



COPPE
UFRJ
Instituto Alberto Luiz Coimbra de
Pós-Graduação e Pesquisa de Engenharia

Técnicas Laboratoriais de análise da fragilização pelo H e Simulação Computacional da Interação H-Metal

DILSON S. DOS SANTOS

PROGRAMA DE ENGENHARIA METALÚRGICA E DE MATERIAIS-PEMM

PROGRAMA DE ENGENHARIA DA NANOTECNOLOGIA-PENT

COPPE- UNIVERSIDADE FEDERAL DO RIO DE JANEIRO

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PEMM-PENT-COPPE/UFRJ

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Conteúdo:

- **Facilidades Laboratoriais no PEMM- COPPE/ UFRJ**
- **Difusão e Interação Hidrogênio microestrutura**
- **Hidrogênio em Ligas de elevada entropia configuracional** Hydrogen in high entropy alloys HEA
- **Hidrogênio em aços inoxidáveis supermartensíticos e aços 9 Ni**
- **Hidrogênio em aços inoxidáveis superduplex**
- **Simulação Multiscale da interação Hidrogenio- metal**

Estrutura de preparação de ligas

Preparação de ligas

Simulação- (termodinâmica, usando Thermocalc)

Fusão- (fornos VAR, VIM e Arco)

Processamento- moagem mecânica , laminação ...

Facilidades Laboratoriais no PEMM- COPPE/ UFRJ

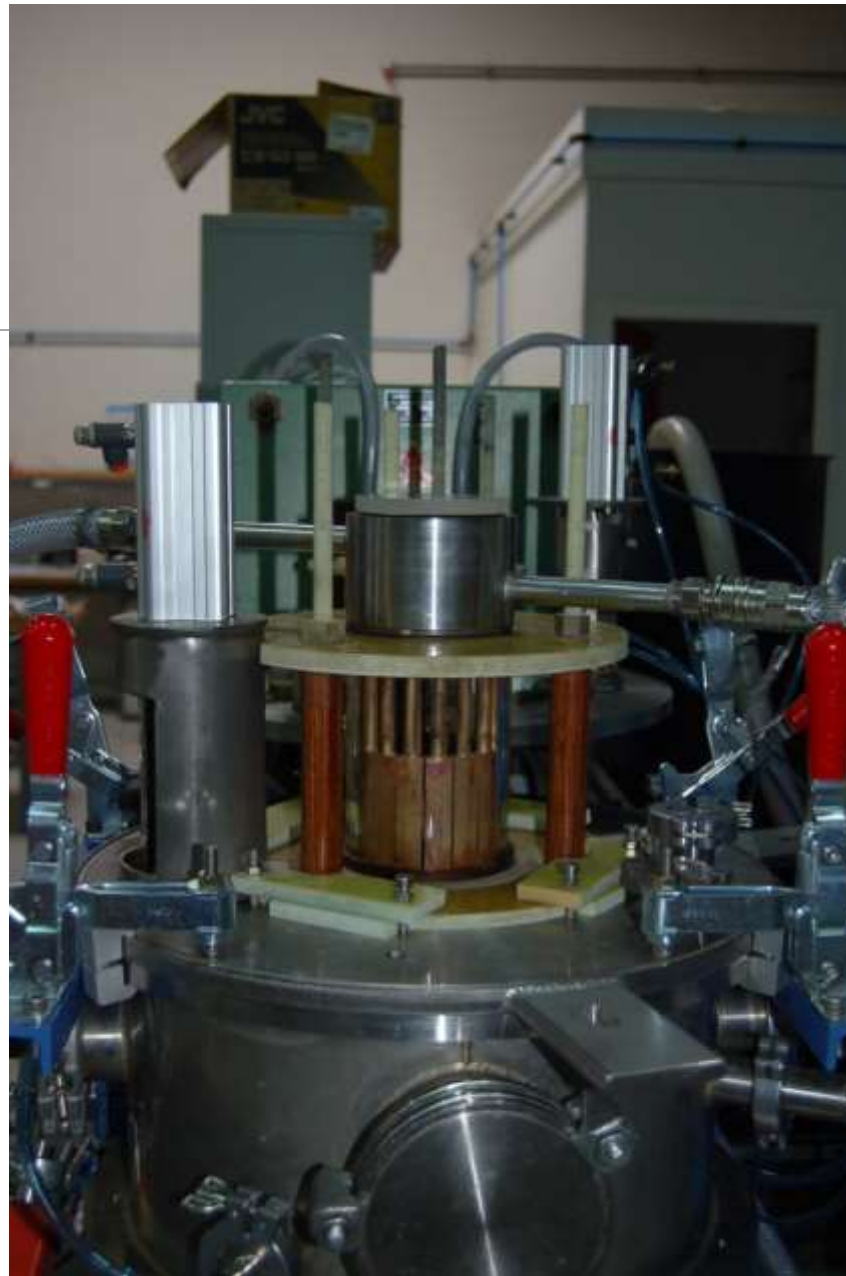
Arc melting furnace
up to 100 g



High- frequency furnace

Temperature up to 2800°C

From 50g to 1 kg.

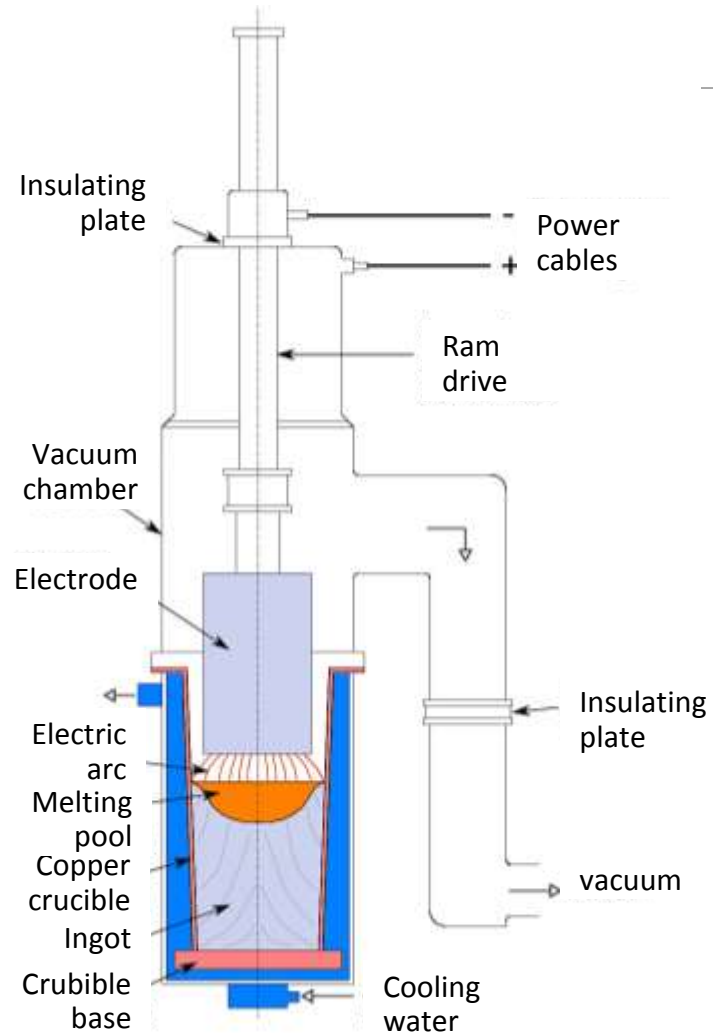


Vacuum Arc-Remelt Furnace (VAR)



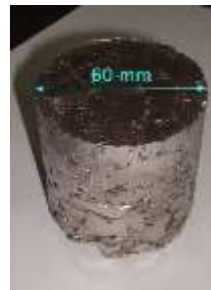
Capacity up to 200 Kg

VAR melting and remelting of alloys



Melting and remelting of special alloys:

- Zirconium alloys;
- Titanium alloys;
- Specialty steels;
- Nickel base superalloys;



Fornecimento global de hidrogênio e demanda (M.ton)

Maior uso do Hidrogênio: na indústria do petróleo e produção de fertilizantes amônia

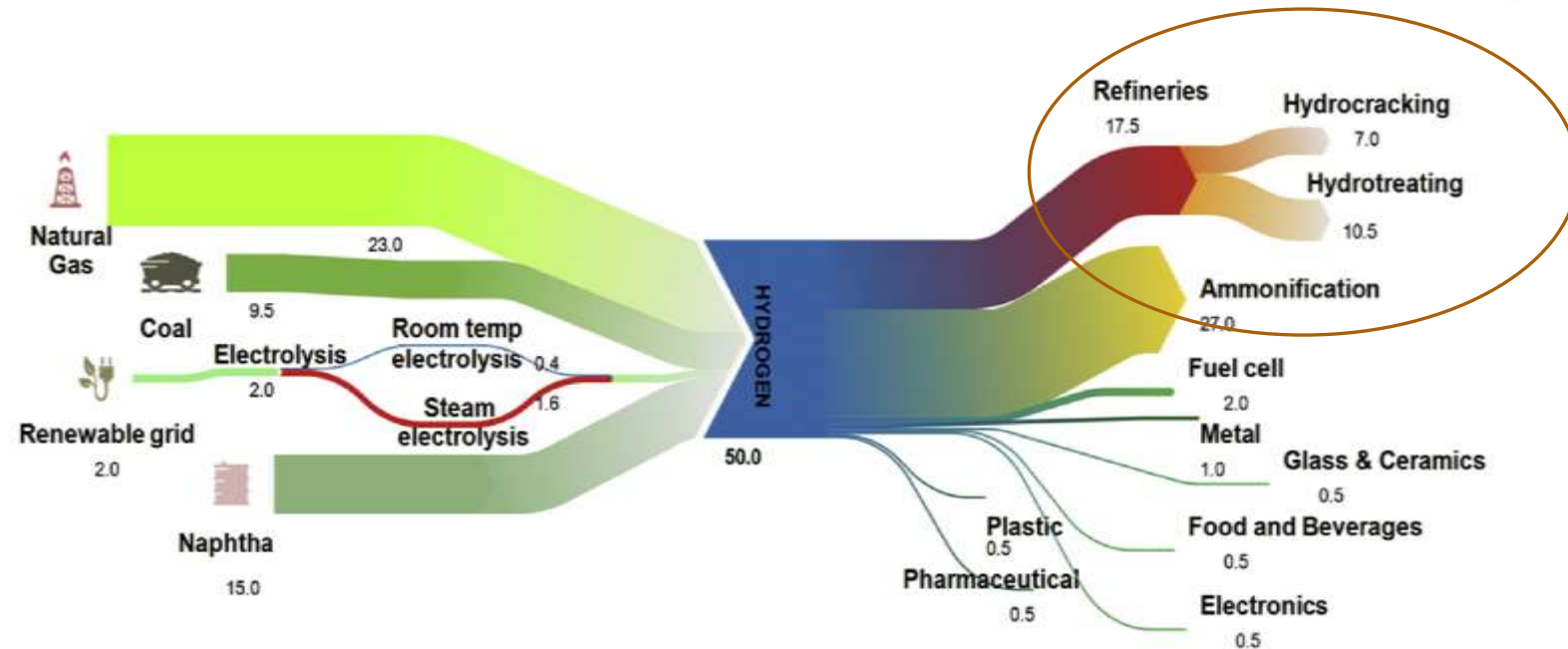


Fig. 4 – The average global hydrogen supply and demand – unit is million metric tons (assembled from multiple sources (2004–2013) in the references section) [4,6,15–17,19–22,28–30,32,33,38–57].

- Motivation:
-

Humber Estuary Killingholme UK – April 16, 2001



- Motivation:
-

Texas City, Texas US – March 23, 2005





- **Difusão e Interação Hidrogênio-microestrutura**

Gas Hydrogen permeation test apparatus

Up to 1000°C
Up to 100 bar

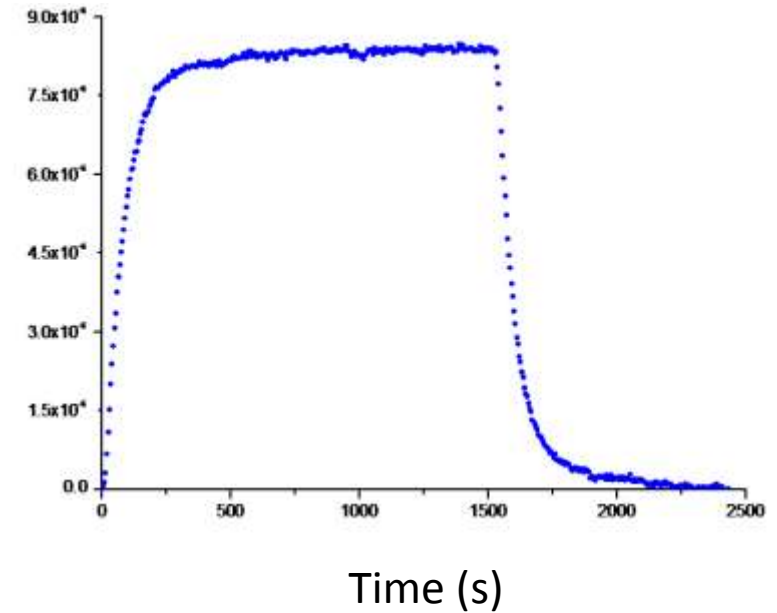
H flux

Capacitive Pressure Transducers



Hydrogen Permeation cell + Furnace

Flow meter 0.5 SCCM



Thermal Desorption System (TDS) with mass spectrometer

Hydrogen trapped (bind energy) related with the microstructure



Electrochemical Hydrogen Permeation test apparatus

1ª Lei de Fick:

$$J = -D \frac{\partial C}{\partial x}$$

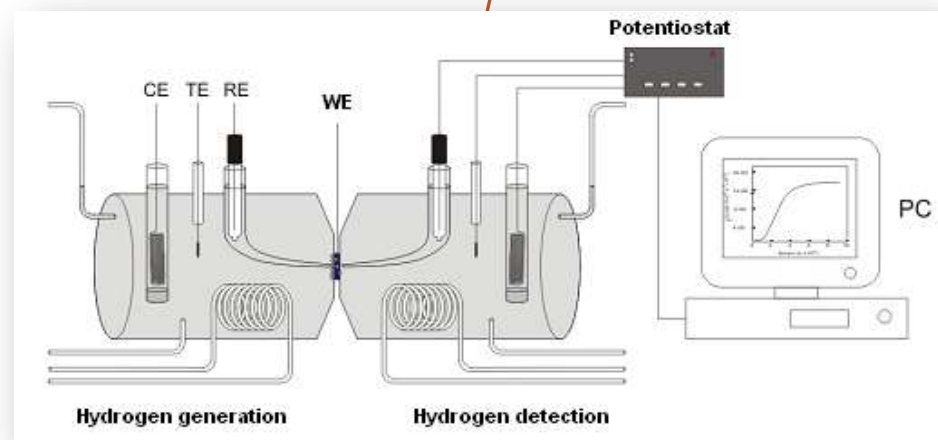
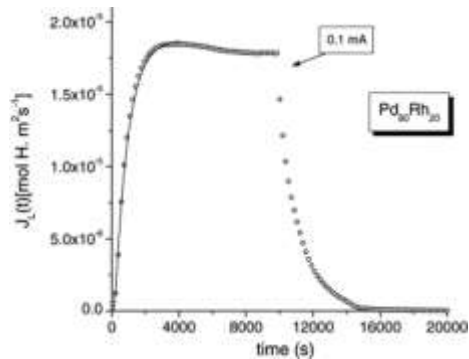
2ª Lei de Fick:

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

Initial & boundaries conditions :

$$C(x,0) = 0 \text{ e } J(0,t) = J_0 C(L,t)_{t>0=\text{cte}}$$

$$\frac{J_L}{J_0} = 1 + \frac{4}{\pi} \sum_{n=1}^{\infty} (-1)^n \exp\left(-\frac{(2n-1)^2 \pi^2 D t}{4L^2}\right)$$



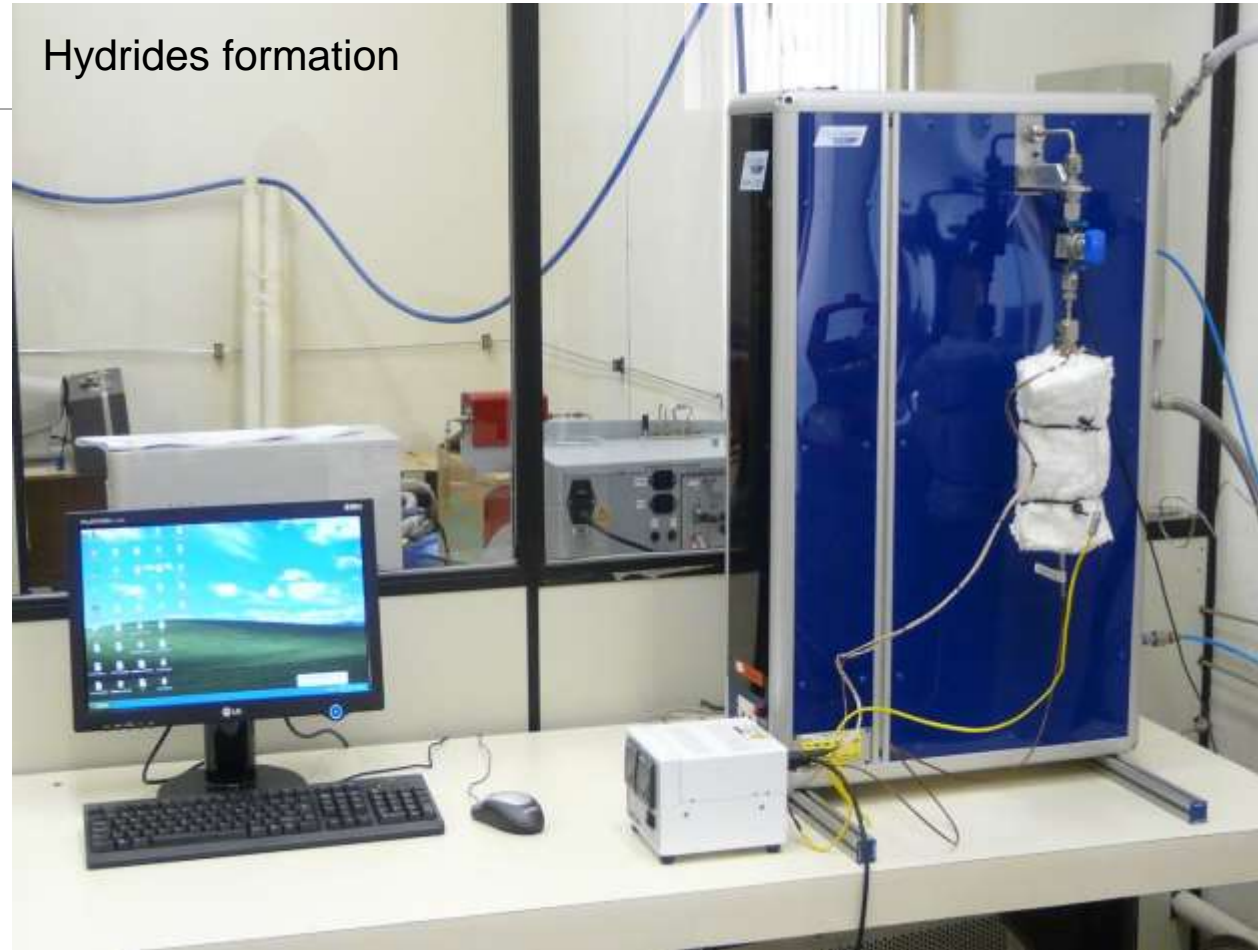
High Pressure DSC



High Pressure Differential Scanning Calorimeter
(DSC-HP)

Phase transformation under high gas pressure
(800°C – 500bar)

PCT equipment



Isothermal Measurements (PCT Pressure – Composition -Temperature)

background

Hydrogen in metals and alloys

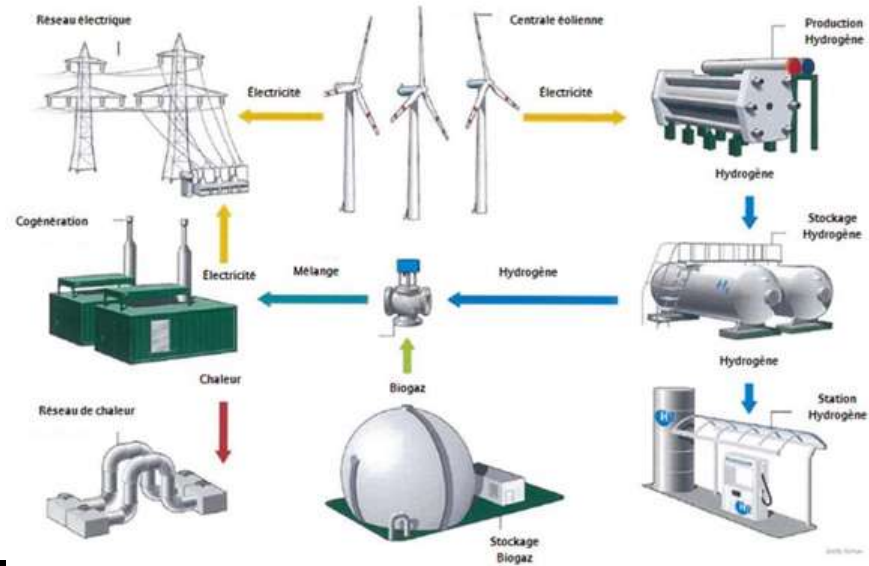
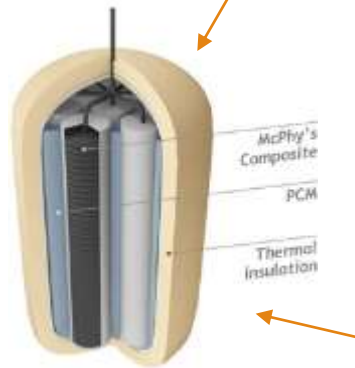
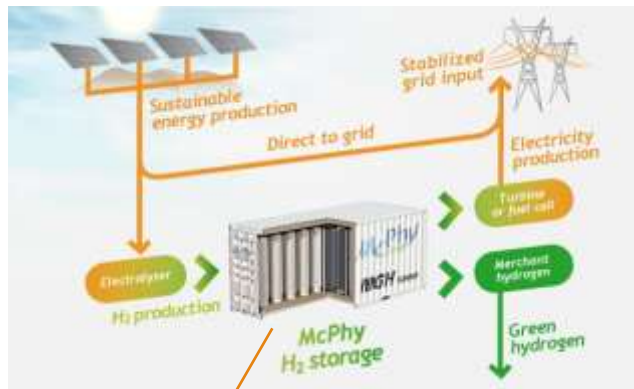
Hydrogen can diffuse through metallic materials

Solid solution (tetrahedral and octahedral sites)

Segregated in defects → Hydrogen embrittlement

As Hydride → energy generation

Hydrogen production & storage



← Hydride Magnesium based alloy

Mcphy Co.

