FROM RESEARCH TO INDUSTRY

cea den

université
PARIS-SACLAY

MECHANICAL BEHAVIOR OF $(\text{Ni,Fe})\text{Cr}_2\text{O}_4$ SPINEL GRAIN BOUNDARIES STUDIED BY MOLECULAR DYNAMICS SIMULATIONS

L. Van Brutzel, A. Chartier, M. Sauzay

DEN, DPC, SCCME, CEA-Saclay, FRANCE

March 11-15, 2018 | Phoenix, Arizona

- **Stress corrosion cracking (SCC): prediction improvement for pressurized water reactors (PWR) primary circuit components**

- Vessel internals
- Steam generators (Ni-based alloys)

Irradiated bolts
stainless steels 8.5 dpa at 300°C
[J.M. Thomas, Fontevraud 2002]

⇒ Reactor shutdown for inspections and replacements

- **Many SCC (and IASCC irradiation assisted) influential parameters**

Several suggested mechanisms but **no consensus** yet

Mechanical solicitation

Material

Irradiation

Environment

⇒ Probably a coupling of several mechanisms

■ One of the most relevant mechanism consists in the grain boundary oxidation

■ Intergranular cracks and surfaces of brittle fractures

316 stainless steel baffle-former bolt
[J.M. Thomas, Fontevraud 2002]

■ Intergranular oxide penetration

Ni-based alloy
[J. Caballero PhD thesis 2016]

■ Slip bands impacting GB

Irradiated stainless steel
[Jiao et al. 2008]

Grain Boundary = preferential diffusion path

⇒ Embrittlement of the interface

Grain Boundary = stress concentration

Finite Element model / cohesive zone model

Improvement of the « pile-up » model (M. Sauzay)

Critical remote stress, Σ_c :

$$\Sigma_c = \frac{1}{m} \left[\tau_0 + \left(\frac{2\lambda}{YC} \right)^{1-\lambda} A^{1-2\lambda} (\theta) \left(\frac{t}{L} \right)^{1/2} \left(\frac{d_0}{t} \right)^{1-\lambda} \sigma_c \right]$$

- Schmid factor, m
- Elastic modulus, YC
- Shear critical stress, slip band, τ_0
- Angle between GB and slip band, θ
- Distance between first atomic planes, d_0
- Slip band length, L
- Slip band thickness, t
- **Critical local stress, σ_c**

Cohesive zone model, FE

[M. Sauzay et al. Int. J Fract 184 (2013) 215]

σ_c ??? $\Rightarrow$ input from lower length-scale

« Universal Binding Energy Relation »

Brittle fracture via cleavage : Rigid separation between two blocks

Hypothesis : Energy localization

Decohesion Energy : $E_{\text{UBER}}(\gamma_{\text{cleavage}}, L_c^*)$

[Rose et al. PRB 28 (1983) 1835]
[Lazar et al. Appl. Phys. Lett. 87 (2005) 261910]

$$\max \left(\frac{dE_{\text{UBER}}}{dl} \right) = \sigma_c = \sqrt{\frac{Y \gamma_{\text{cleavage}}}{e^2 L_c^*}}$$

Application to grain boundaries ?

$$\gamma_{\text{cleavage}} = G_c^{\text{Griffith}} = 2\gamma_S - \gamma_{GB}$$

Different uniaxial loadings

- $\langle 100 \rangle$, $\langle 110 \rangle$, $\langle 111 \rangle$

Different systems

- without defect (bulk)
- $\Sigma 5$, $\Sigma 13$, $\Sigma 17$, $\Sigma 25$, $\Sigma 29$, $\Sigma 41$, $\tau 5$, $\tau 13$, $\tau 25$
- random (poly-crystal)

Spinel
 AB_2O_4

Cation A : Ni, Fe

Cation B : Cr

System size
 $13 \times 5 \times 5$ nm

Relaxation **NPT**
0 GPa, 300 K

uniaxial
deformation

$\dot{\epsilon}$

Relaxation **NσT**
300 K
 σ_{xx} free, others 0 GPa

output

$$G_c = L_x \int_0^{\epsilon_c} d\epsilon \sigma(\epsilon)$$

$$G_c^{\text{Griffith}} = 2\gamma_S - \gamma_{GB}$$

SOME GRAIN BONDARIES, $Fd\bar{3}m$

CLS name	$\Sigma 41$	$\Sigma 25$	$\Sigma 13$	$\Sigma 5$	$\Sigma 29$	$\Sigma 17$	$\tau 25$	$\tau 13$	$\tau 5$
nomenclature	$\Sigma 41(190)[001]$	$\Sigma 25(170)[001]$	$\Sigma 13(150)[001]$	$\Sigma 5(130)[001]$	$\Sigma 29(370)[001]$	$\Sigma 17(350)[001]$	$\Sigma 25[001]$	$\Sigma 13[001]$	$\Sigma 5[001]$
angle	12.68	16.26	22.61	36.86	46.39	61.92	16.26	22.61	36.86

symetric tilt $\Sigma 17(350)[001]$

CLS 17

→ surface (350)

⊙ direction [001]

$\Sigma 13(150)[001]$ symetric twist $\Sigma 5[001]$

CLS 5

→ surface (100)

⊙ direction [010] / [035]

