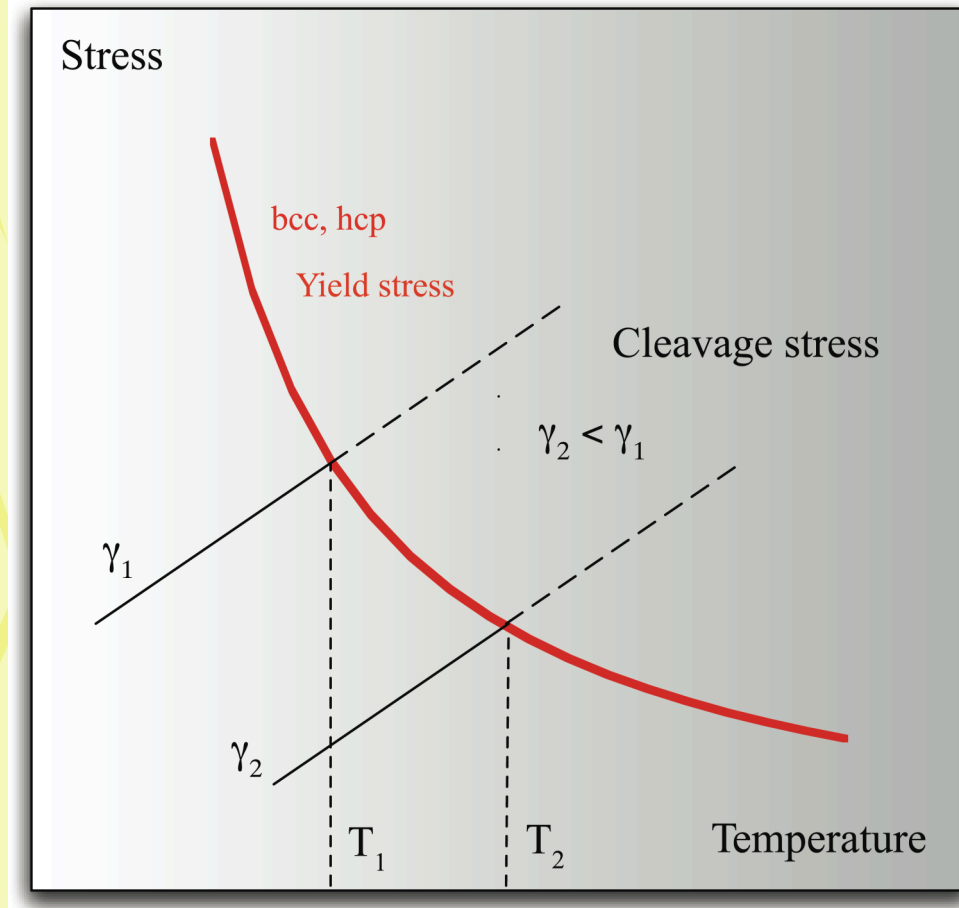
**BUT ...**

- No mechanisms
- No microscopic description of the SL interface
- No kinetics
- No understanding of plasticity at the crack tip