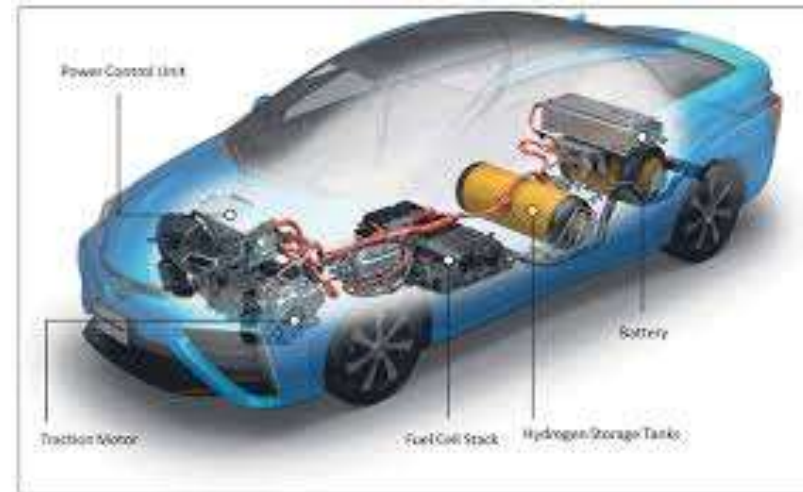
H2 fuel and power station



Technology of Hydrogen cars



Toyota



Hydride

Effects of Nb_2O_5 and (Niobate) $\text{Na}_2\text{Nb}_2\text{O}_5\text{H}_2\text{O}$ addition on the MgH_2

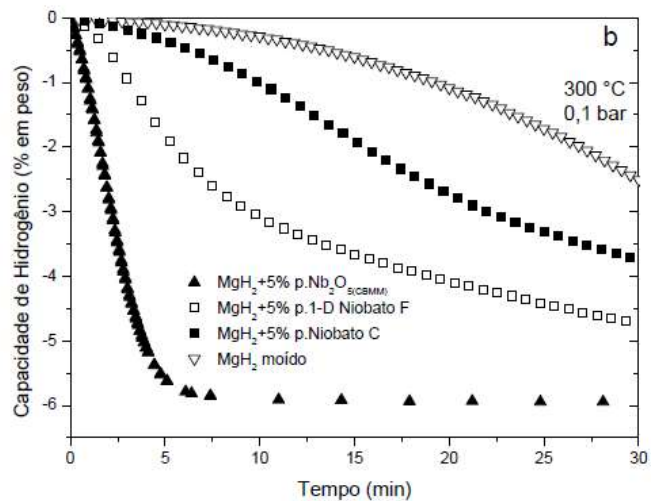
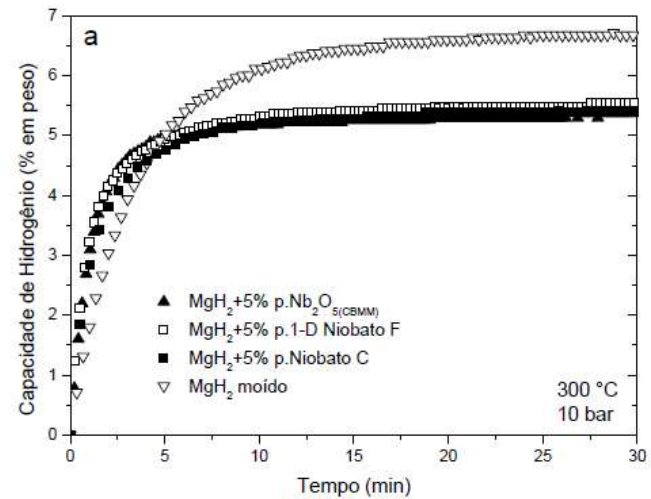
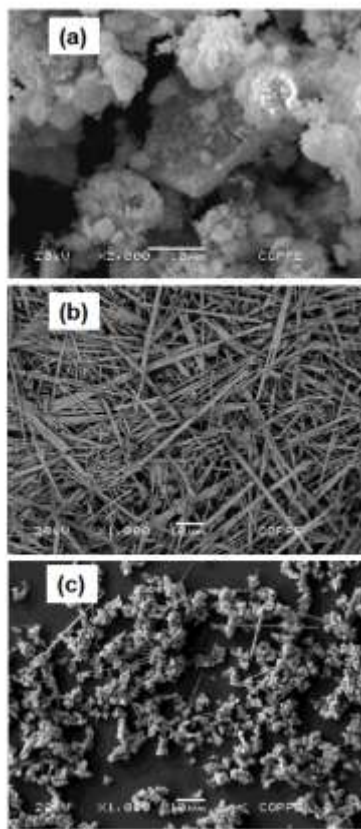
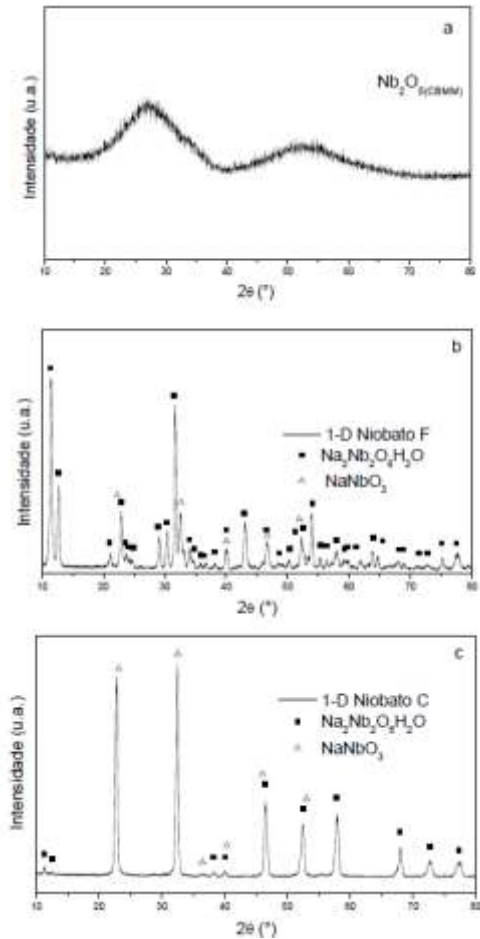


Fig. 18. Curvas de cinética de absorção (a) e dessorção (b) de H_2 das amostras MgH_2

First hydrogenation enhancement in TiFe alloys for hydrogen storage

Catherine Gosselin¹, Dilson Santos² and Jacques Huot¹

¹Hydrogen Research Institute, Université du Québec à Trois-Rivières, 3351 des Forges, Trois-Rivières, QC, G9A 5H7, Canada; jacques.huot@uqtr.ca

²Program of Metallurgical and Materials Engineering – COPPE/Federal University of Rio de Janeiro, P.O. Box 68505, 21941-972 Rio de Janeiro, RJ, Brazil

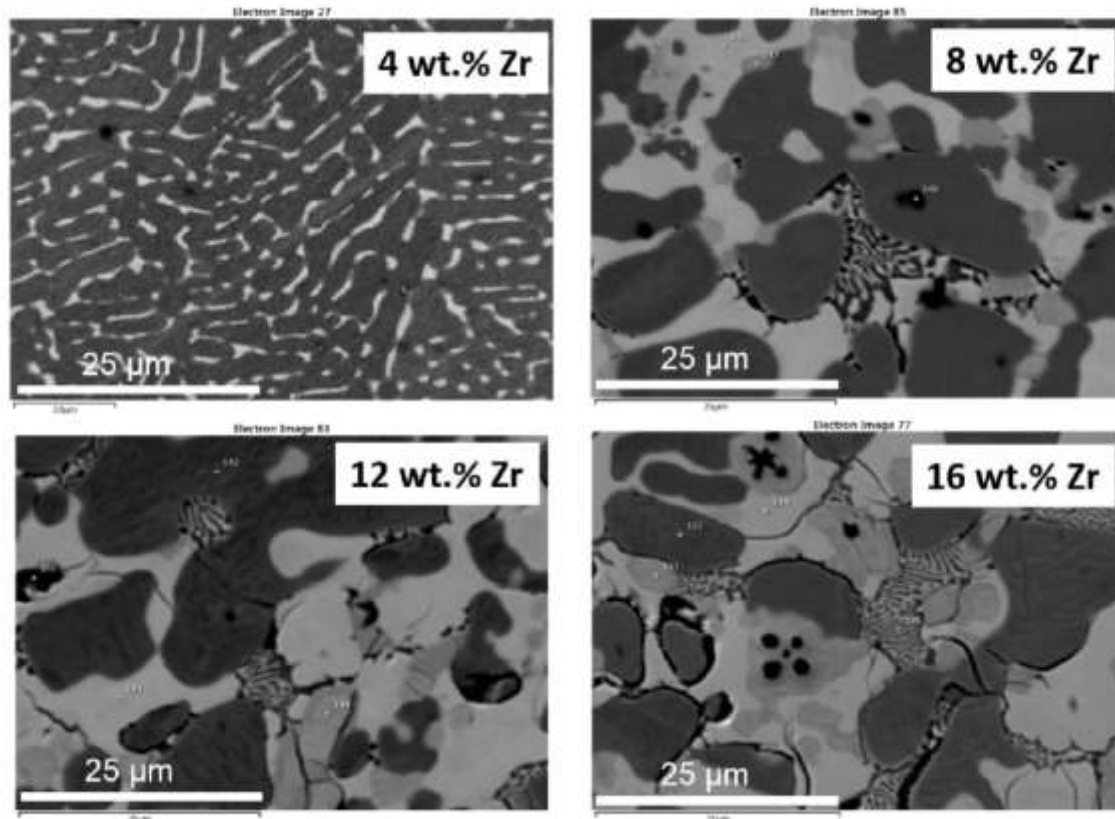


Figure 3. Backscattered radiation micrographs of as-cast TiFe + x wt.% Zr for x = 4, 8, 12, and 16.

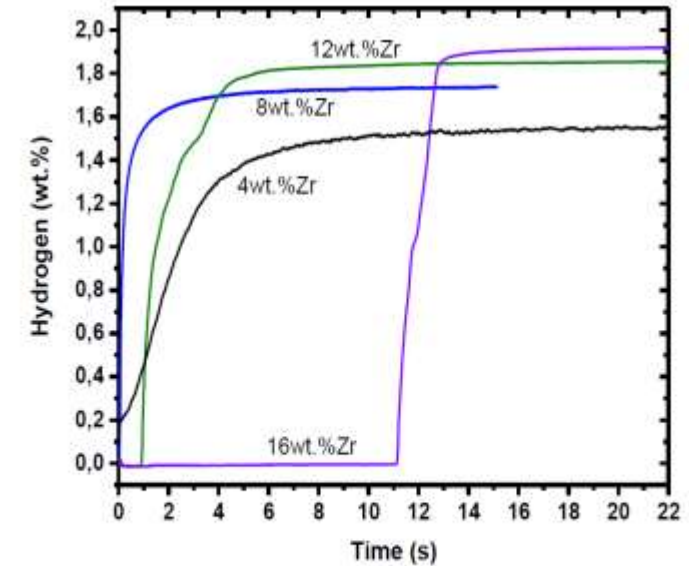
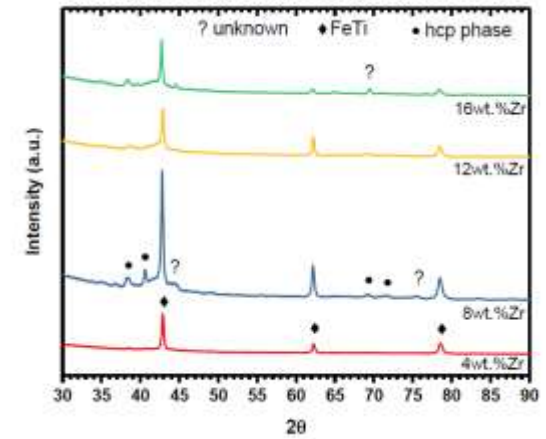


Figure 5. First hydrogenation kinetics at room temperature and under 4500 kPa of hydrogen of as-cast alloys TiFe + x wt.% Zr for x = 4, 8, 12, and 16.

Ligas de elevada entropia configuracional

High Entropy Alloys- HEA

(Alunas MSc: Sara Marques e Ligia Yassuda)

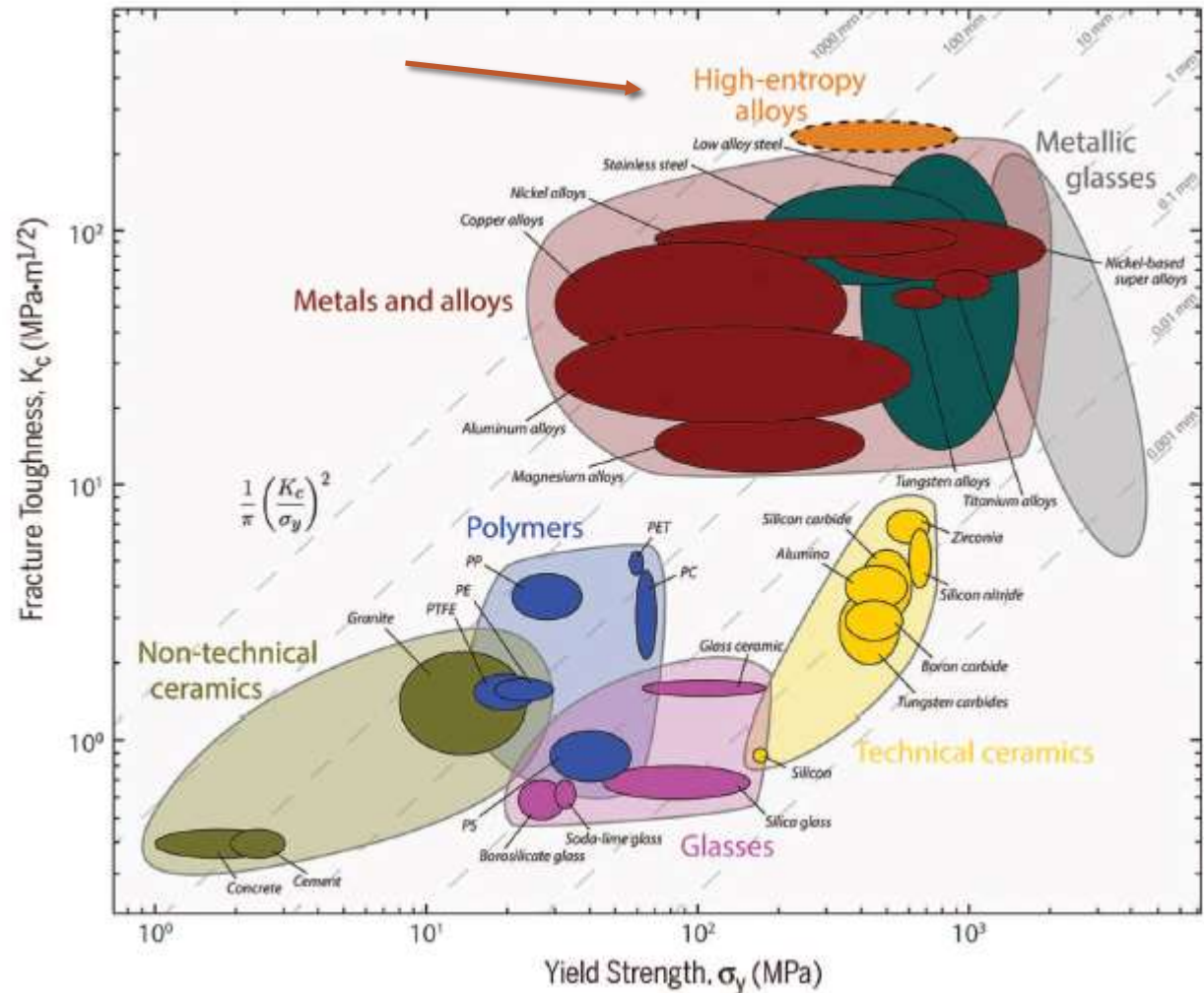
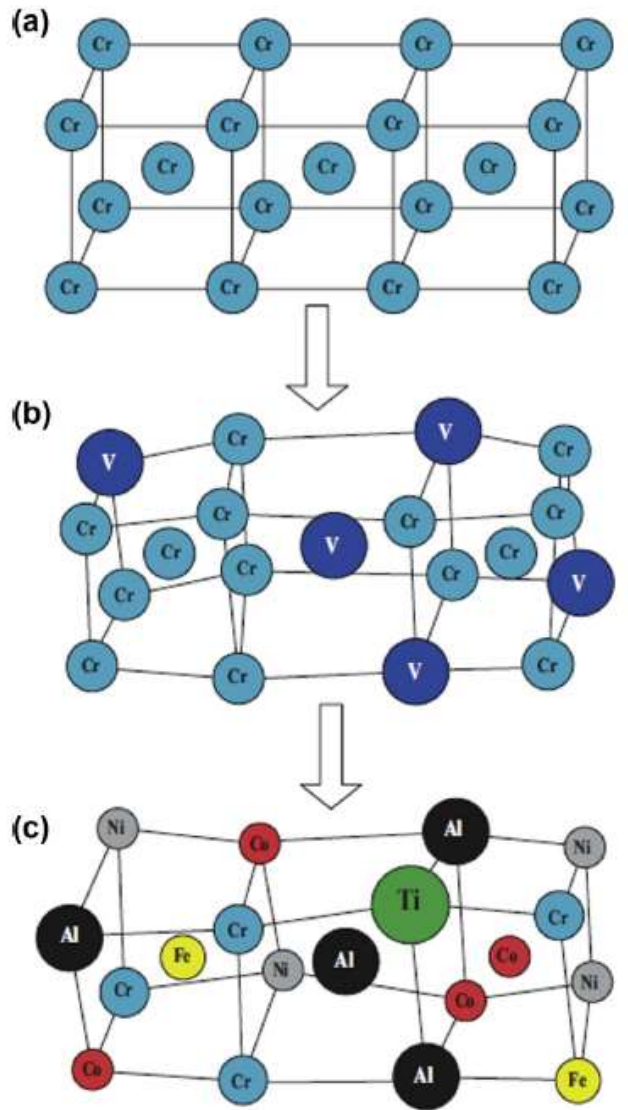
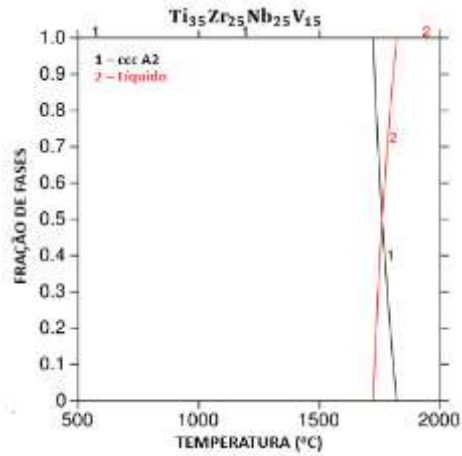


Fig. 4. Ashby map showing fracture toughness as a function of yield strength for high-entropy alloys in relation to a wide range of material systems. The excellent damage tolerance (toughness combined with strength) of the CrMnFeCoNi alloy is evident in that the high-entropy alloy exceeds the toughness of most pure metals and most metallic alloys (9, 49) and has a strength comparable to that of structural ceramics (49) and close to that of some bulk-metallic glasses (51–55).

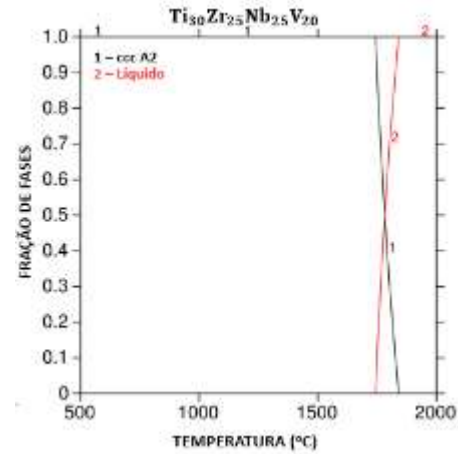


HEA phase diagram

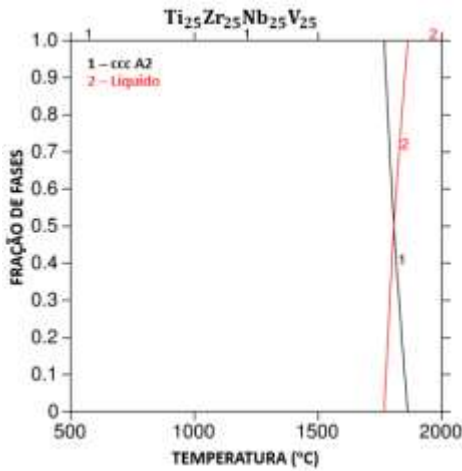
(a)



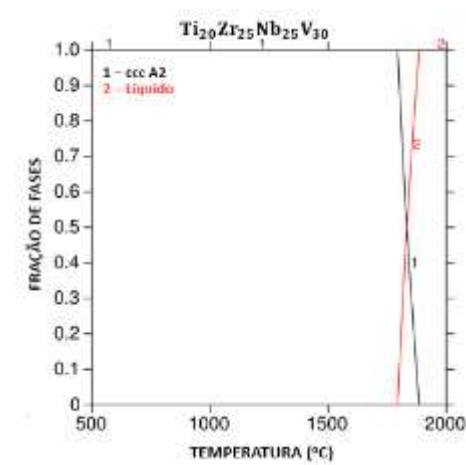
(b)



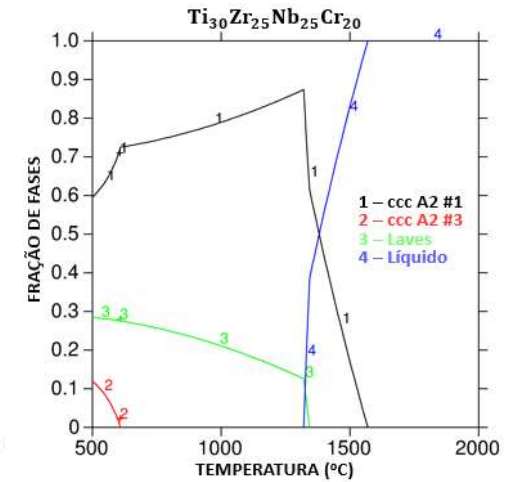
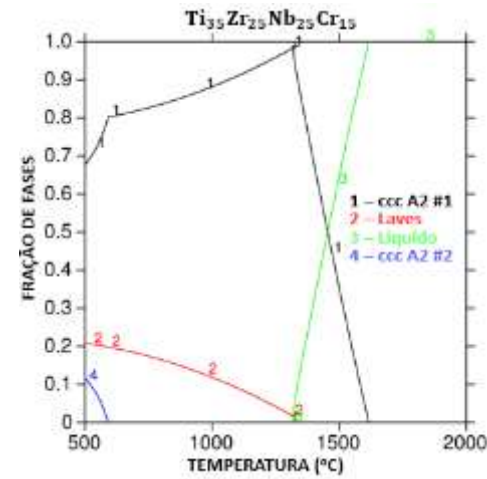
(c)



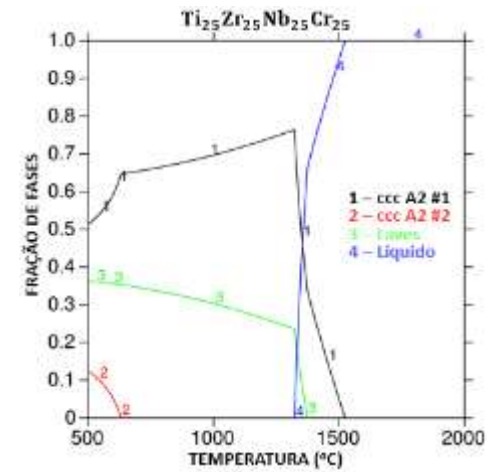
(d)