Random GB

GRAIN BOUNDARY RUPTURE

$\Sigma 5 - \text{FeCr}_2\text{O}_4$

Fracture via decohesion = Cleavage
Final state : 2 free surfaces

Use of periodic boundary conditions $\Rightarrow$ 2 GBs

$$G_c = L_x^* \int_0^{\epsilon_c} d\epsilon \sigma(\epsilon)$$

STRAIN/STRESS CURVES

Random GB $\rightarrow$ smallest σ_c

Local disorder increase = harder to break

$$\Delta CN = \frac{CN_{GB} - CN_{ref}}{CN_{ref}}$$

$\frac{\sigma_c \text{ (grain boundary)}}{\sigma_c \text{ (bulk[oriented])}}$ as a function of the misorientation angle

ex. $\sigma_c(\Sigma 5)/\sigma_c(\text{bulk}[130])$

$\sigma_c \text{ (grain boundary)} \ll \sigma_c \text{ (bulk)}$

Importance of the loading direction : anisotropic elasticity

$\text{FeCr}_2\text{O}_4 - \Sigma 5$

$$E_{\text{elast}} = \frac{N}{2V} Y_{xx} \epsilon_{xx}^2 + E_{\text{bulk}}$$

Localization criteria

$$L_x^* = L_{GB}(\epsilon_c) - L_{GB}(\epsilon_0)$$

Comparison of σ_c from MD and σ_c calculated with UBER

Universal Binding Energy Relation :

$$\sigma_c = \sqrt{\frac{Y_{xx} G_c^{\text{Griffith}}}{e^2 L_x^*}}$$

$$G_c^{\text{Griffith}} = 2\gamma_S - \gamma_{GB}$$

with

$$L_x^* = L_{GB}(\epsilon_c) - L_{GB}(\epsilon_0)$$

Very good agreement between UBER theory and MD

Oxidized grain boundary fracture criteria ?

Verification of UBER theory applied to GBs
via MD simulations of oxidized GBs (Σ , τ , random)

- Brittle fracture, cleavage
- Verification of the energy localization hypothesis
- Calculate critical local stresses, σ_c

Effect of the local disorder on the GB: $\sigma_c(\text{NiCr}_2\text{O}_4) > \sigma_c(\text{FeCr}_2\text{O}_4)$

Effect of the crystallographic orientation: anisotropic elasticity

With characteristic length: $L^* = L_{\text{GB}}(\varepsilon_c) - L_{\text{GB}}(\varepsilon_0)$

→ UBER theory agrees well with MD results

Studying other interfaces (metal/oxide, metal/metal)

⇒ Implementation in FE-CZM

■ B. Sicaud PhD thesis

$$\Sigma_c = \frac{1}{m} \left[\tau_0 + \left(\frac{2\lambda}{YC} \right)^{1-\lambda} A^{1-2\lambda}(\theta) \left(\frac{t}{L} \right)^{1/2} \left(\frac{d_0}{t} \right)^{1-\lambda} \sigma_c \right]$$

 Σ_c (MPa)
IASCC exp. results:

[Fournier 2007]

[Gupta 2016]

[Chung 2001]

[Stephenson 2012]

[Fukuya 2008]

[Hide 1995]

[Cookson 1993]

[Massoud 2005]

[Busby 2003]

Acknowledgments

A. Chartier, M. Sauzay,

B. Sicaud

Challenge project – mtt7073

Thank you for your attention

Questions ?

Laurent.vanbrutzel @cea.fr
Commissariat à l'énergie atomique et aux énergies alternatives
DEN/DANS/DPC/SCCME/LM2T bât. 450S
Centre de Saclay | 91191 Gif-sur-Yvette Cedex
T. +33 (0)1 69 08 79 15 | F. +33 (0)1 69 08 92 21

Direction de l'énergie Nucléaire
Département de Physico-Chimie
Service de Corrosion et du
Comportement des Matériaux dans
leur Environnement

INTERATOMIC POTENTIAL - SPINEL

We consider cubic structure $Fd\bar{3}m$, normal

No Jahn-Teller effect, No magnetism:

$$T_C(\text{FeCr}_2\text{O}_4) = 88 \text{ K}, \quad T_C(\text{NiCr}_2\text{O}_4) = 320 \text{ K}$$

Interactions between ions $(\text{Ni, Fe, Cr})_3\text{O}_4$ in spinel structure

$$U_{ij}(r) = \frac{q_i q_j}{4\pi\epsilon_0 r} + A_{ij} \exp\left(-\frac{r}{\rho_{ij}}\right) - \frac{C_{ij}}{r^6} + D_{ij} \{ \exp[-2\beta_{ij}(r - r_0)] - 2\exp[-\beta_{ij}(r - r_0)] \}$$

Parameter fitted to reproduce the structure and the Bulk modulus

Verified on thermal expansion and disordered system formation energies

Lattice parameter as function of temperature

		a (Å)		B ₀ (GPa)		α (10 ⁻⁵ K ⁻¹)	
		calc.	exp.	calc.	exp.	calc.	exp.
NiCr ₂ O ₄	N	8.284	8.3155 8.305	231	204 333	2.2	2.1-2.3
	D	8.298		224			
	I	8.297		228			
FeCr ₂ O ₄	N	8.370	8.377 8.392	183	203 204	3.0	1.8-2.3
	D	8.404		179			
	I	8.410		185			

N = normal D = disordered I = inverse

STRAIN RATE EFFECT

No influence of the strain-rate: $10^9 \rightarrow 10^6 \text{ s}^{-1}$

But $\gg$ to experiments

V. Yamakov et al. (2006)

$$\langle \sigma_{yy}(\lambda, t) \rangle,$$

$$\begin{aligned} \Gamma_{\text{clivage}} &= 2\gamma_S - \gamma_{GB} + \gamma_{\text{plastique}} \\ &= \int_0^{\gamma_0} \sigma_{yy}(\lambda) d\lambda \end{aligned}$$