# LME & Cracks & Ductile Brittle Transition Temp

System	$\gamma_s$ (J/m <sup>2</sup> )
Al	1.0
Al-Pb	0.344
Al-Cd	0.298
Al-Bi	0.288

*Old & Trevena (1979)*



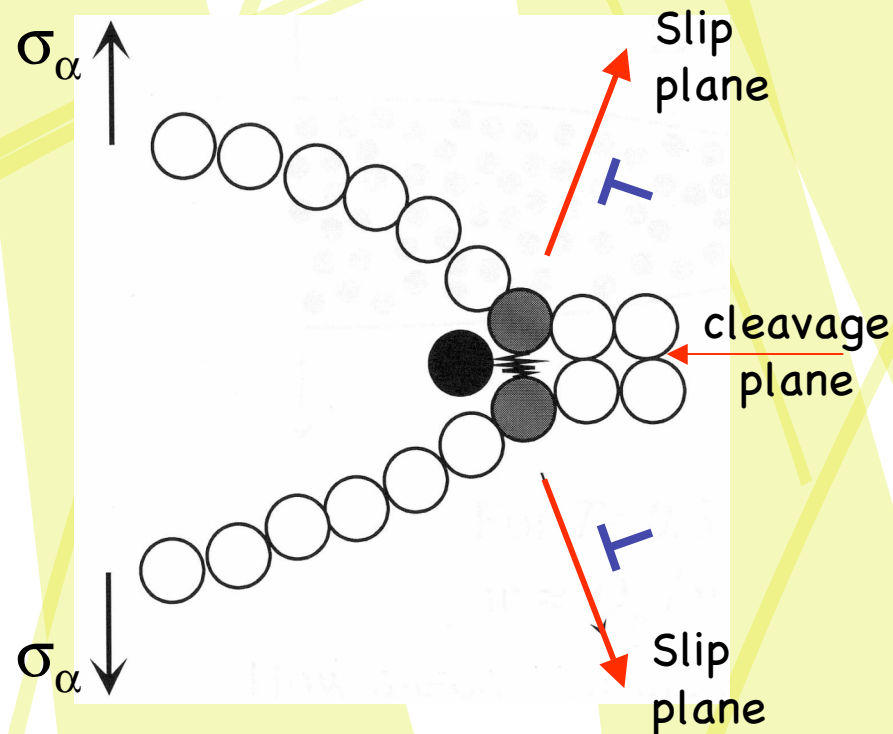
## Limitations of this approach

- Lack of surface energy data (ab-initio ?)
- Physical parameters influencing LME do not appear in the model (e.g. microstructure)
- No insight into the mechanisms (atomistic scale)

Consensus: reduction in  $\gamma_s$  is necessary but not sufficient

# AIRC

## Adsorption Induced Reduction in Cohesion



- Bond breaking  $\sigma_m = \sqrt{\frac{\gamma_s E}{x_0}}$
- Crack length  $2a$   
Stress at the tip  $\sigma = 2\sigma_a \sqrt{\frac{a}{\rho}}$
- $\rho = x_0 \longrightarrow \sigma_{prop} = \sqrt{\frac{\gamma_s E}{4a}}$

$$\sigma_{prop(blunted)} = \sqrt{\frac{E\gamma_{fracture}}{4a}} = \sqrt{\frac{E\gamma_s \xi}{4a}}$$

AIRC: the atoms of the liquid (black) reduce/increase the bond strength

## AIRC: present situation

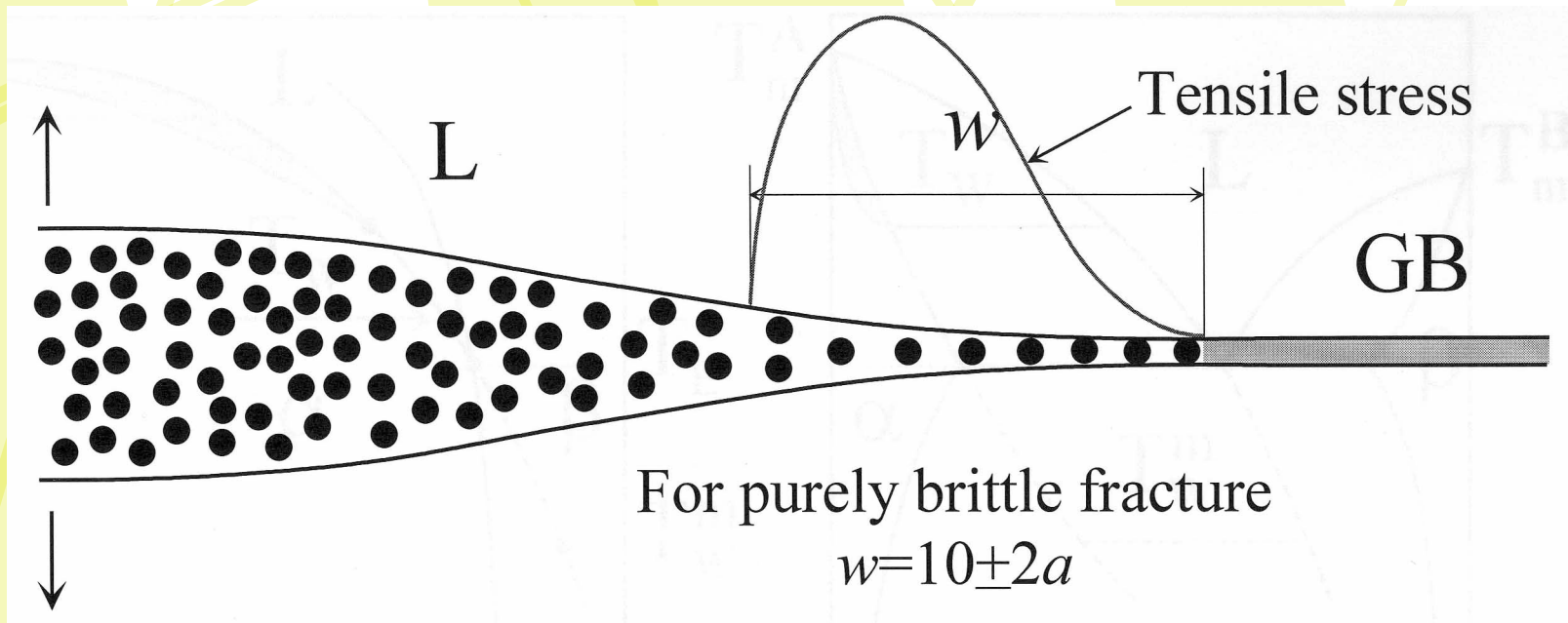
- AIRC is widely accepted
- Consistent with several experimental findings (Zn-Hg, Zn-Ga, hydrogen, ...)
- Explains impurity action