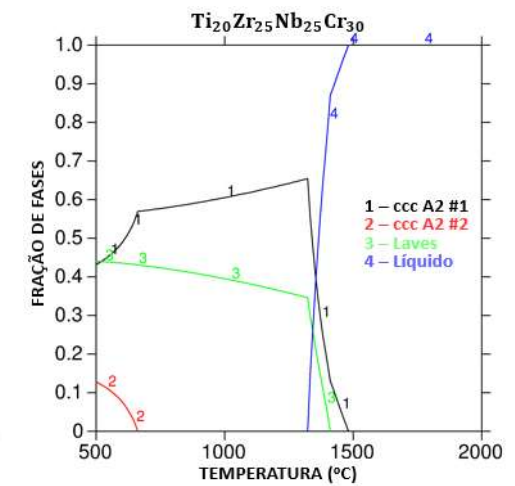
(e)



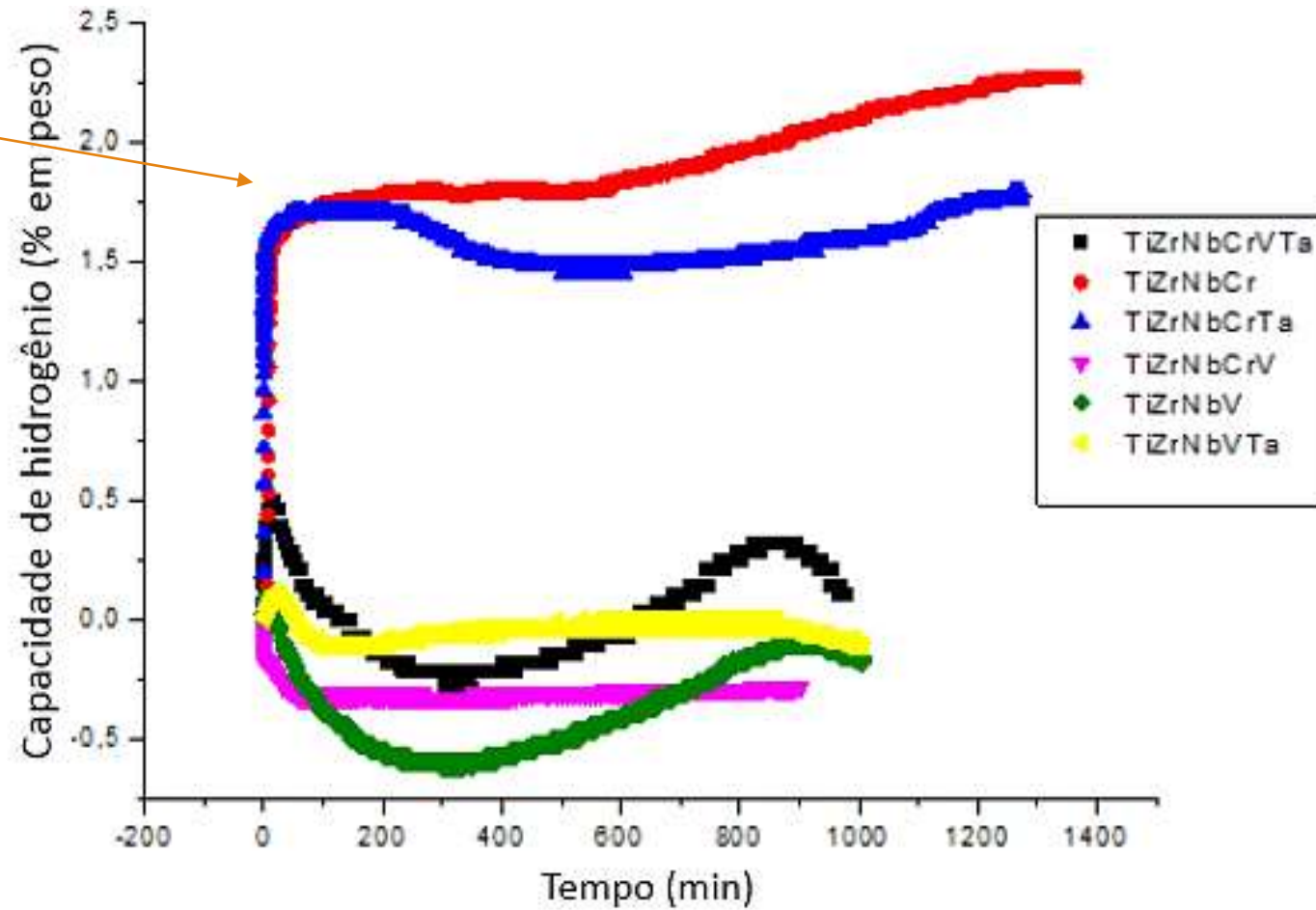
(c)



(d)



absortion



Fragilização pelo Hidrogênio



Hidrogênio em 2.25Cr-1Mo-0.25V

T= 450°C

t- 20 a 30 anos

ataque pelo hidrogênio

Hydrocracking reactor for Petrochemical Industry

2 ¼ Cr-1Mo V steel (300 mm thickness)

Fabrication of heavy wall reactors made in CrMo(V)

walter tosto

Shipping



Federal University of Rio De Janeiro 24th - 26th November 2010

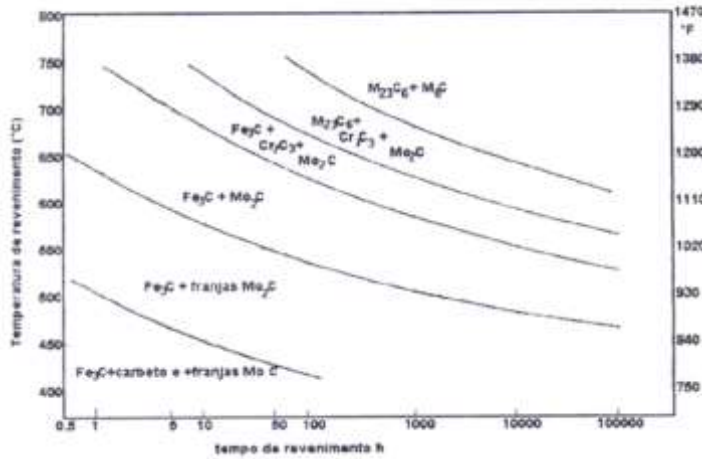
T= 450 to 550°C, 200 bar (H₂)

Oil + H₂

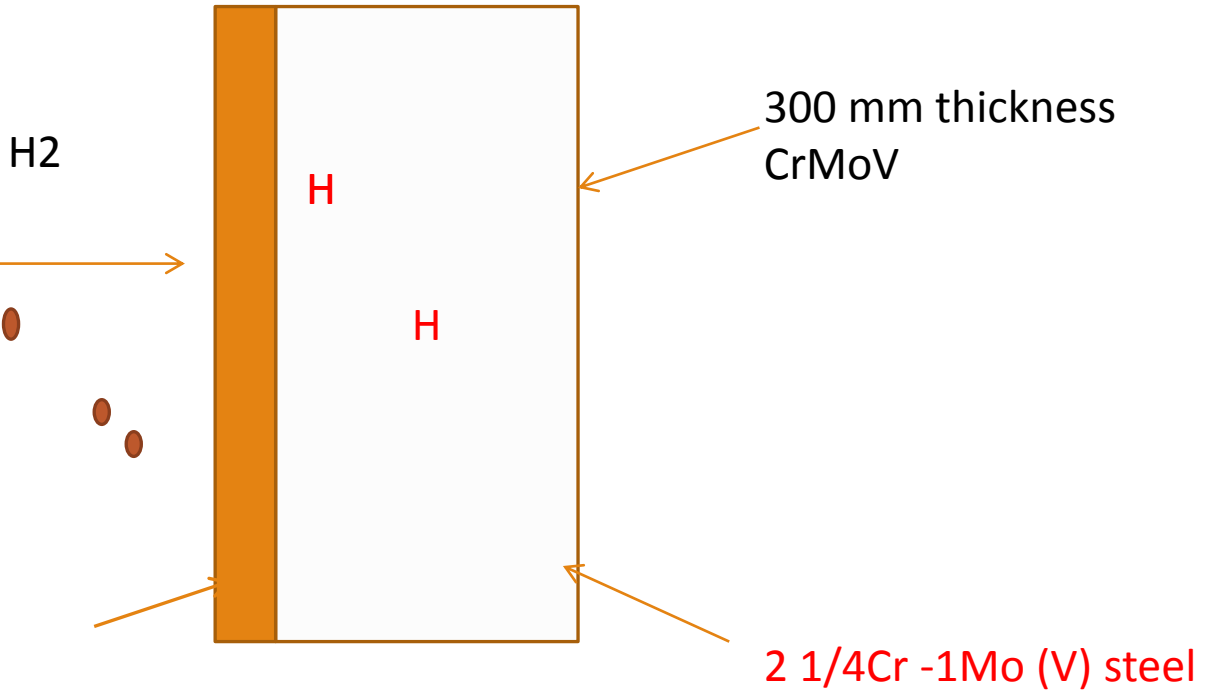
Hydrogen permeation through CrMo(V) steels

25°C
450°C

$D_{\gamma}=10^{-16} \text{ m}^2/\text{s}$
 $D_{\gamma}=10^{-13}-10^{-12} \text{ m}^2/\text{s}$

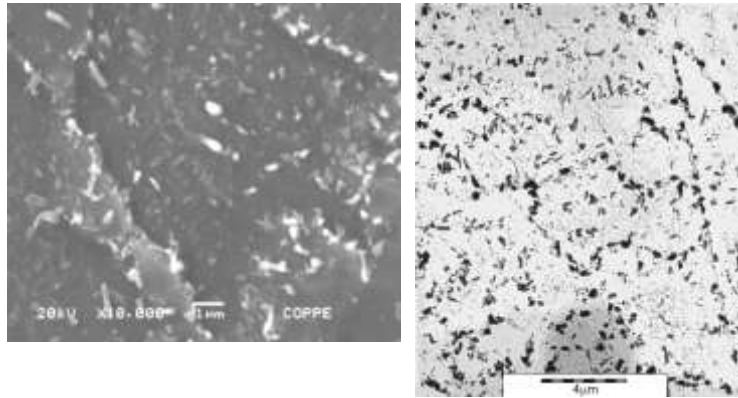


Stainless steel
Coating (cladding)
6 to 10 mm thickness



2,25Cr-1Mo Heat treated

SEM & TEM - Analysis



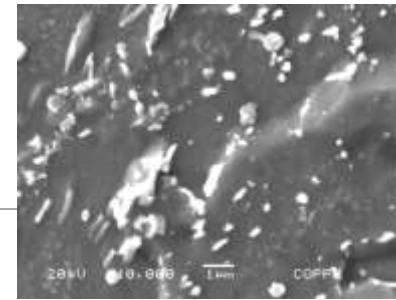
SEM

TEM

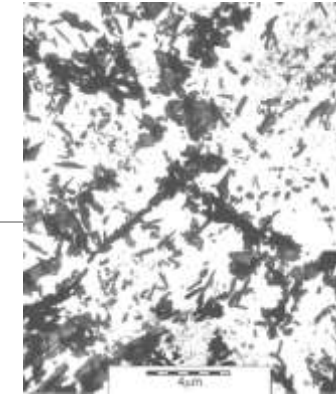
a) As-received sample

Table 1. Chemical composition (in wt.%) of the 2¼Cr-1Mo steel.

C	Mo	Cr	Mn	P	S	Si
0.121	0.96	2.13	0.590	0.005	0.001	0.232

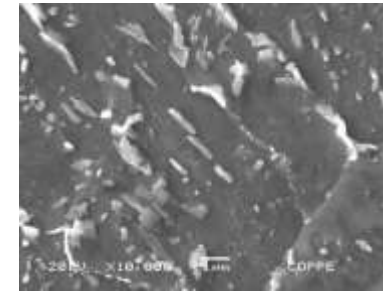


SEM

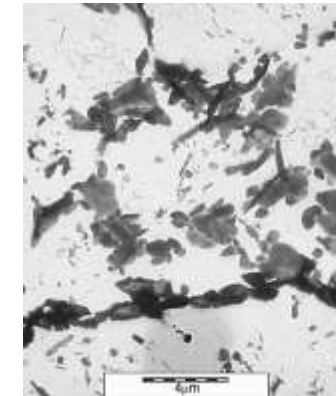


TEM

(b) Heat treated under Ar (1bar- 600°C) 2000 h



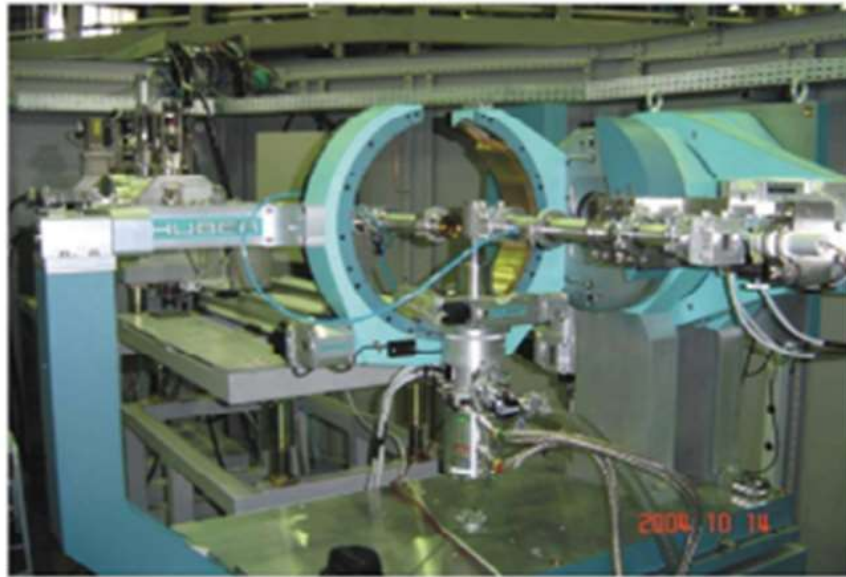
SEM



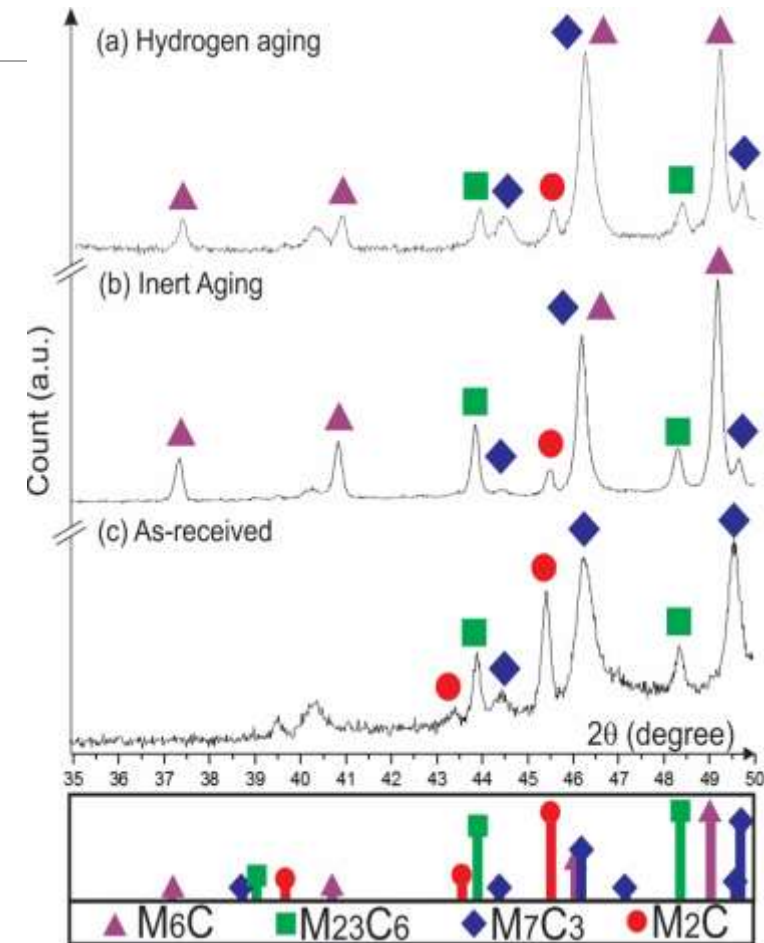
TEM

(c) Heat treated under H2 (10bar – 600°C) 2000h

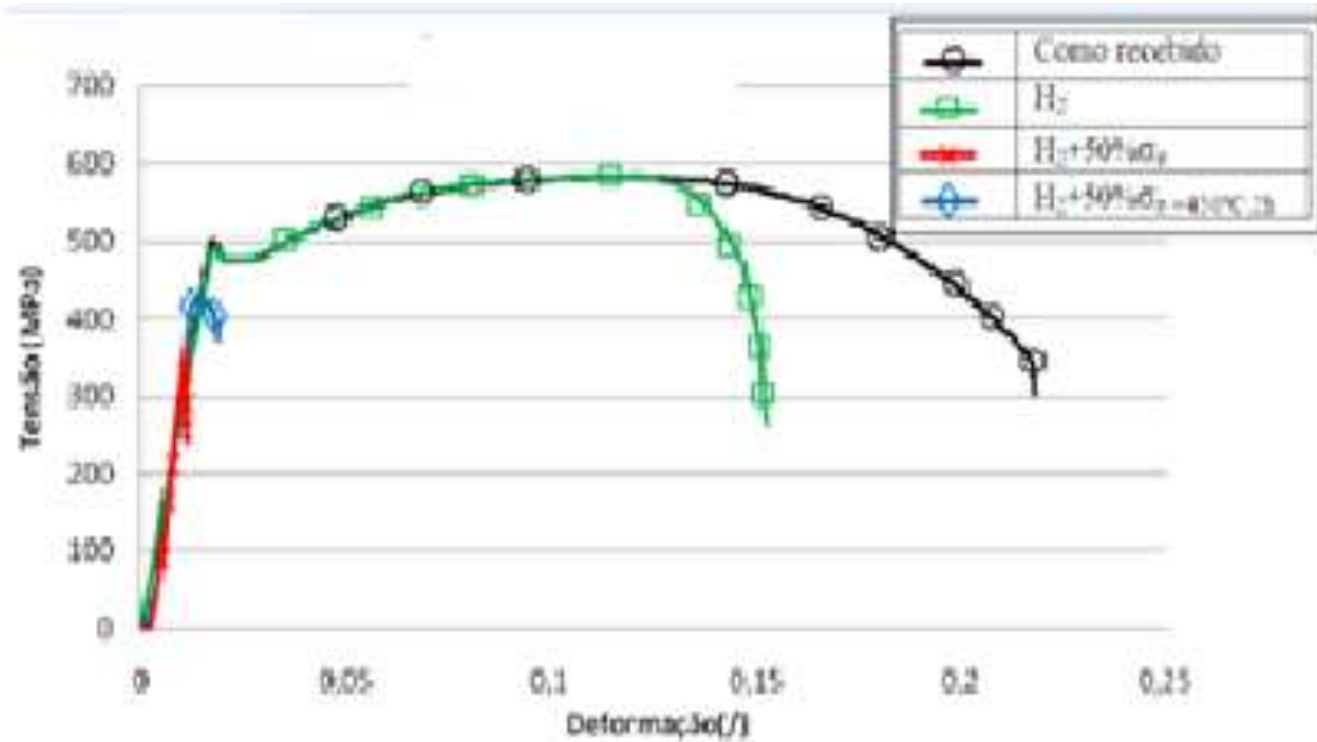
X- Ray Diffraction in the of Synchrotron Radiation in the Lab. ,LNLS Brazil



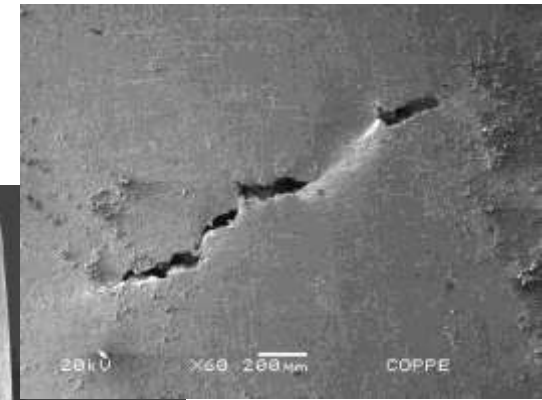
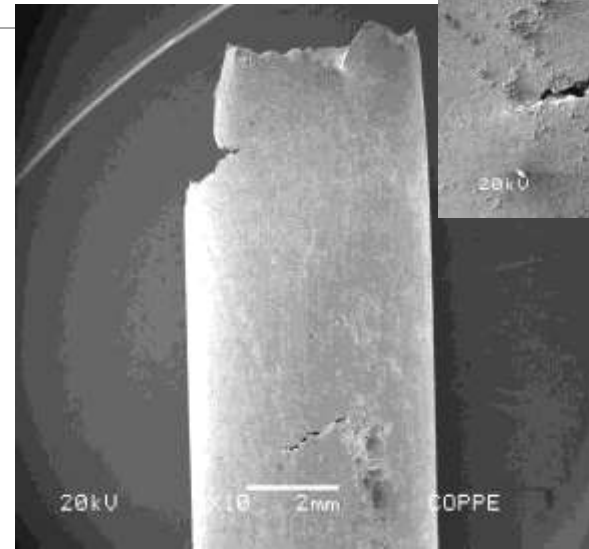
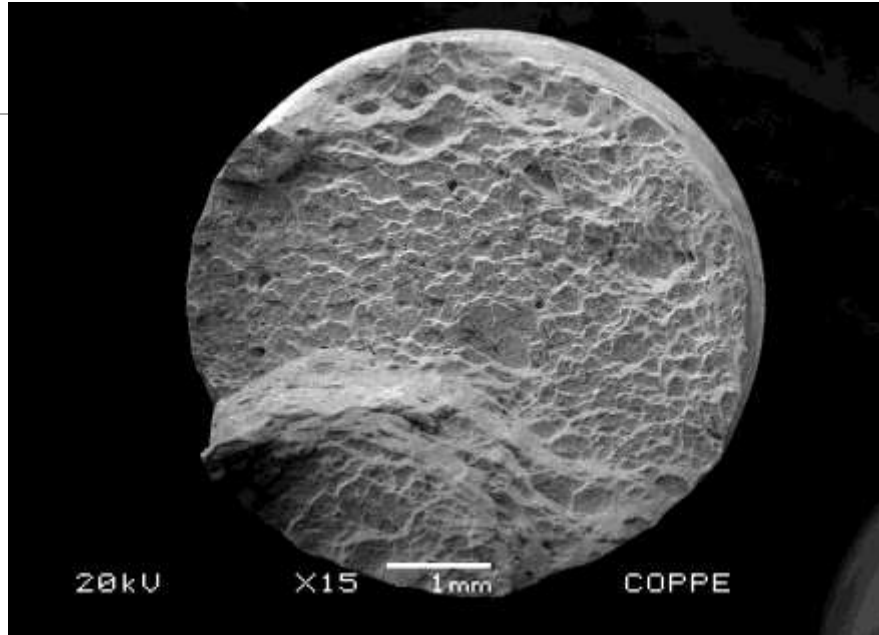
LNLS – Brazil XRD beam line



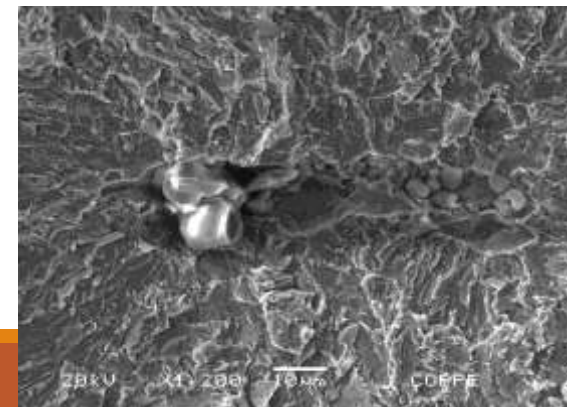
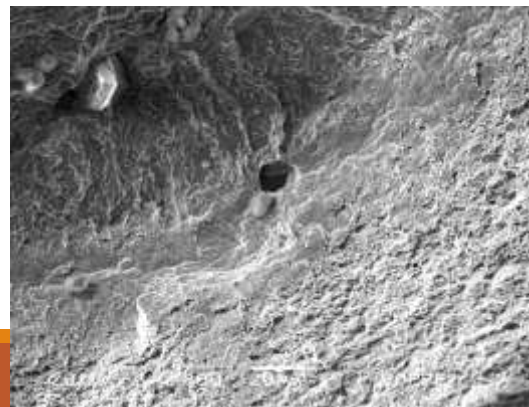
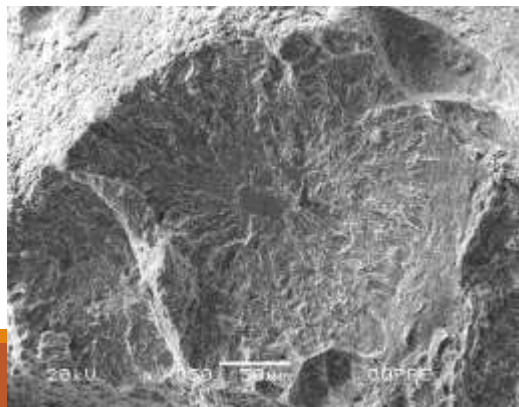
Stress-Strain curves with hydrogen



Fracture surface of 2 ¼ Cr -1Mo-0.25V

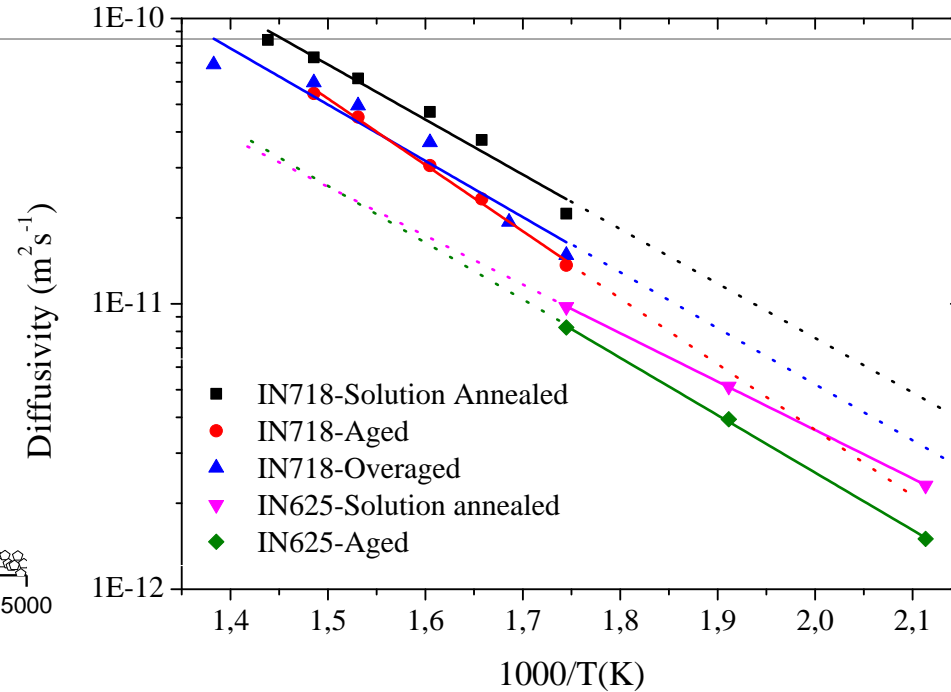
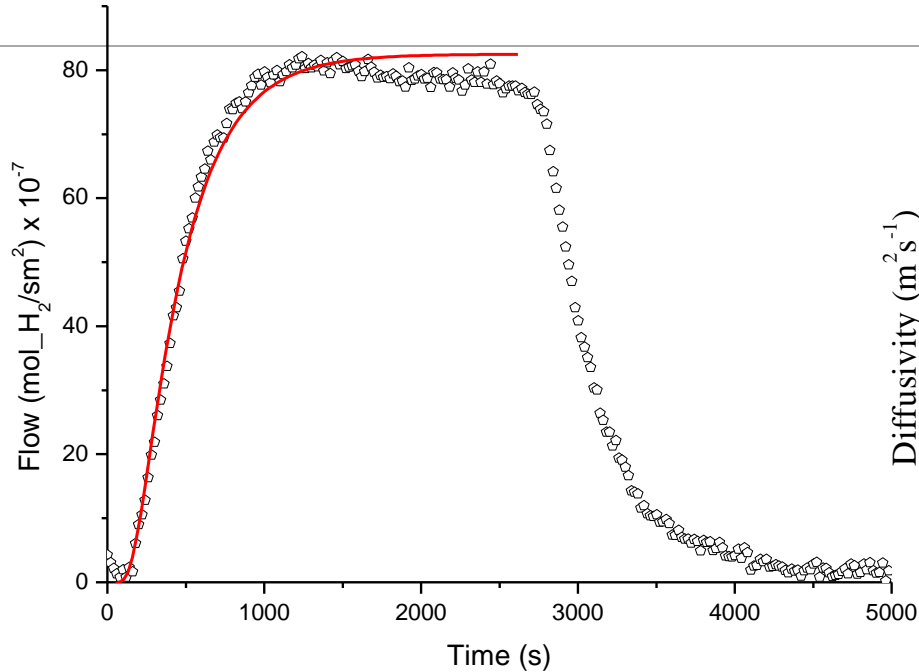


Effects of inclusion on the fracture in samples hydrogenated



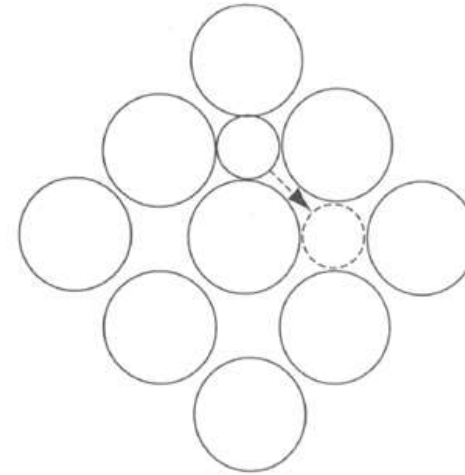
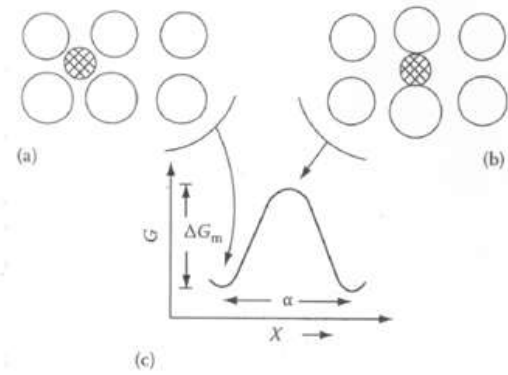
Ni superalloy

Hydrogen diffusion Ni-base superalloys



Attribute	718 SA	718 A	718 OA	625 SA	625 A
D_0 (m ² /s)	$5,38 \times 10^{-8}$	$1,20 \times 10^{-8}$	$4,52 \times 10^{-8}$	$9,62 \times 10^{-9}$	$2,37 \times 10^{-8}$
E_D (kJ/mol K)	36,92	31,36	37,32	32,81	29,95
F_0 (mol H/m s MPa ^{1/2})	$4,94 \times 10^{-4}$	$9,34 \times 10^{-5}$	$8,80 \times 10^{-5}$	$5,54 \times 10^{-7}$	$8,51 \times 10^{-4}$
E_F (kJ/mol K)	59,75	55,24	55,28	32,28	68,91

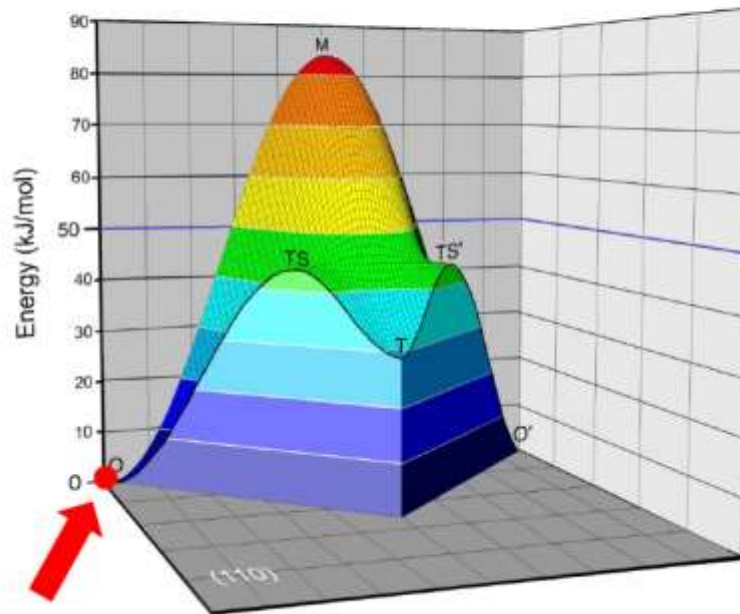
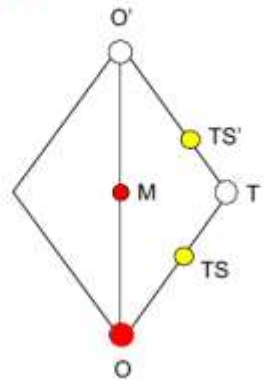
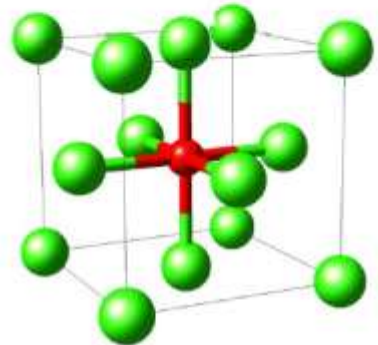
Interstitial Diffusion



J. Philibert Ed de Physique

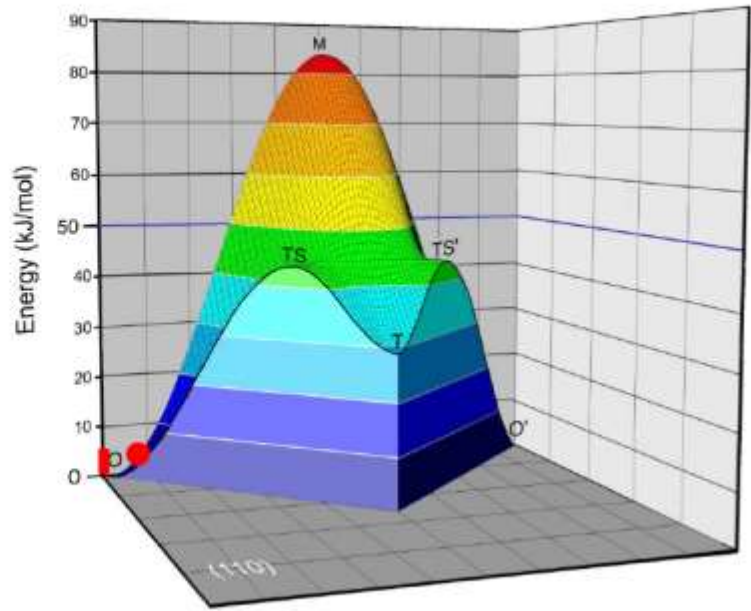
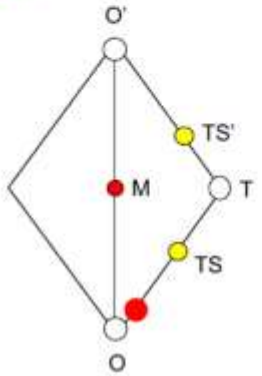
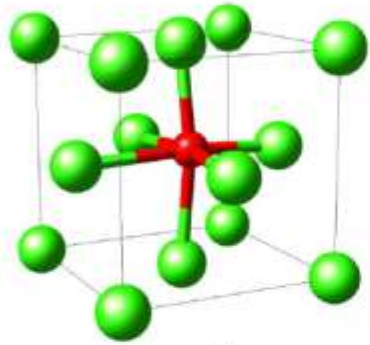


Diffusion of Interstitial Impurities



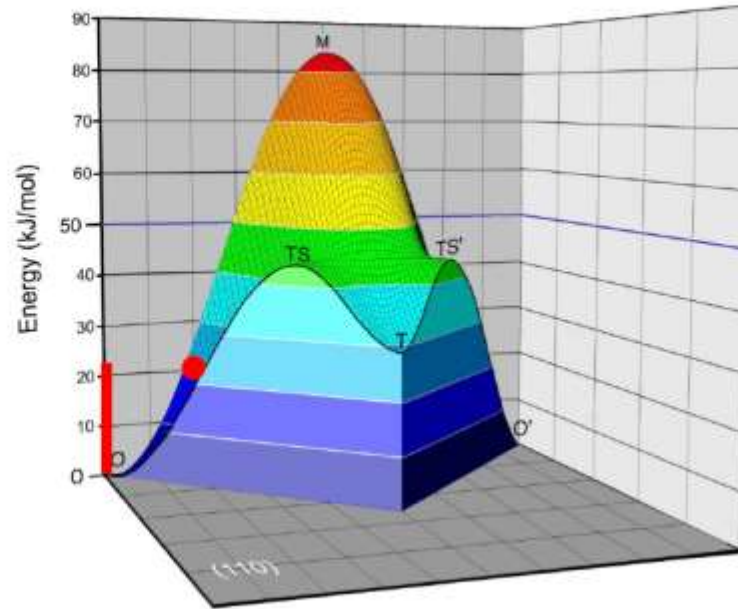
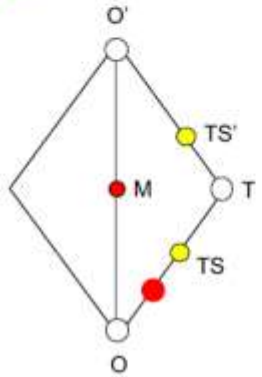
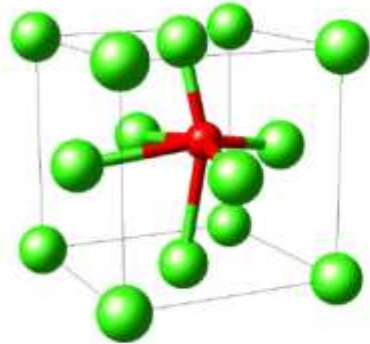
MedeA

Diffusion of Interstitial Impurities



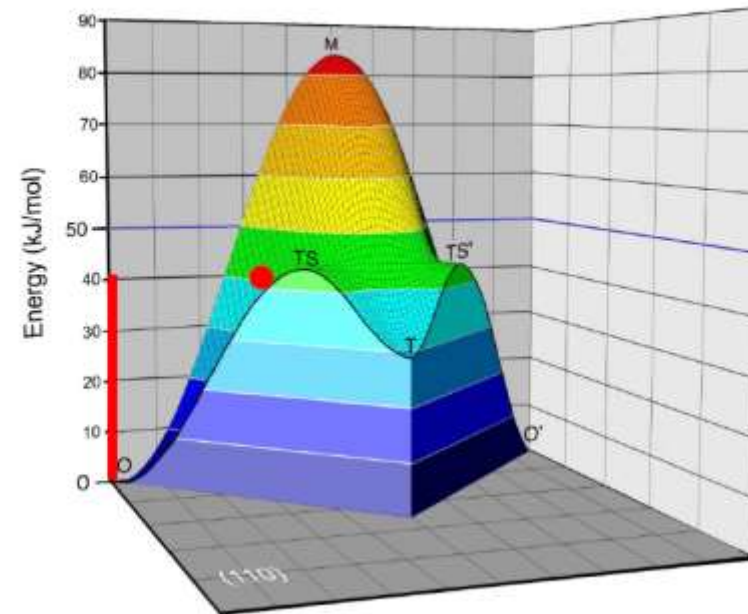
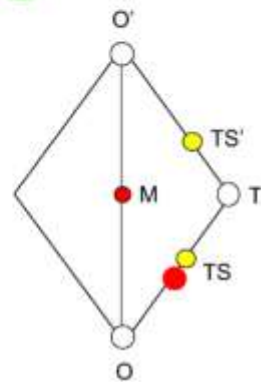
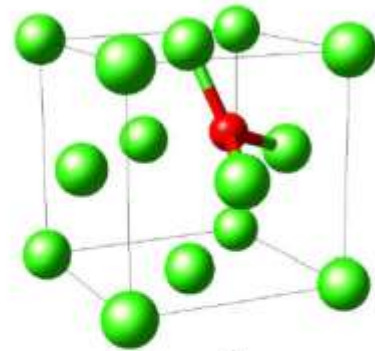
MedeA

Diffusion of Interstitial Impurities





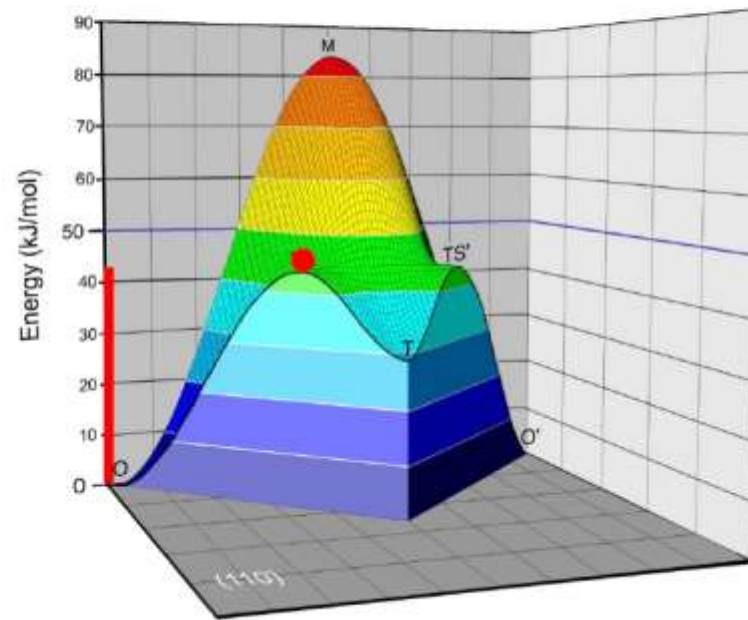
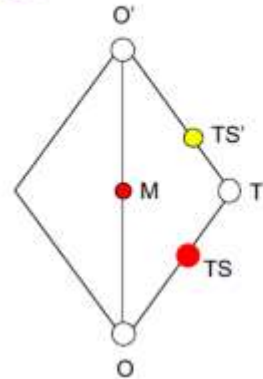
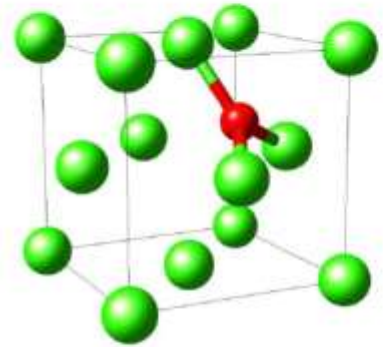
Diffusion of Interstitial Impurities



MedeA



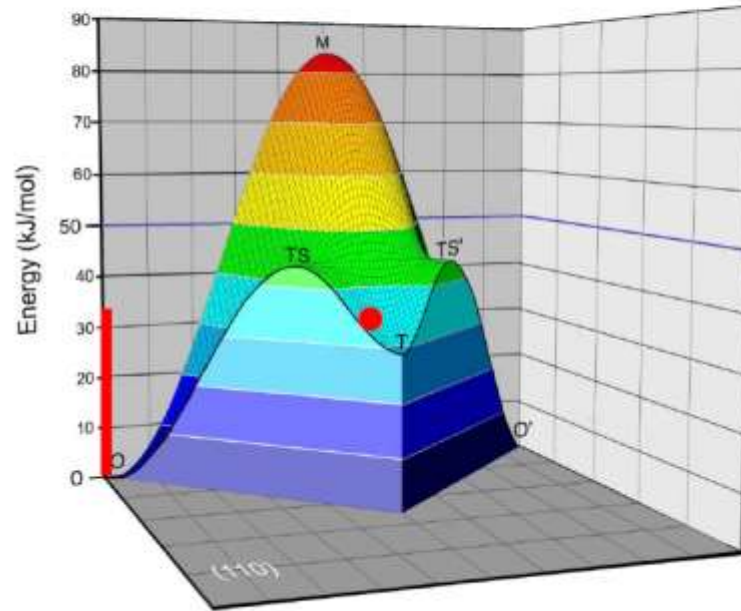
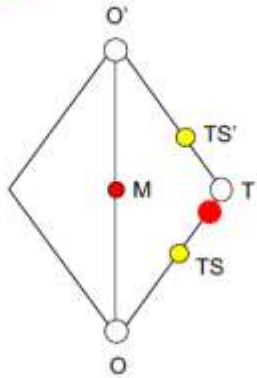
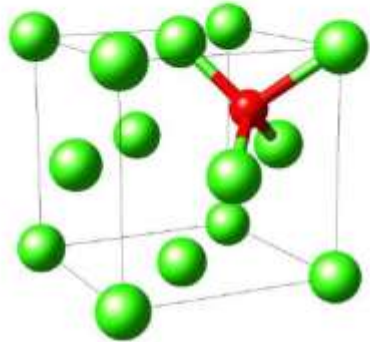
Diffusion of Interstitial Impurities