**BUT ...**

- Hardening is absent
- Enhanced plasticity at the crack tip and HT LME are not explained
- Transport mechanisms are not considered
- No realistic prediction of the crack velocity



# AIRC variants & improvements

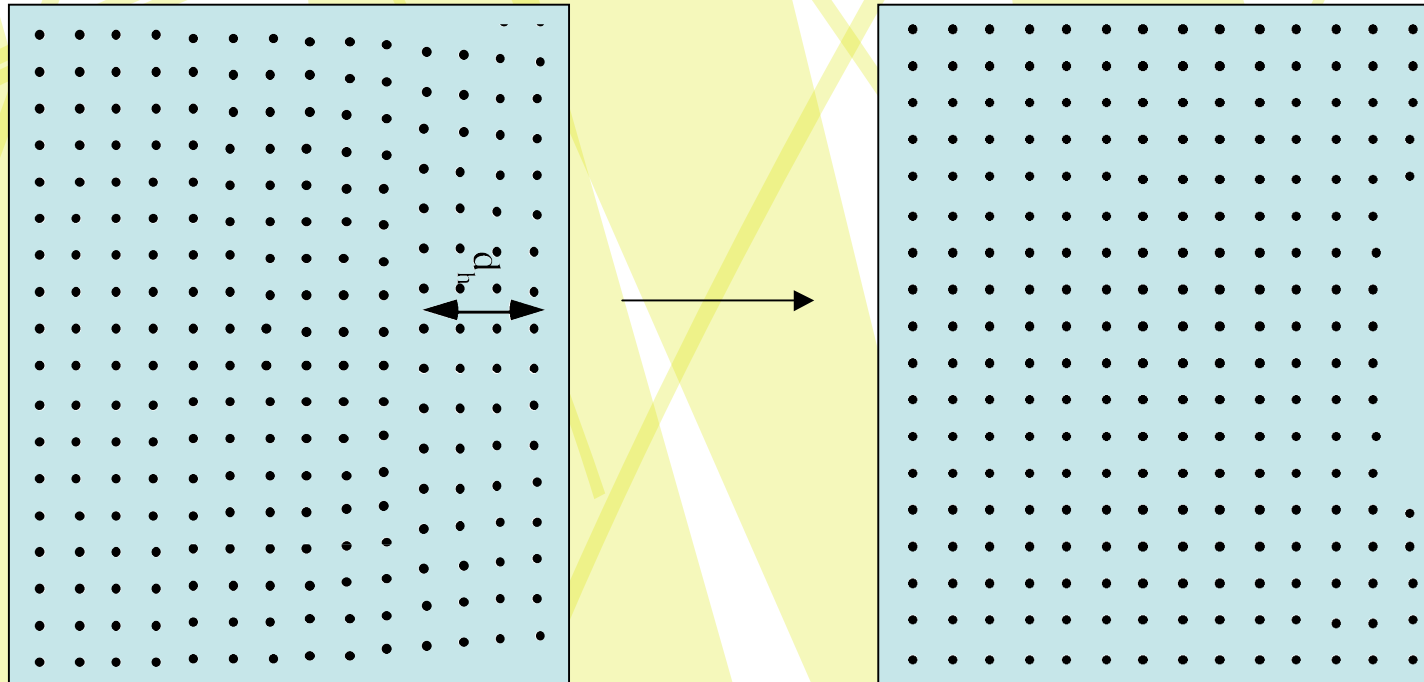


Wetting effects

*Rabkin et al, (19..)*

# Modeling PIN: nano-cracks

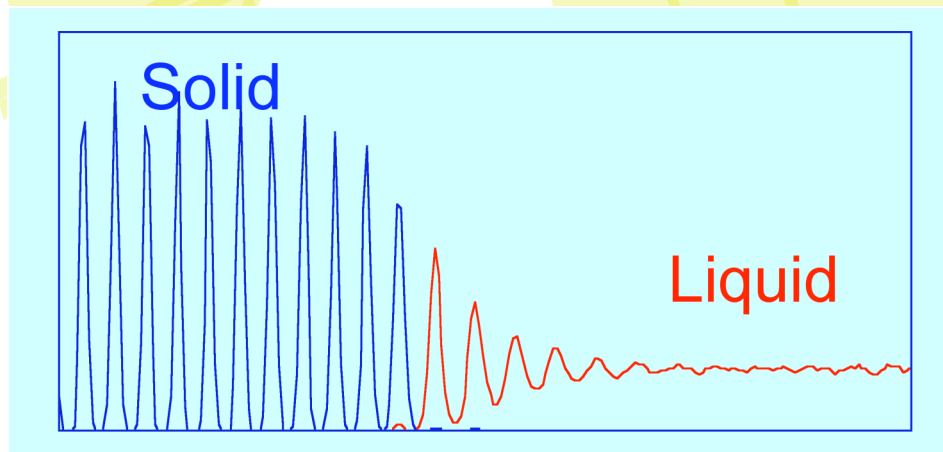
*Geysermans et al. (2003)*



$$d_h \leq \frac{\mu b^4}{4\sqrt{2}\pi(1-\nu)E_v^f}$$

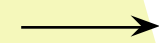
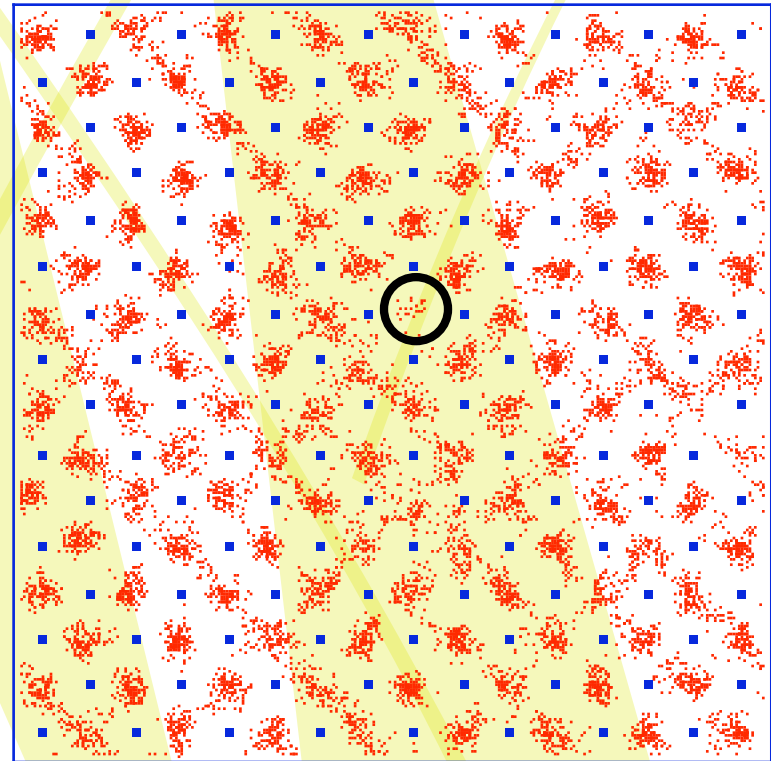
*(Friedel, 1964)*

# Modeling: Crystal-Liquid interface



$$\tilde{\rho}(x) = \left\langle \sum_i \delta(x - x_i) \right\rangle$$

[001]



[010]

*Geysermans et al. (2005)*

# Conclusive remarks

- LME can affect several structural materials and be a major cause of damage
- Understanding of LME is still limited
- No general agreement exists about mechanisms
- There is lack of atomic scale description
- No predictions can be made i.e. which liquid metal embrittles which solid metal
- Research on LME could result in decisive advances in the physics & chemistry of interfaces

# Origins of Illustrations

1. [http://www.tech.plym.ac.uk/sme/Interactive\\_Resources/tutorials/FailureAnalysis/Fractography/Fractography\\_Resource4.htm](http://www.tech.plym.ac.uk/sme/Interactive_Resources/tutorials/FailureAnalysis/Fractography/Fractography_Resource4.htm)