MedeA



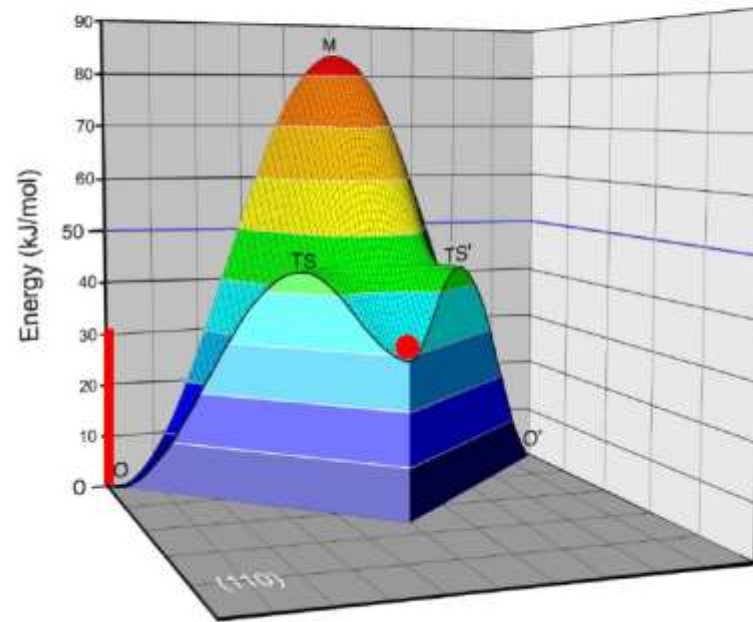
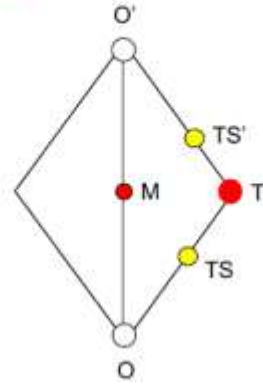
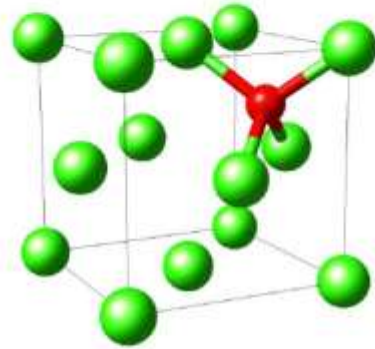
Diffusion of Interstitial Impurities



MedeA



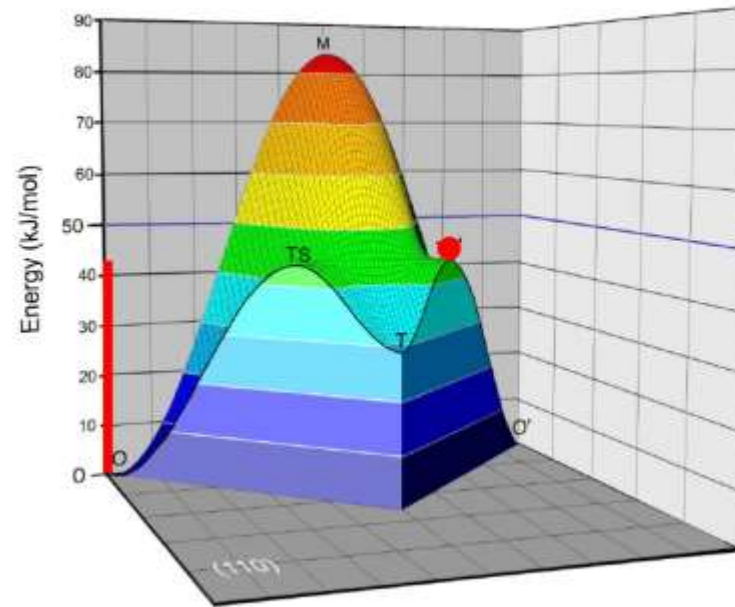
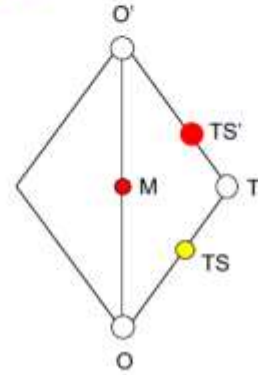
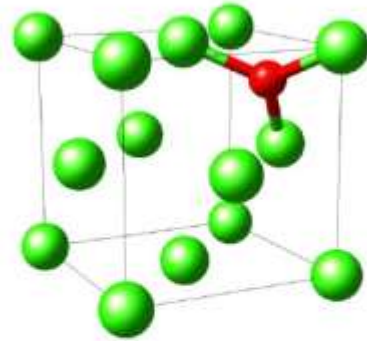
Diffusion of Interstitial Impurities



MedeA



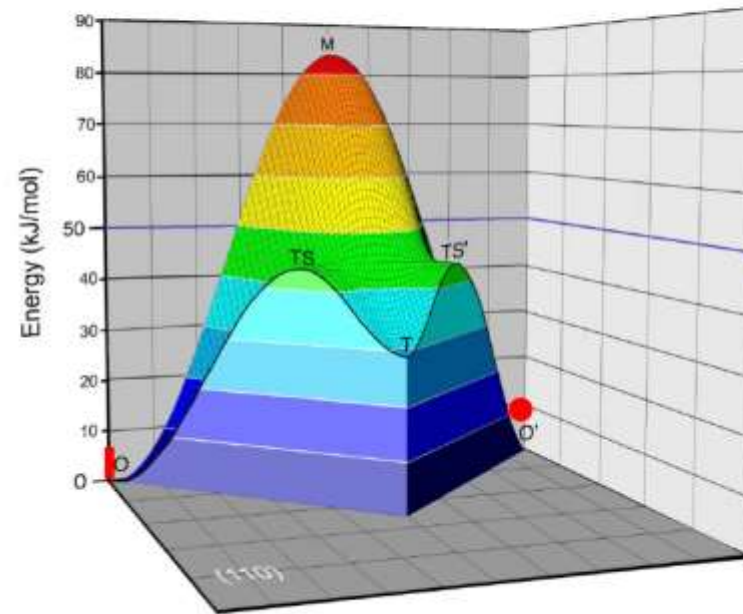
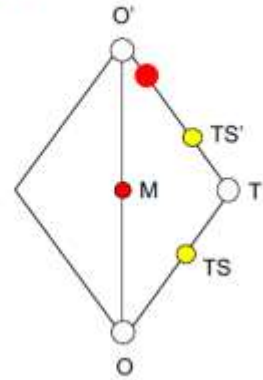
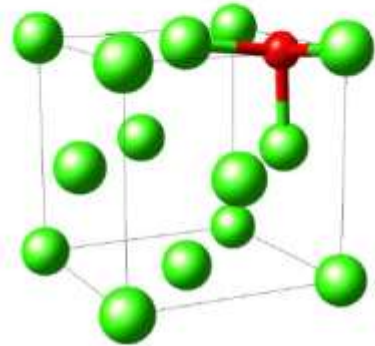
Diffusion of Interstitial Impurities



MedeA

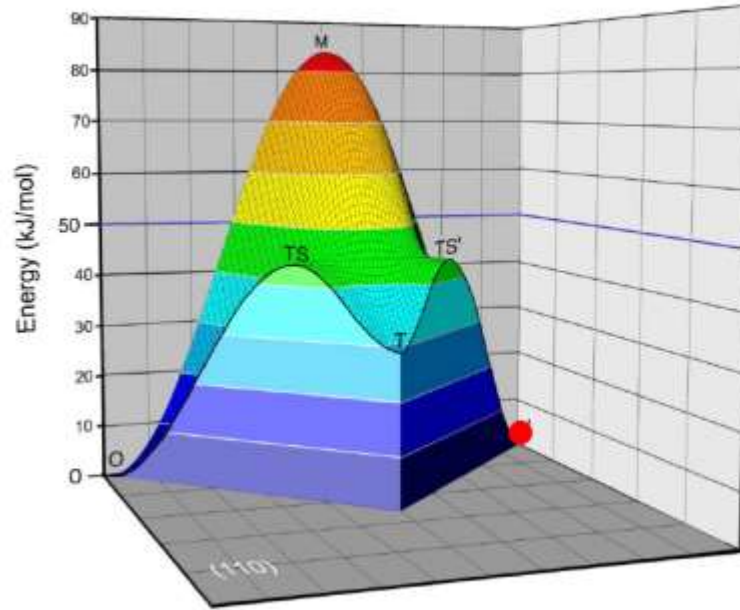
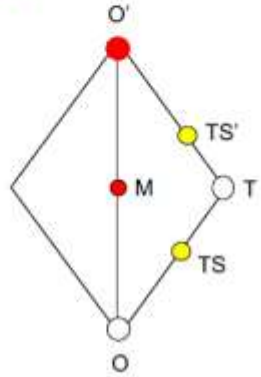
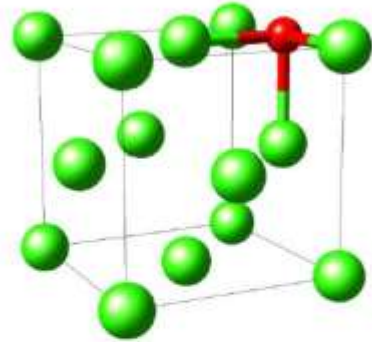


Diffusion of Interstitial Impurities



MedeA

Diffusion of Interstitial Impurities



Interação H- Defeitos

Discordâncias: emaranhadas, livres subgrãos, discordâncias geometricamente necessárias...

lacunas, vazios poros

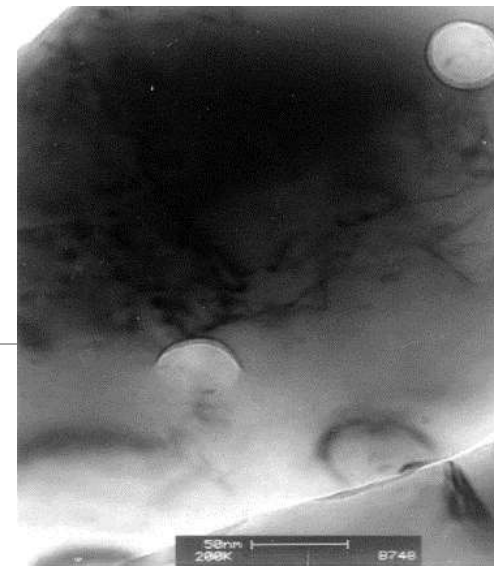
Contornos de grãos: aleatórios e coincidentes

Hydrogen induced superabundant
vacancies

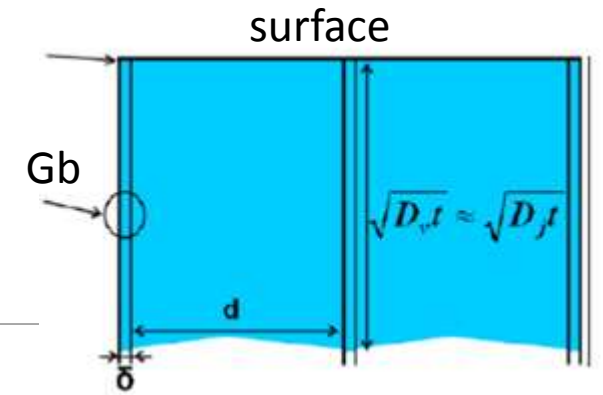
Hydrogen induced dislocations & vacancies

D. S dos Santos; S. Miraglia and Daniel Fruchart
Jalcom 1999

Increasing temperature more vacancies are formed



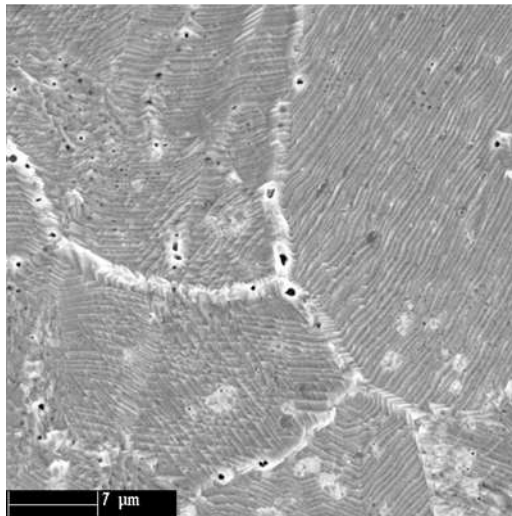
TEM for Pure Pd at 800C, 3.5GPa



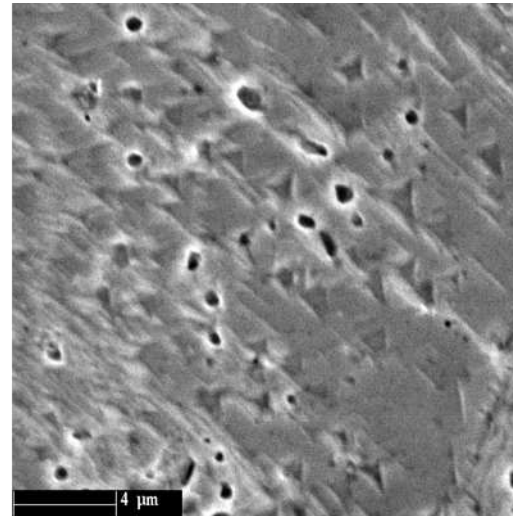
$$D_{\text{eff}} = (1 - f)D_v + f_{\text{gb}} \cdot D_j$$

Diffusion equal in whole volume sample

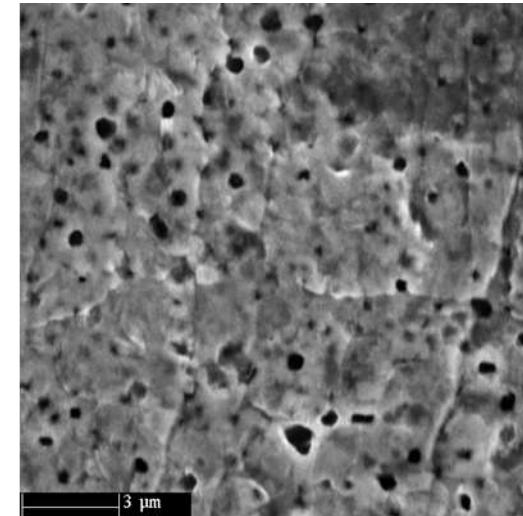
Pure Pd at 450C, 3.5GPa



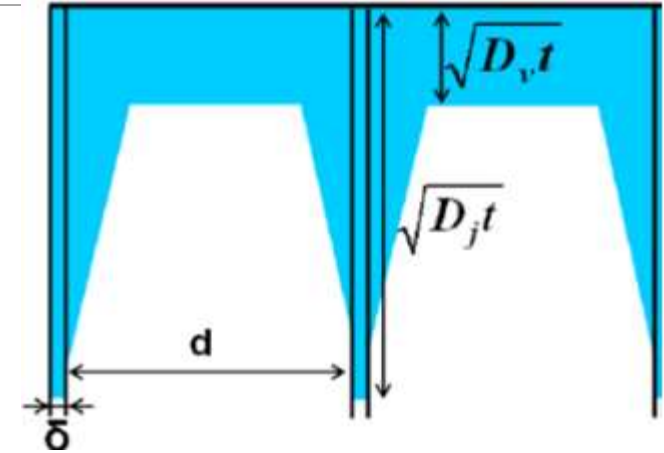
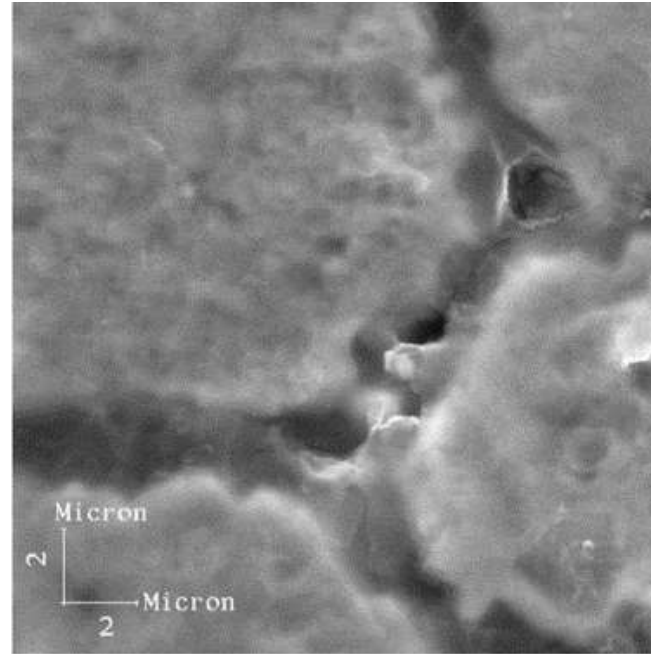
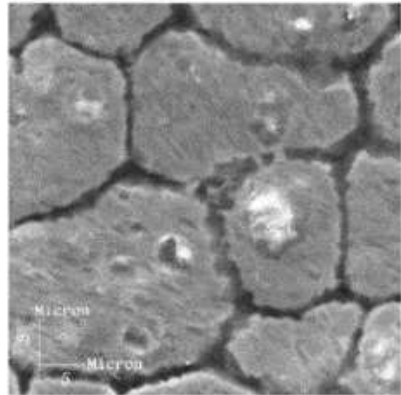
Pure Pd at 600C, 3.5GPa



SEM for Pure Pd at 800C, 3.5GPa



High Pressure Hydrogenation Pure Ni at 800 °C - 3.5GPa

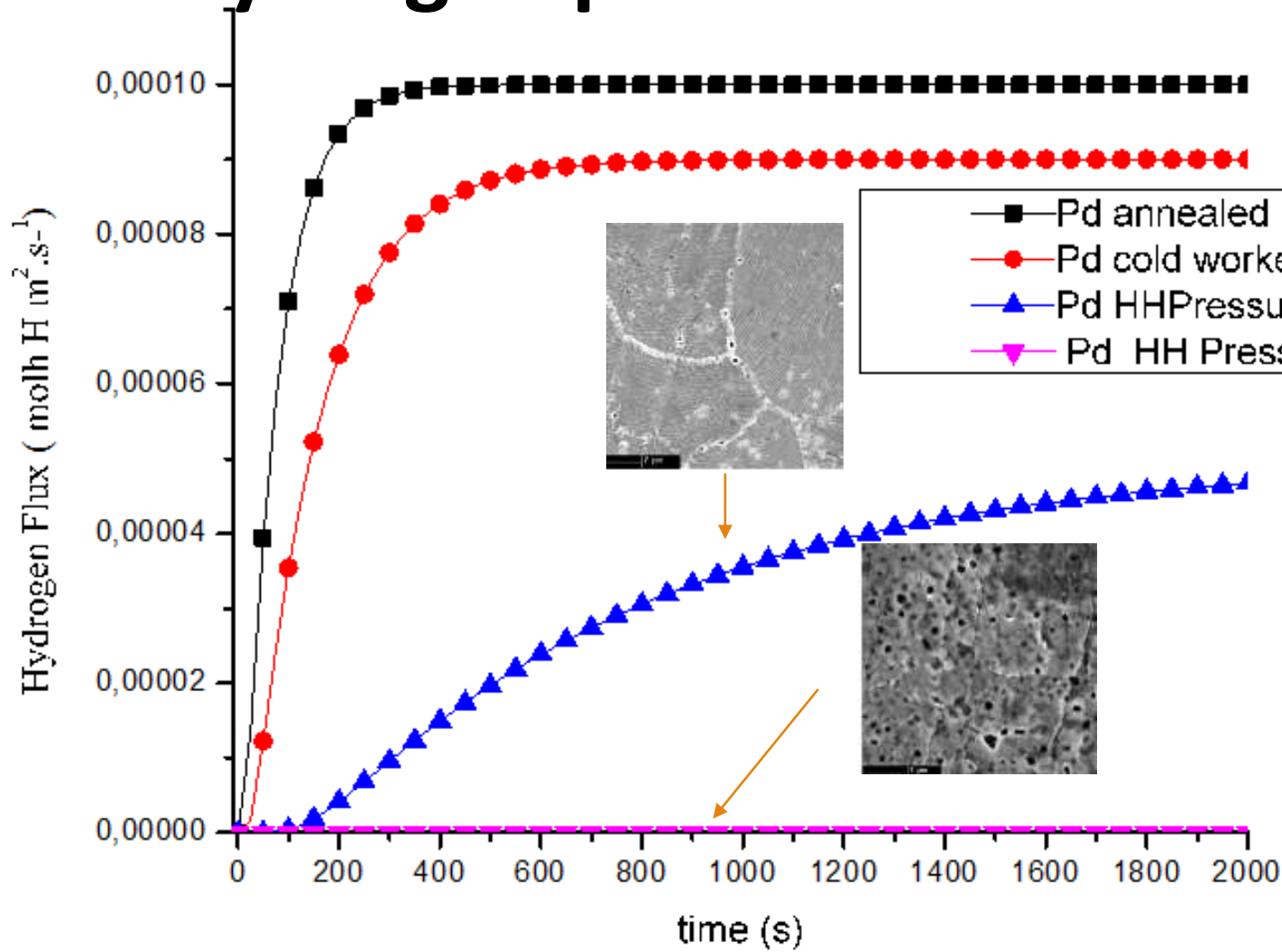


$$\text{If } \frac{\delta}{2} \ll \sqrt{D_v t} \ll d,$$

Diffusion in grain boundaries is faster

In this case vacancies are generated in Grain boundaries

Hydrogen permeation through Defective Palladium



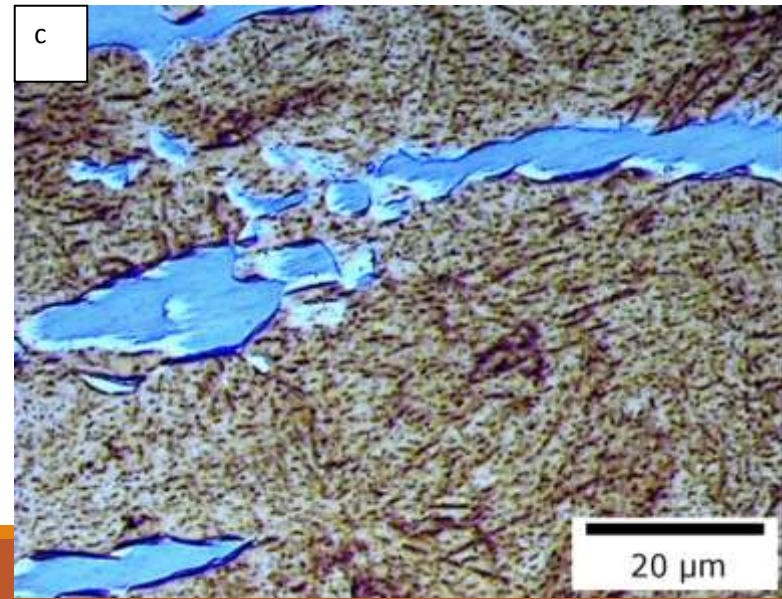
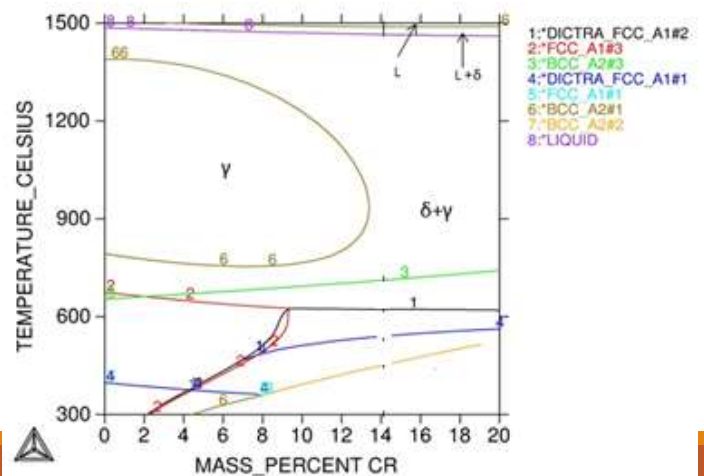
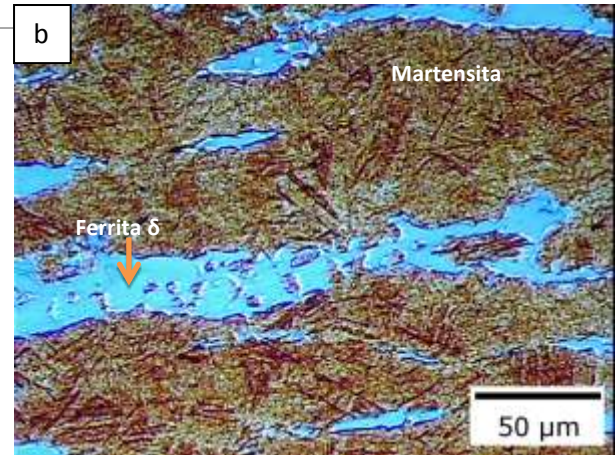
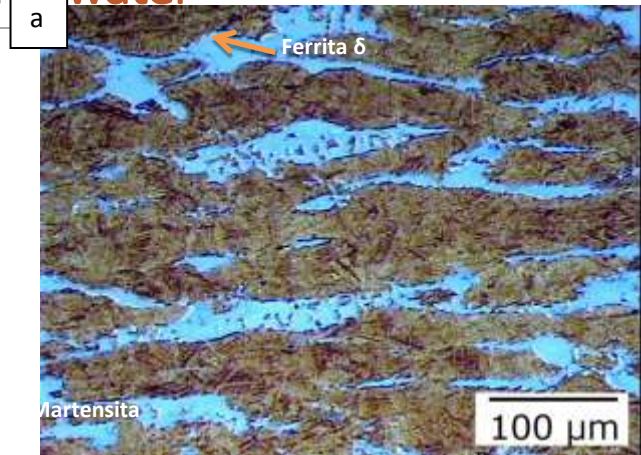
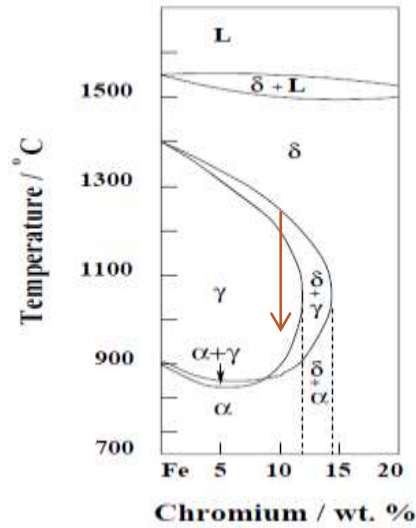
palladium	Difusivity m ² /s	Solubility molH/m ³
Heat treat	5 x 10 ⁻¹¹	310
Cold work	2 x 10 ⁻¹¹	400
HHP 500 C	6 x 10 ⁻¹²	900
HHP 800C	1x 10 ⁻¹²	2800

Hydrogen in supermartensitic stainless steels

Supermartensitic steel (optical microscopy)

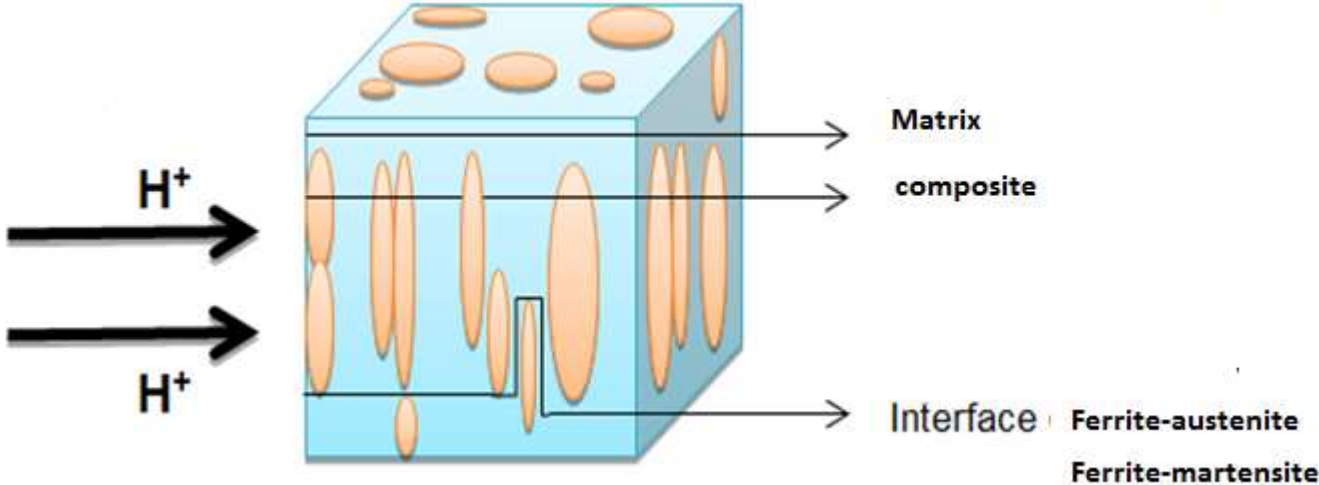
HT

cooled in water



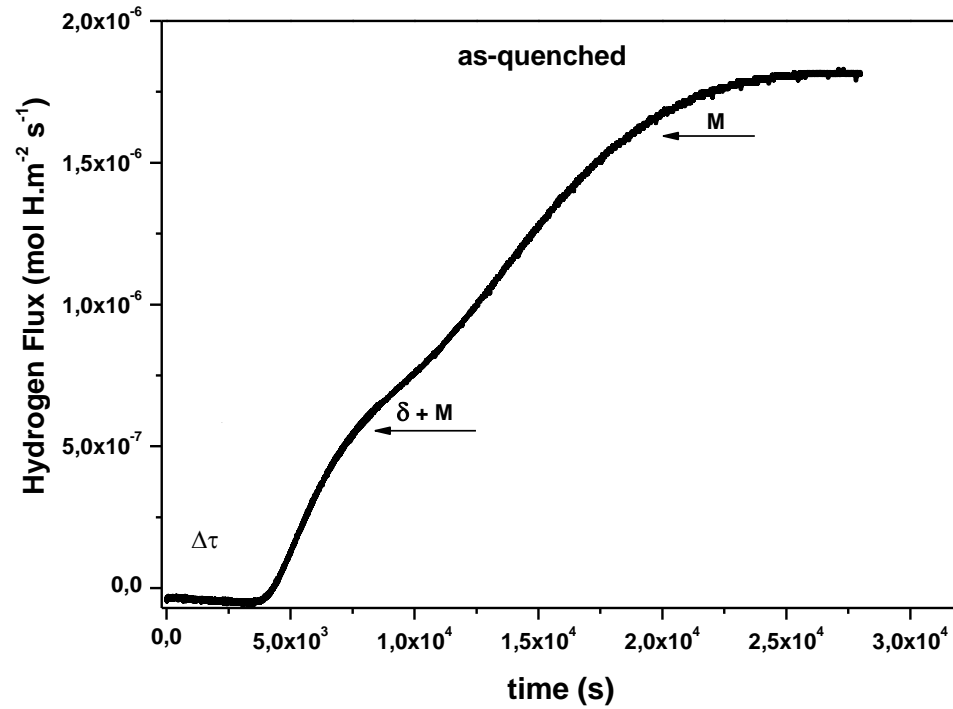
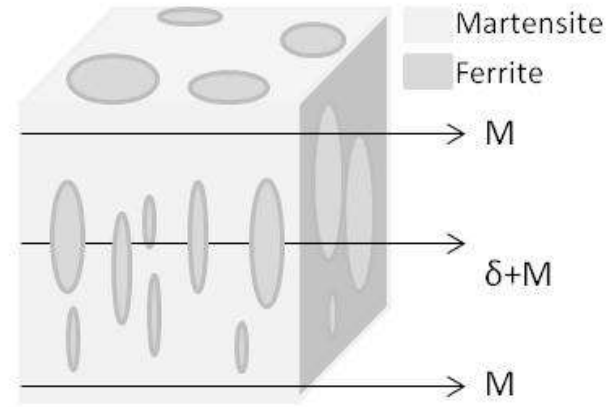
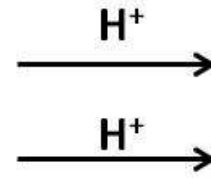
Hydrogen permeation through composite alloy

Pre-existing two phases

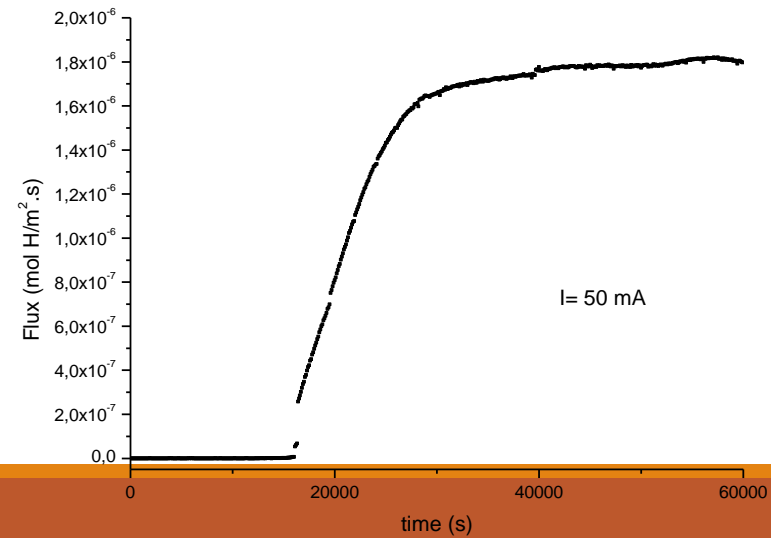
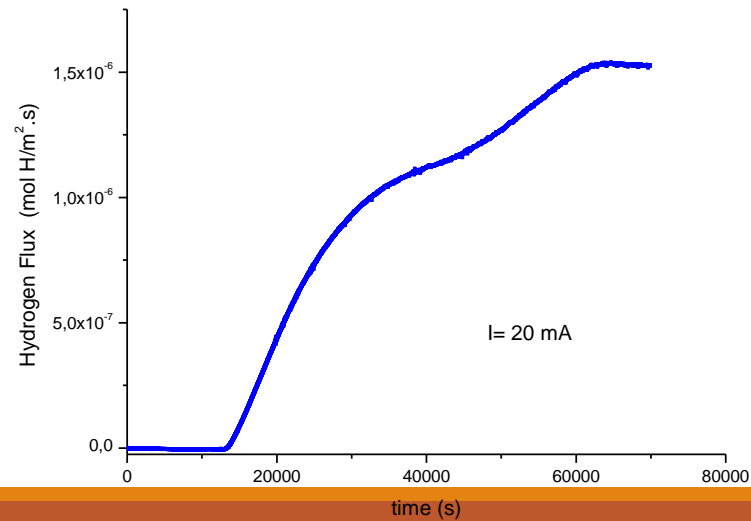
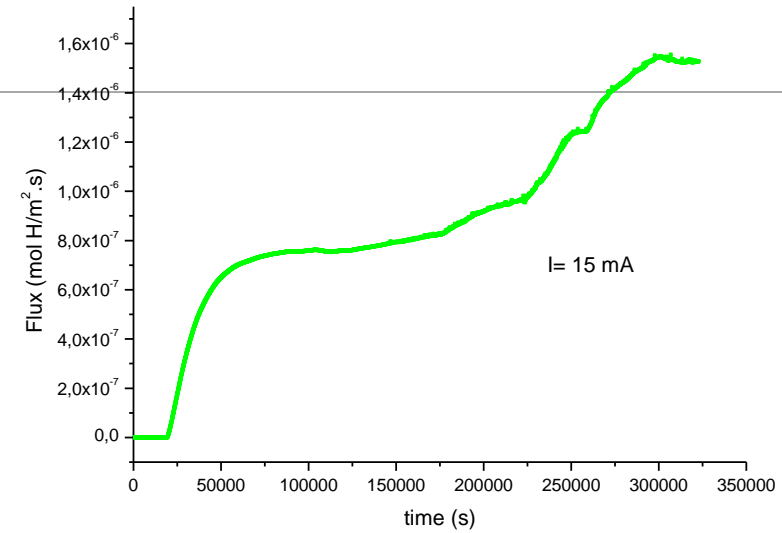
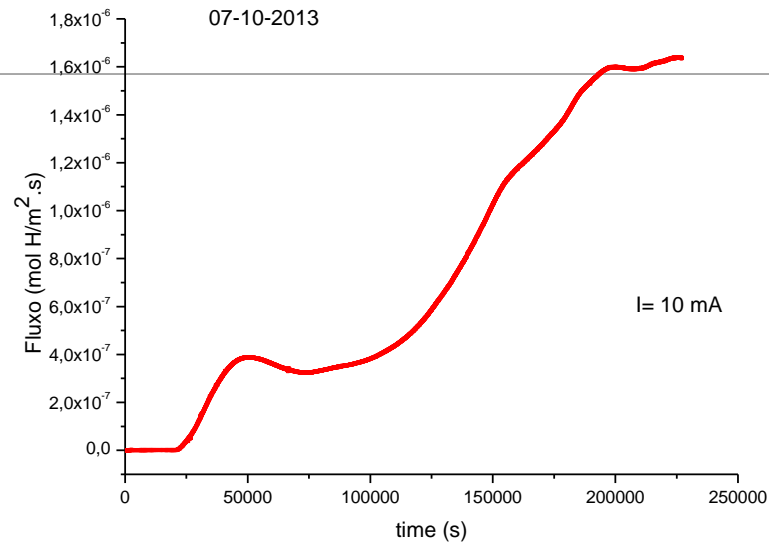


Mechanism

Diffusion path

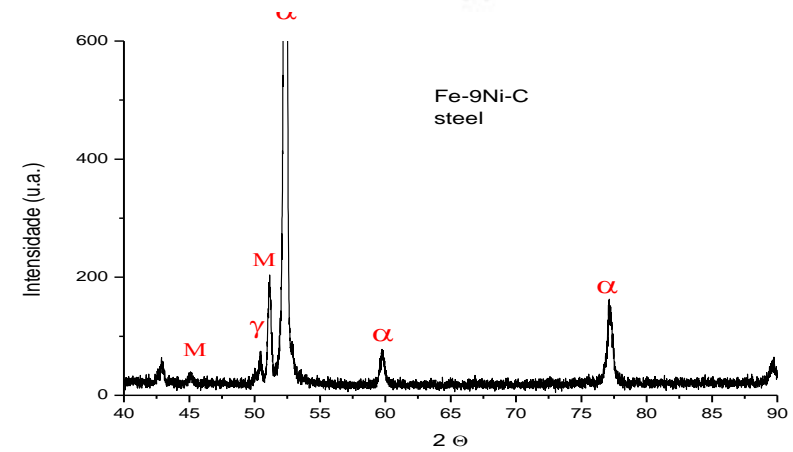
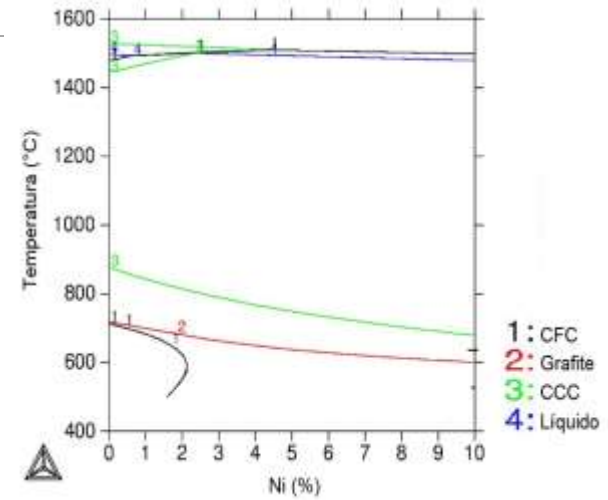
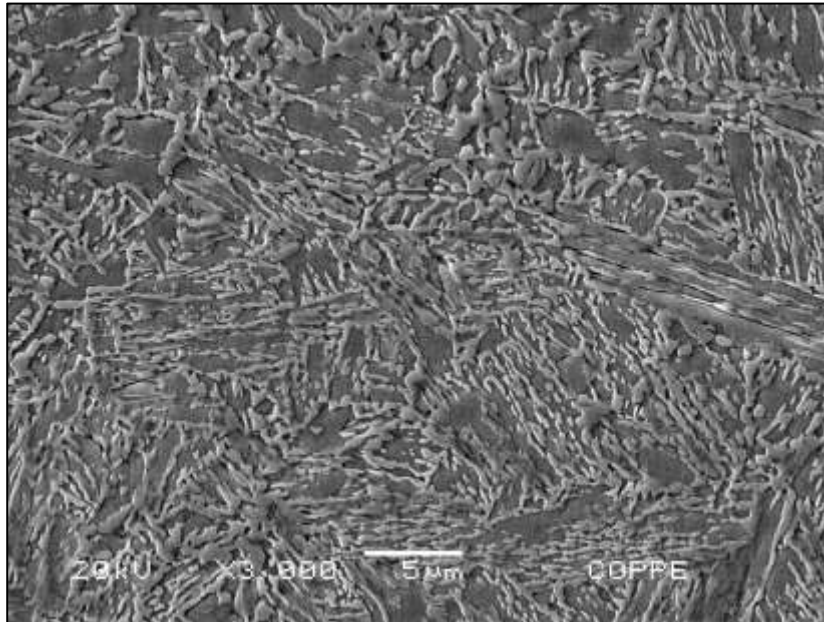


Effect of cathodic charging on the H- Permeation curves (H_2SO_4 0.1M)



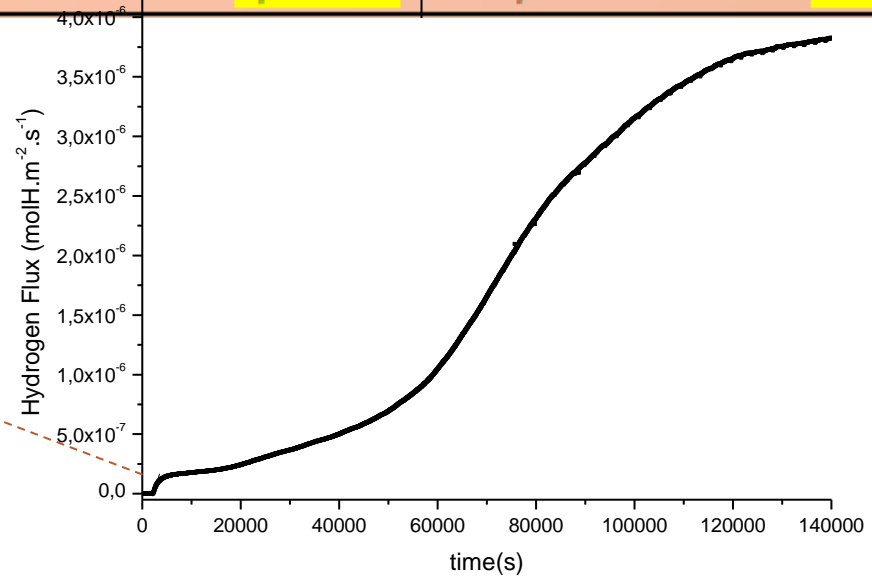
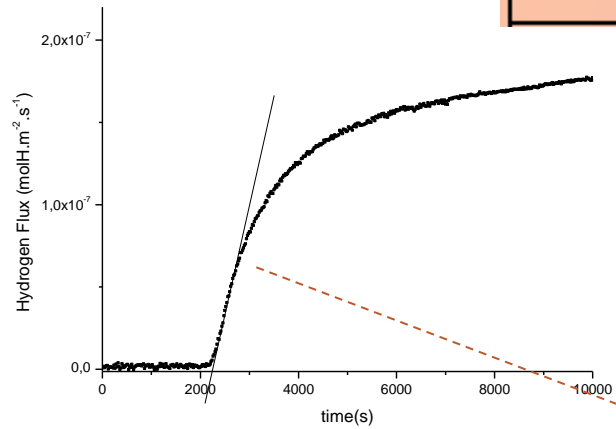
Fe-9Ni-C steel

Bainite-Martensite + Retained Austenite Structure



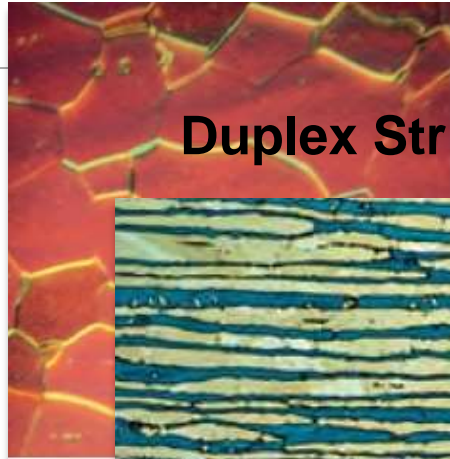
Electrochemical Hydrogen permeation curve (room temperature)

condition	t_0 (s)	D_{app} (m^2/s)	J_{max} ($mol\ H/m^2s$)	S_{app} ($mol\ H/m^3$)
CR 0,8	2258	$2,2 \times 10^{-11}$	$1,7 \times 10^{-7}$	6,2
	48637	$1,0 \times 10^{-12}$	$3,8 \times 10^{-6}$	167,4



-
- Hydrogen diffusion and interaction with defects
 - **Hydrogen in duplex stainless steels**

Duplex Stainless Steels



Ferrite (α)

Duplex Structure

BCC
High H diffusivity
Low solubility

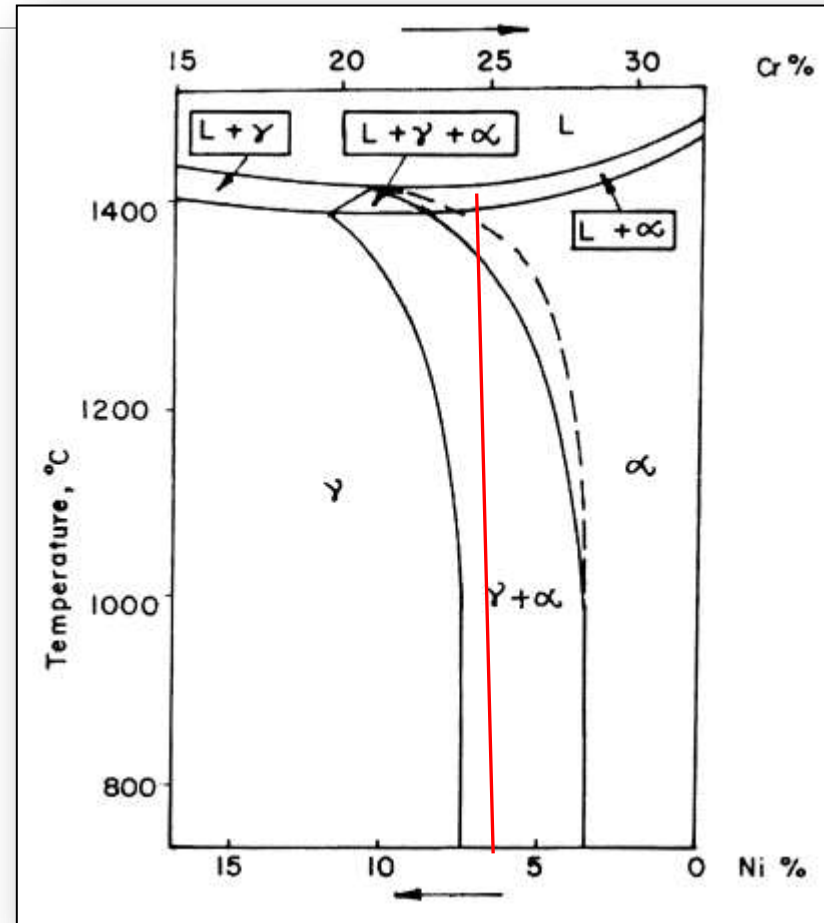


Austenite (γ)

FCC
High H diffusivity

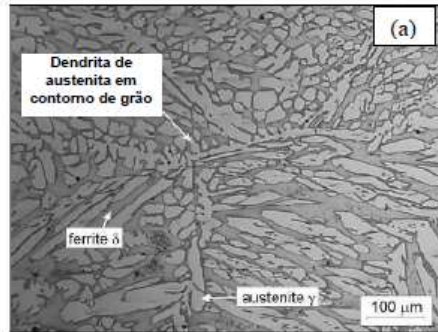
Austenite - Ferrite

High H solubility



Hydrogen diffusion in multi-phase steels

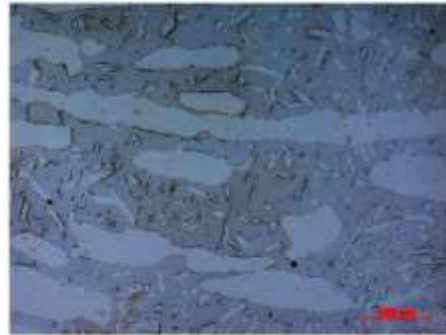
Super duplex stainless steel



As cast

$$D = 8 \times 10^{-14} \text{ m}^2/\text{s}$$

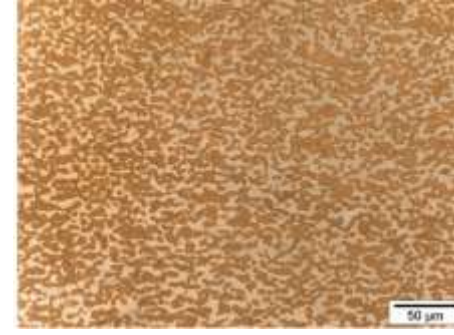
25 C



forged

$$D = 6 \times 10^{-14} \text{ m}^2/\text{s}$$

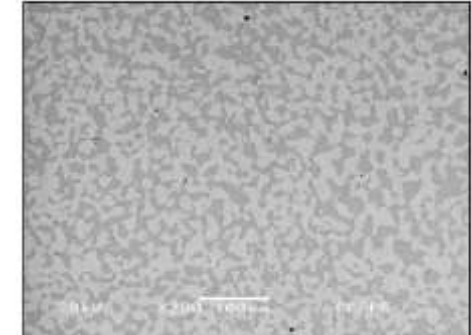
25 C



Cold rolled

$$D = 9 \times 10^{-15} \text{ m}^2/\text{s}$$

25 C



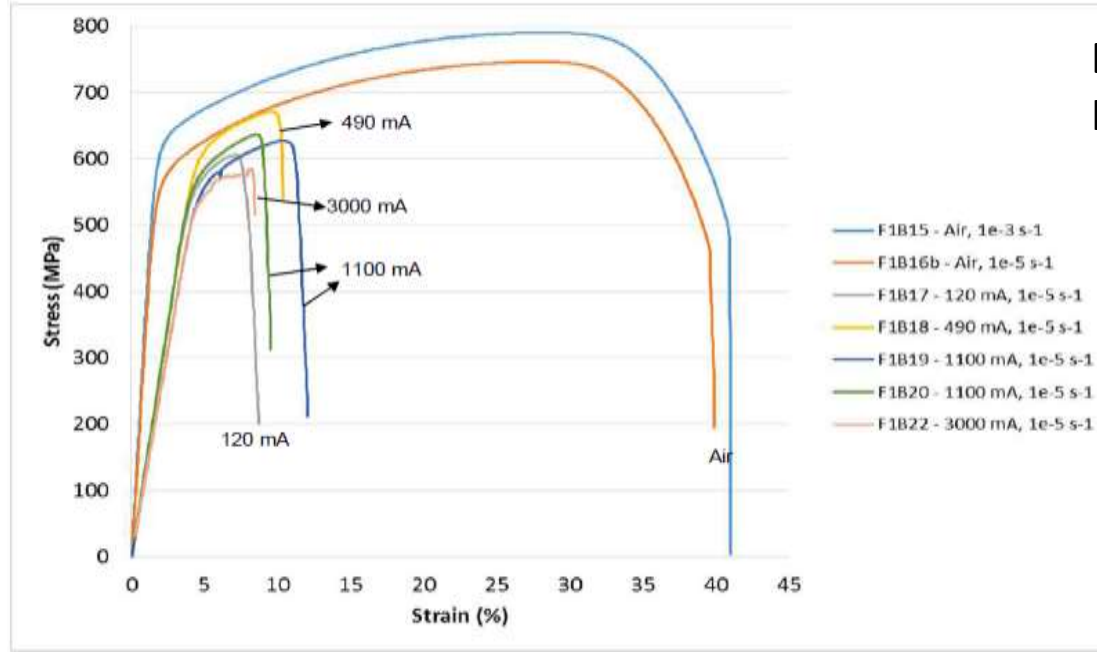
HIP

Hot isostatic pressed

$$D = 5 \times 10^{-15} \text{ m}^2/\text{s}$$

25 C

Tensile Tests under In-Situ Hydrogen Charging

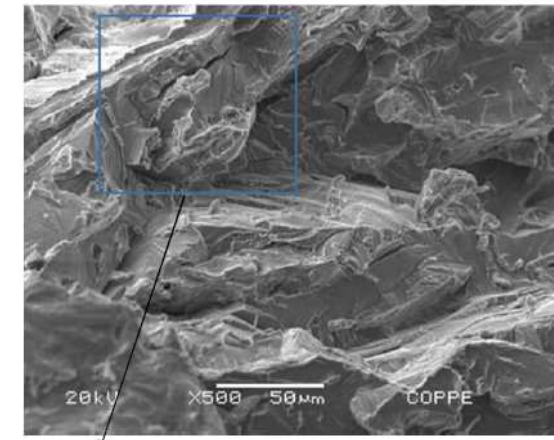
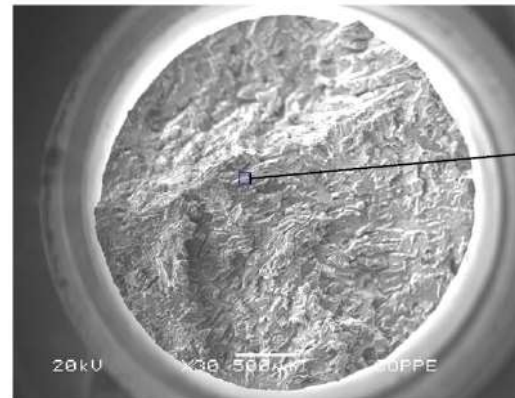
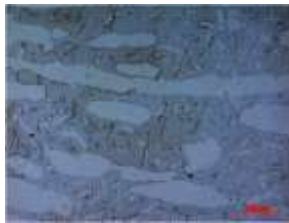


Electrochemical cathodic charging Hydrogen transport by dislocations in SSDS

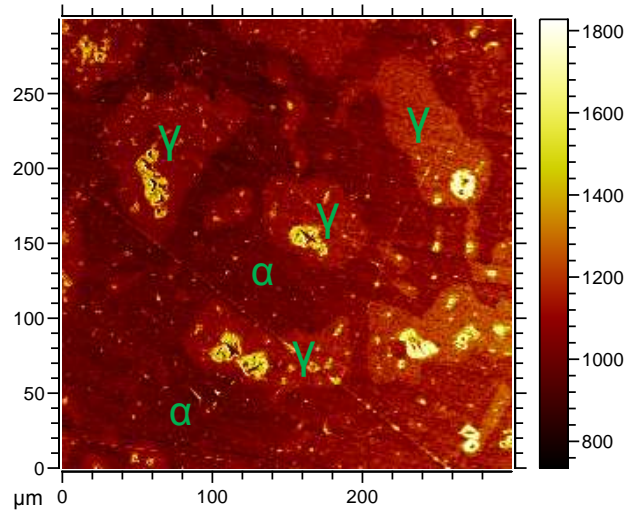
Tensile Tests under In-Situ Hydrogen Charging



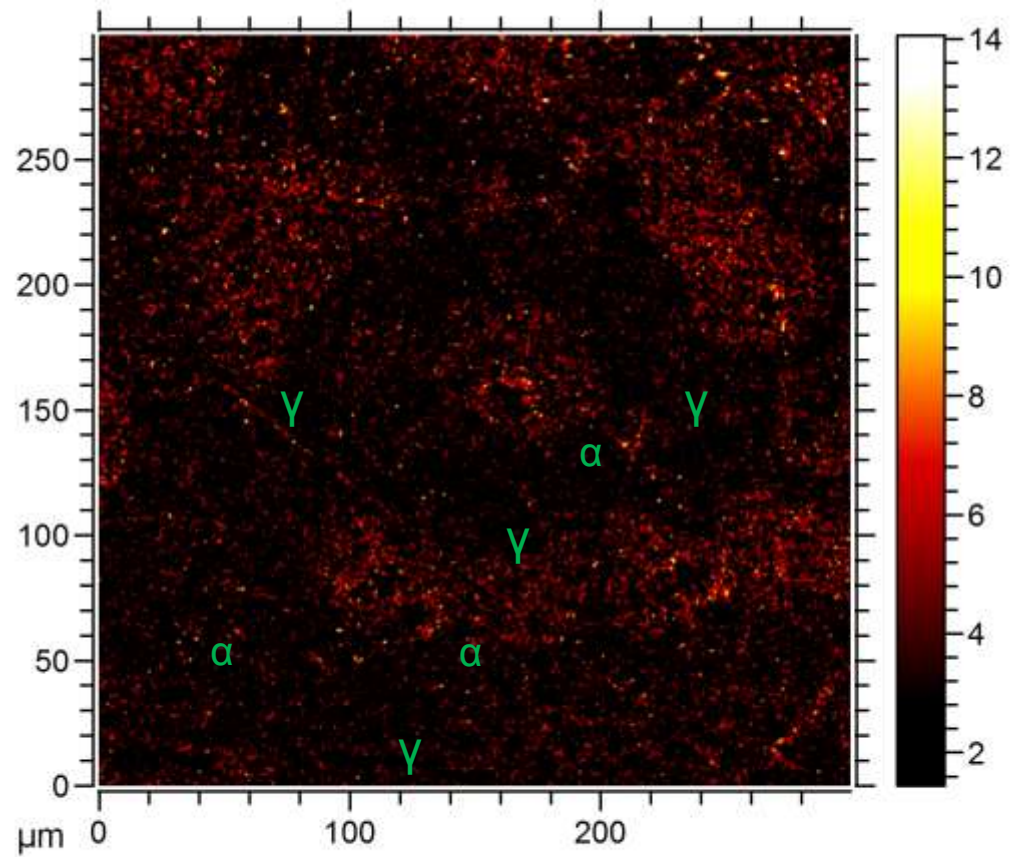
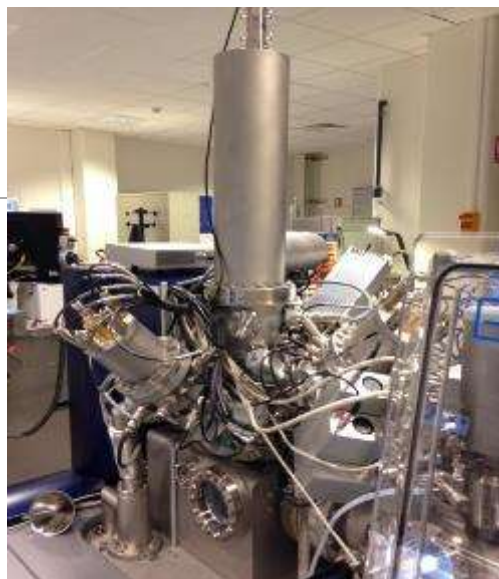
- All tests at room temperature.
- Only 30 min pre-charging without loading.
- Slow strain rate of 10^{-5} s^{-1} .
- Specimens with gauge diameter of 3,73-3,84 mm and gauge length of 16,74-18,01 mm.
- 3.5% NaCl solution with cathodic currents between 120 and 3000 mA – current densities of 0,56-14,9 mA/mm² (560-14900 A/m²) – potentials of -5 up to -19,6 V_{SCE}.



TOF SIMS Test in cryogenic condition (-100C)



total
MC: 1827; TC: 6.981e+007



H₂-
MC: 14; TC: 1.809e+005

Collaboration with L. Briottet
CEA- Grenoble
P. Craidy Thesis



Figura 105 – Ensaio de tração em baixa taxa de deformação. Em (a), teste no material como recebido. Em (b), teste realizado sob corrente catódica em célula de hidrogenação.

Super duplex stainless steel
Hot isostatic pressed
(Hydrogenated)

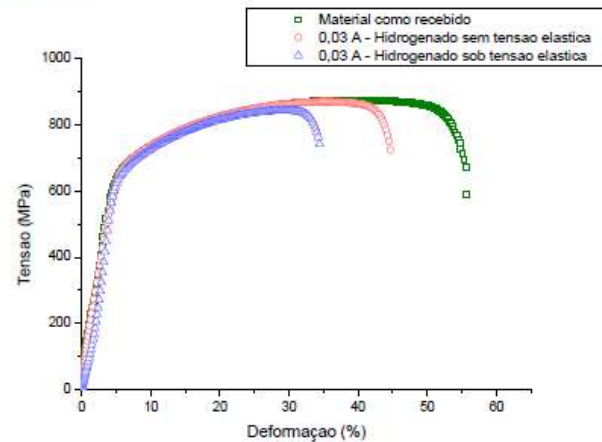


Figura 95 - Ensaio de tração no AISD HIP SAF 2507 nas condições como recebido, após hidrogenação eletrolítica por 12 dias em corrente catódica de 0,03A e após hidrogenação eletrolítica por 7 dias em corrente catódica de 0,03A sob tensão elástica (75% σ_y).

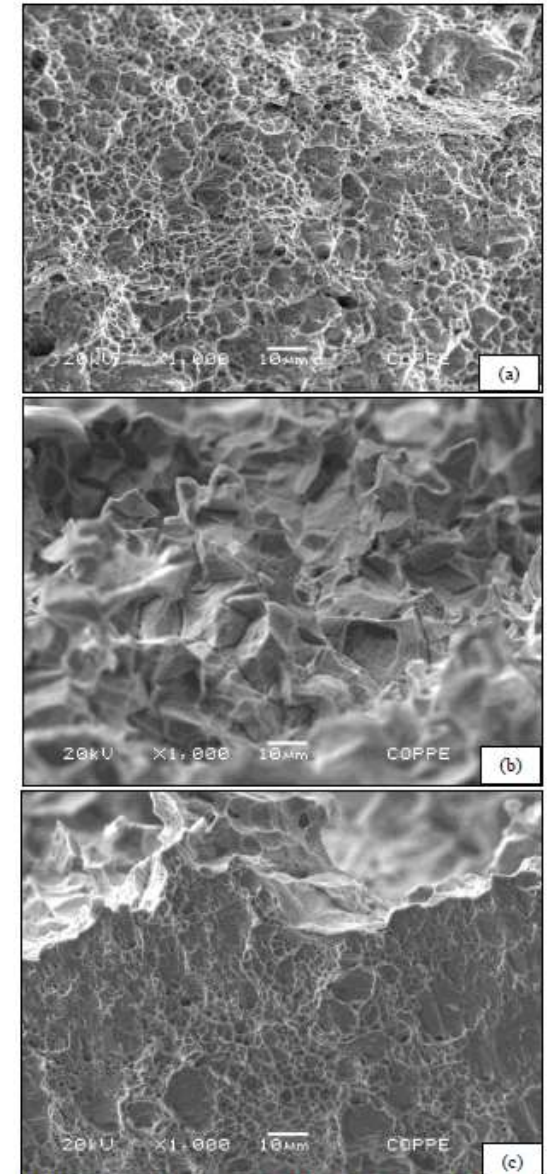


Figura 112 - Superfícies de fratura da amostra hidrogenada a 2A. Em (a) região central. Em (b) região periférica (borda) retirada na zona identificada como frágil. Em (c), zona dúctil da borda.

SDSS- HIP

HYDROGEN GAS PERMEATION TEST

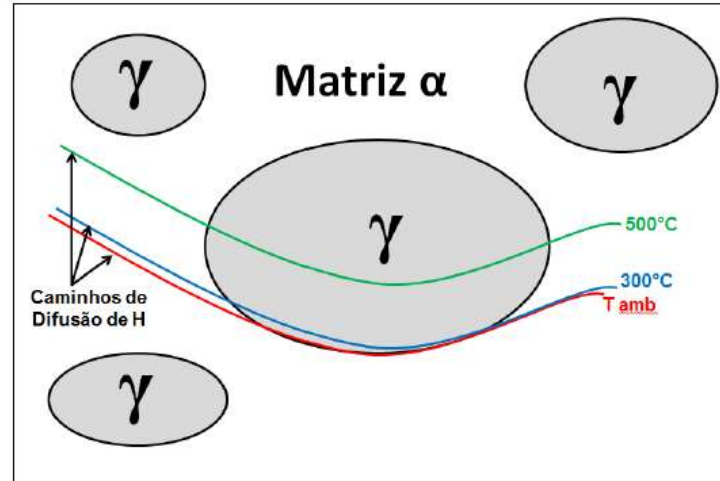
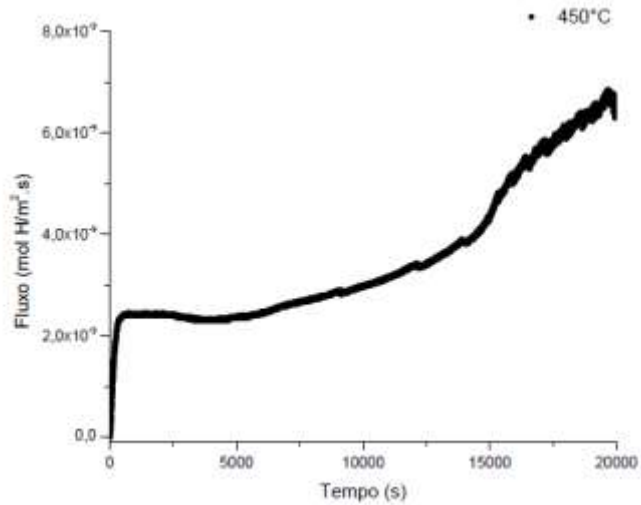
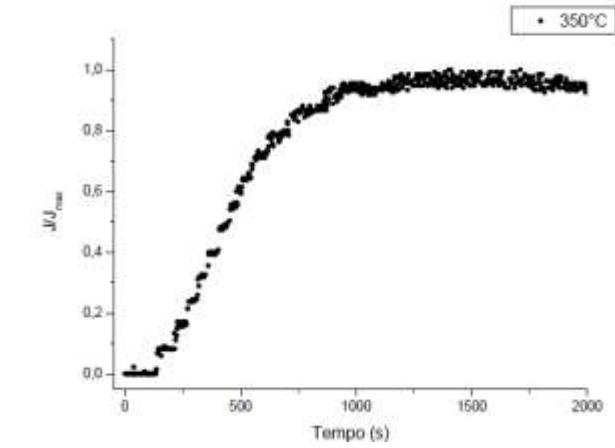


Figura 124 – Esquema representando o comportamento duplo-sigmoidal no AISD HIP em altas temperaturas de teste.

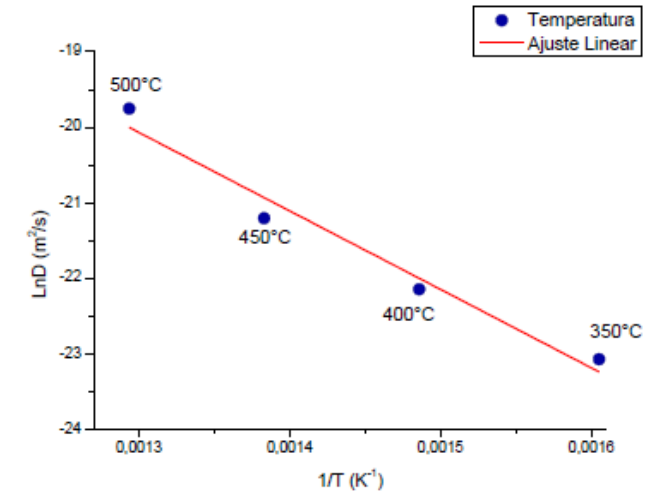


Figura 125 – Curva experimental do AISD HIP para cálculo da energia de ativação E_D e para difusão e constante D_0 .

Tabela 29 – Cálculo de parâmetros de difusão para AISD HIP SAF 2507.

Material	D_0 (m ² /s)	Energia de Ativação E_D (kJ/mol)
AISD HIP SAF 2507	$1,5 \cdot 10^{-3}$	86,4

TDS Super duplex HIP

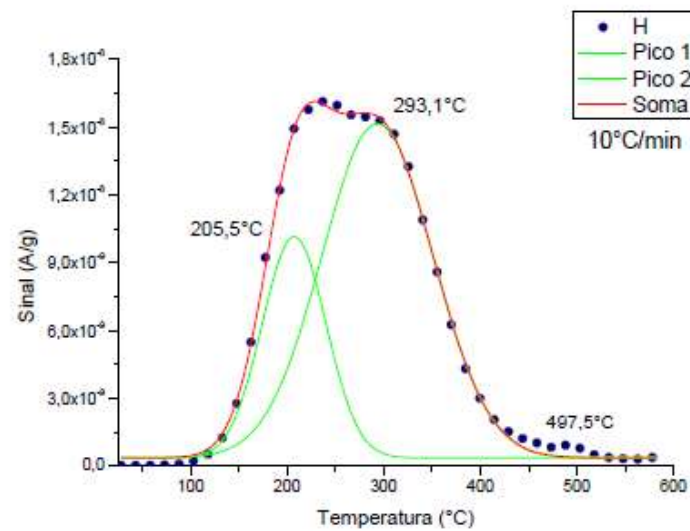


Figura 127 - Resultados da análise TDS e picos obtidos para AISD HIP SAF 2507. Taxa de aquecimento: 10°C/min.

Hydrogenated eletrolitively

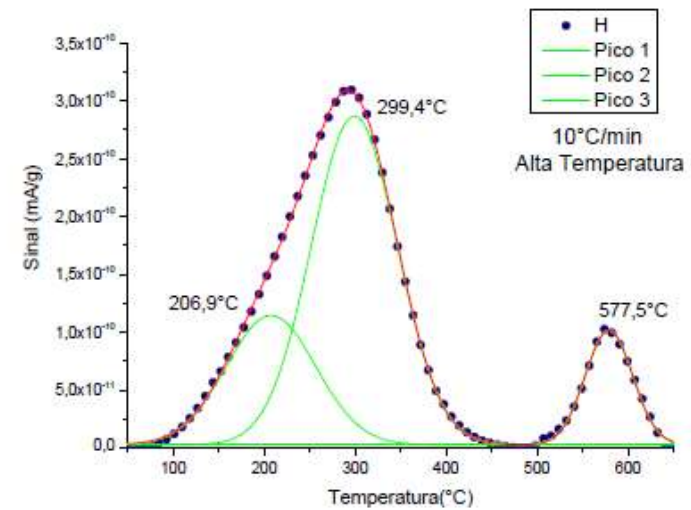


Figura 134 - Resultados da análise TDS e picos obtidos para AISD HIP SAF 2507 utilizando amostra hidrogenada em alta temperatura via permeação gasosa. Taxa de aquecimento: 10°C/min.

Hydrogenated H pressure high T



Figure 4 - Lateral view of as-received tensile specimen rupture: (a) H-free condition; (b) H-charged condition; (c) H-charged under stress condition

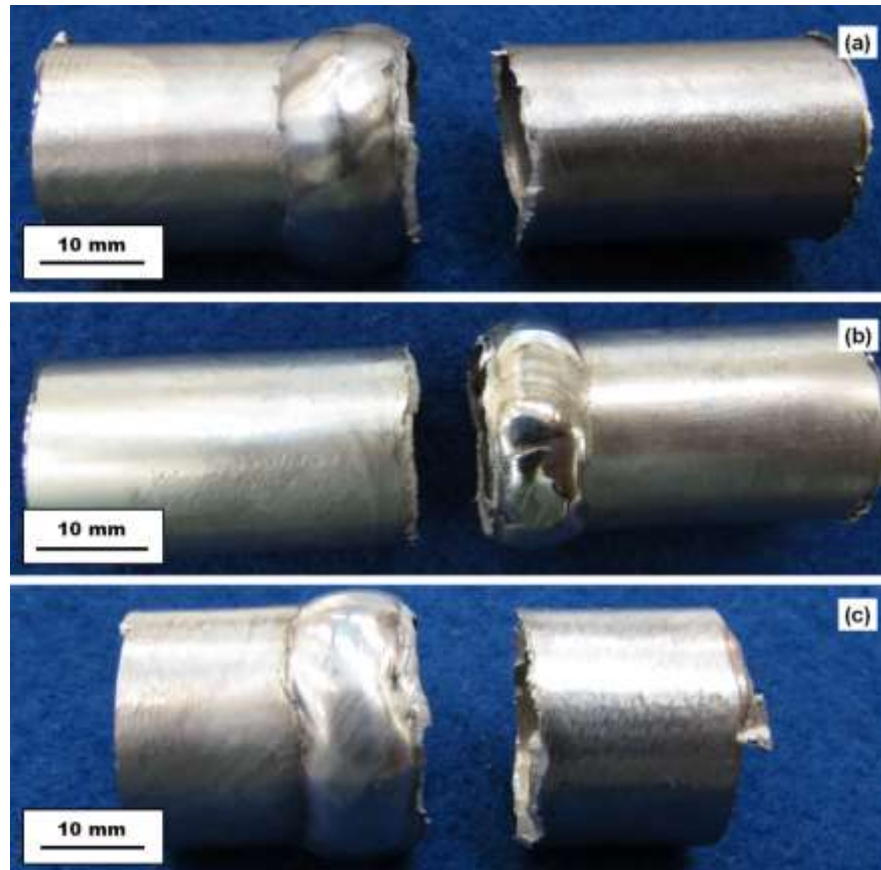
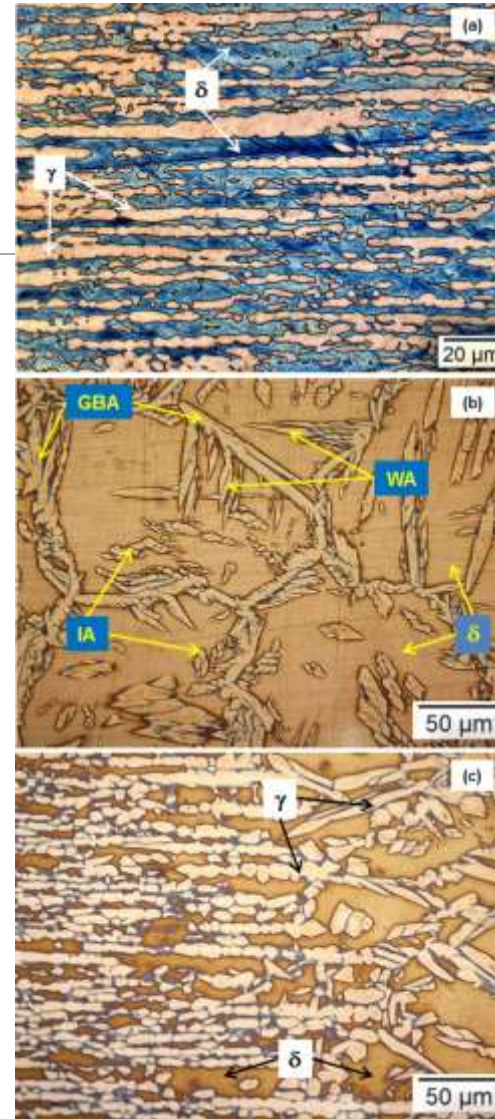


Figure 5 - Lateral view of welded tensile specimen rupture: (a) H-free condition; (b) H-charged condition; (c) H-charged under stress condition

Superduplex *tubing welded*



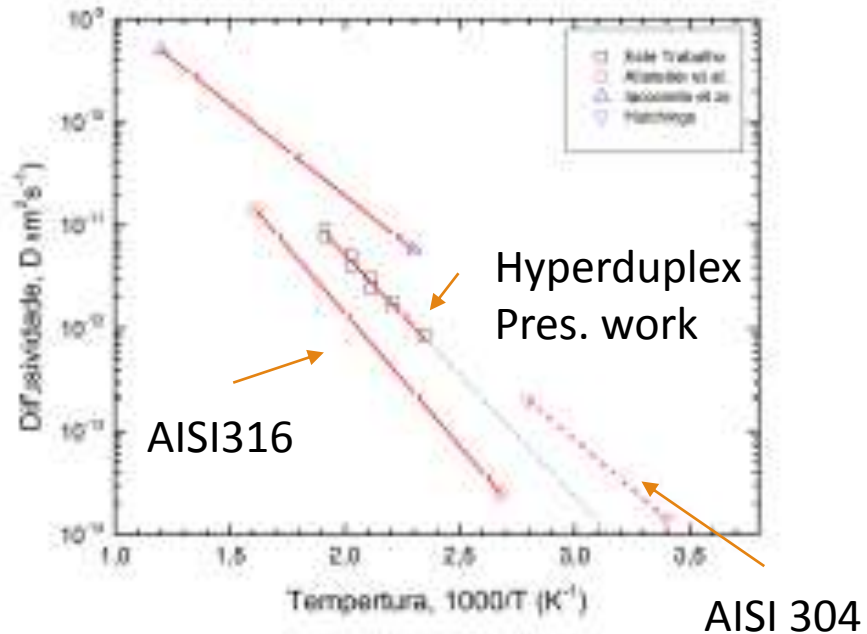
superduplex 2507



Detalhe da microestrutura do aço superduplex pós-soldado (a) metal de base, (b) metal de solda e c) ZTA

Hydrogen Diffusivity x Temperature Hyperduplex stainless steel SAF 3207

Amostra (L) [μm]	D_{ap} [$\text{m}^2 \cdot \text{s}^{-1}$]				
	150°C	180°C	200°C	220°C	250°C
104	$9,00 \cdot 10^{-13}$	$1,56 \cdot 10^{-12}$	$3,19 \cdot 10^{-12}$	$5,35 \cdot 10^{-12}$	$8,48 \cdot 10^{-12}$
249	*	$1,80 \cdot 10^{-12}$	$2,76 \cdot 10^{-12}$	$4,33 \cdot 10^{-12}$	$9,40 \cdot 10^{-12}$

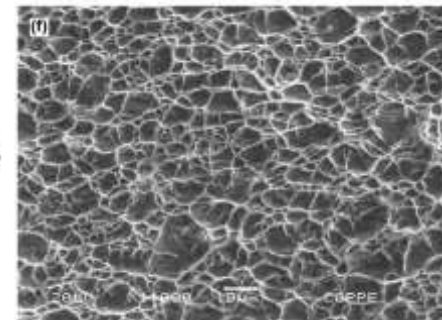
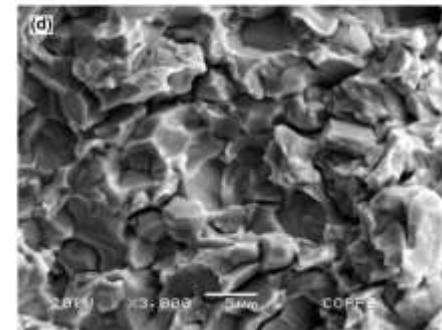
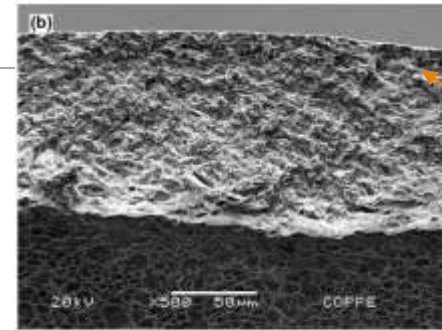
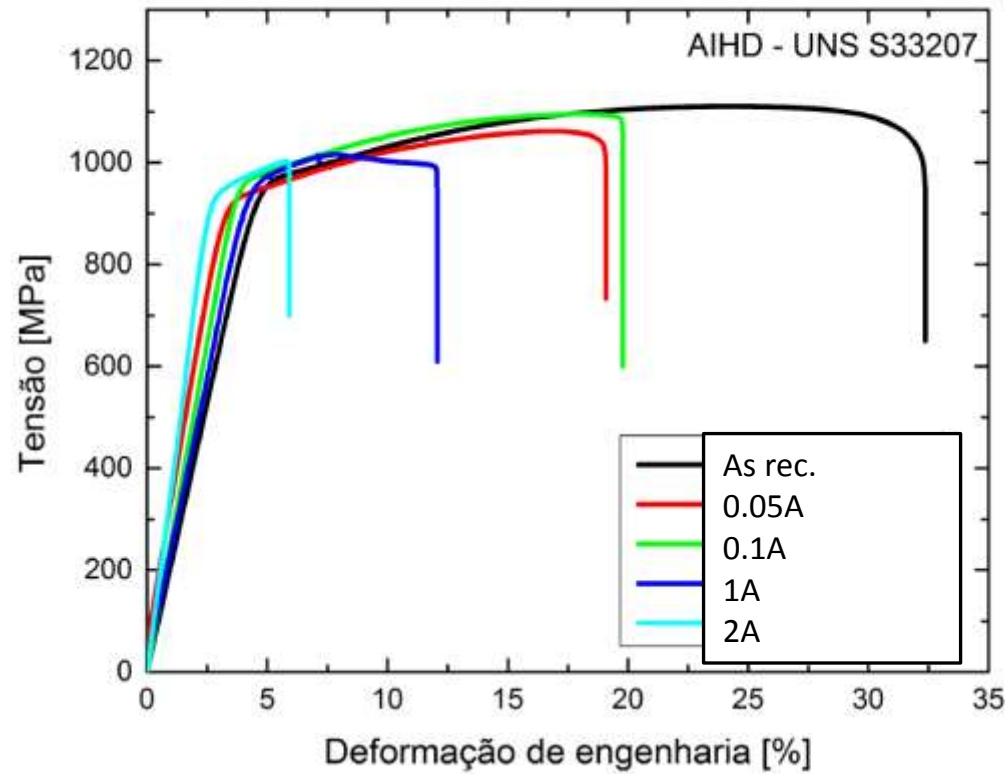


$$D = 2,50 \cdot 10^{-7} \exp\left(\frac{-44,74}{RT}\right) \left(\text{m}^2 \cdot \text{s}^{-1}\right)$$

$$\Phi = 2,96 \cdot 10^{-5} \exp\left(\frac{-41,22}{RT}\right) \left(\frac{\text{molH}}{\text{m} \cdot \text{s} \cdot \text{MPa}^{1/2}}\right)$$

$$S = 117,93 \exp\left(\frac{-3,52}{RT}\right) \left(\frac{\text{molH}}{\text{m}^3 \cdot \text{MPa}^{1/2}}\right)$$

Hydrogenation under elastic stress (75 % yield strength) (150h)



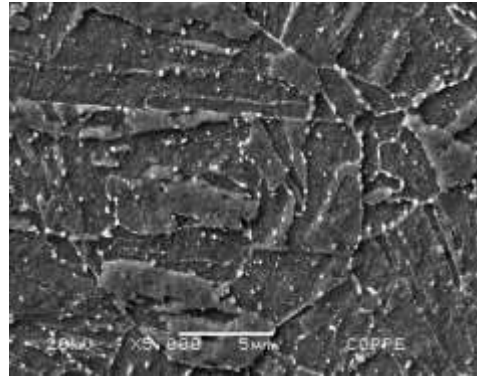
Quem é quem?



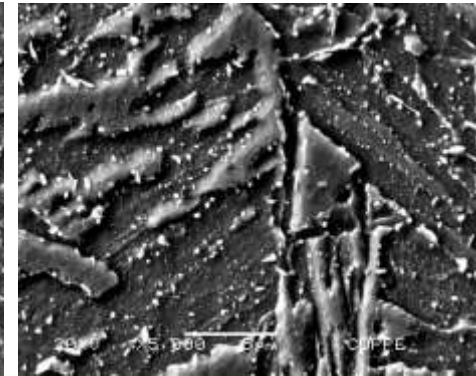


Angela Lorena
Cardenas M.
Estudante DSc

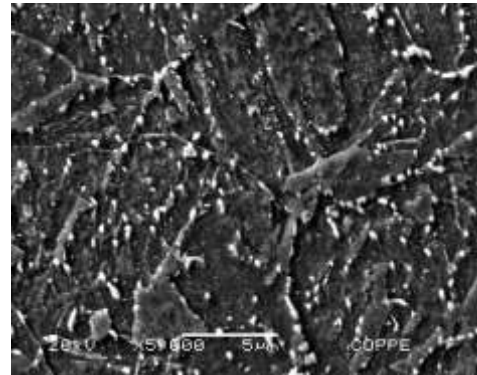
Efeitos do H no aço 2,25Cr-1Mo-0,25V



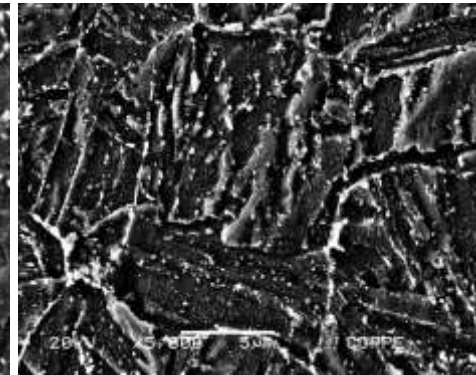
1C



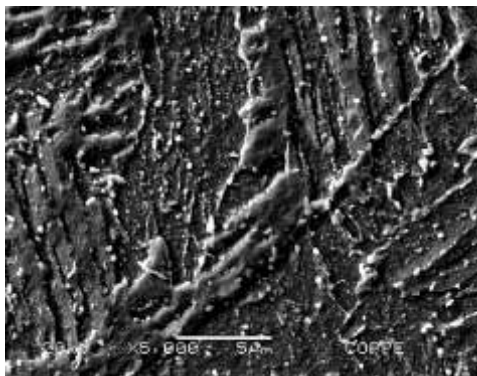
3C



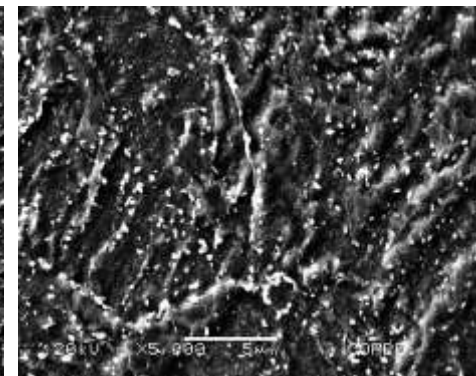
1C-ENV600



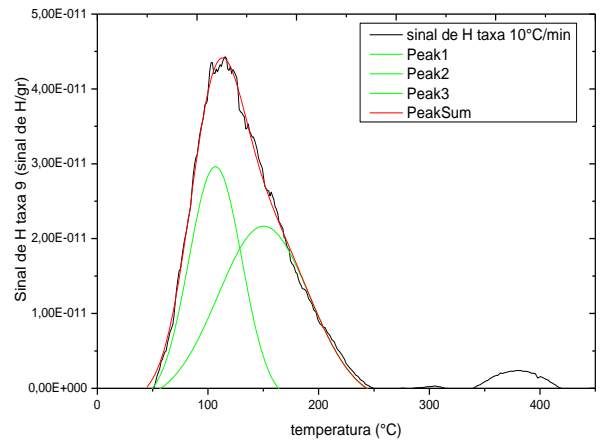
ENV600



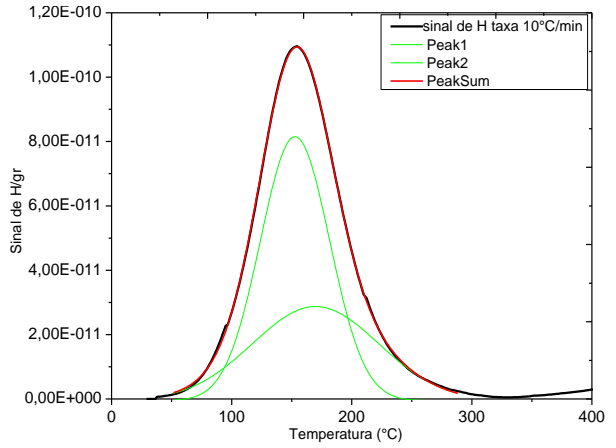
1C-ENV1000



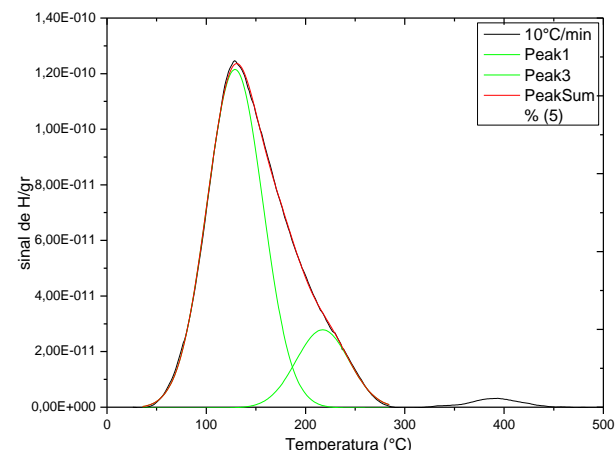
1C+ENV1000-PWHT



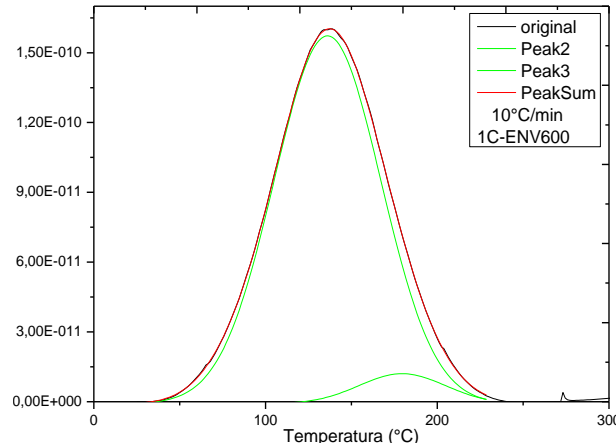
1C



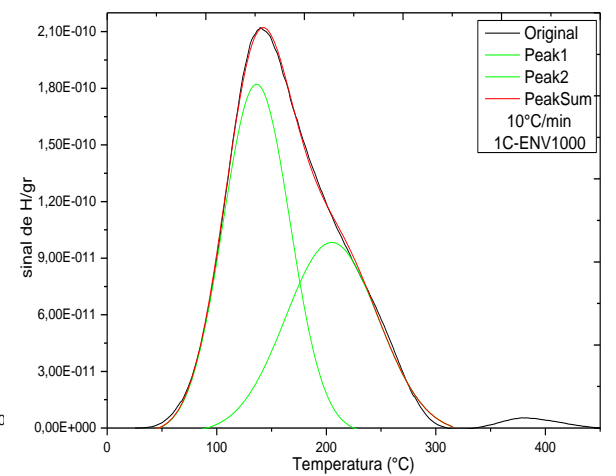
3C



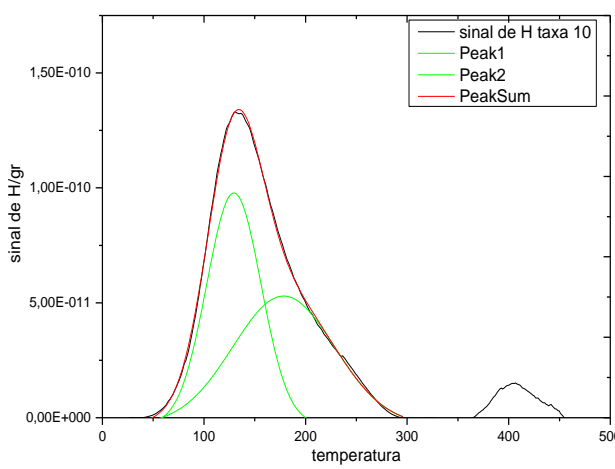
Env 600°C/600h



1C.Env600°C/600h

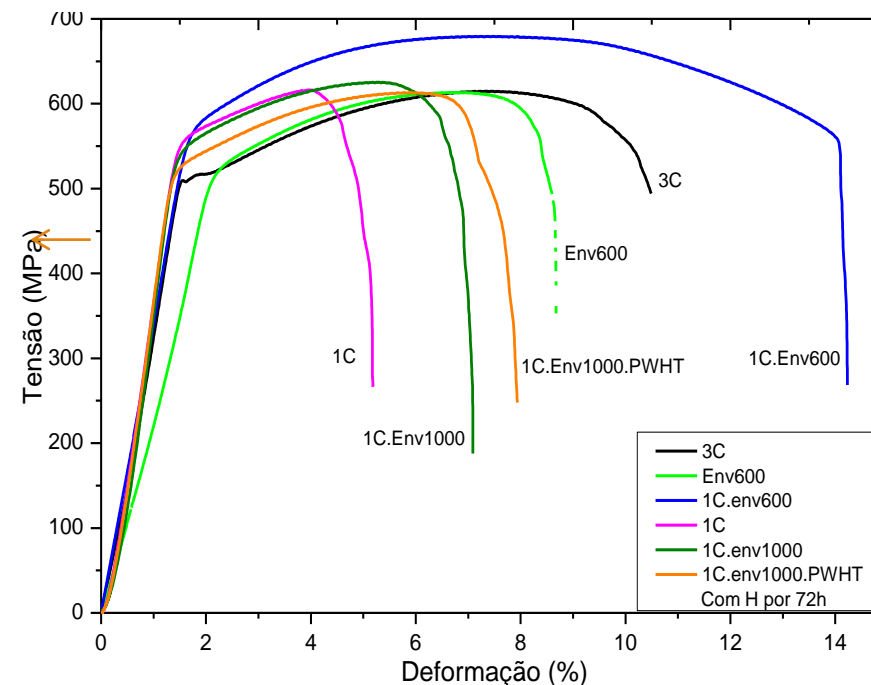
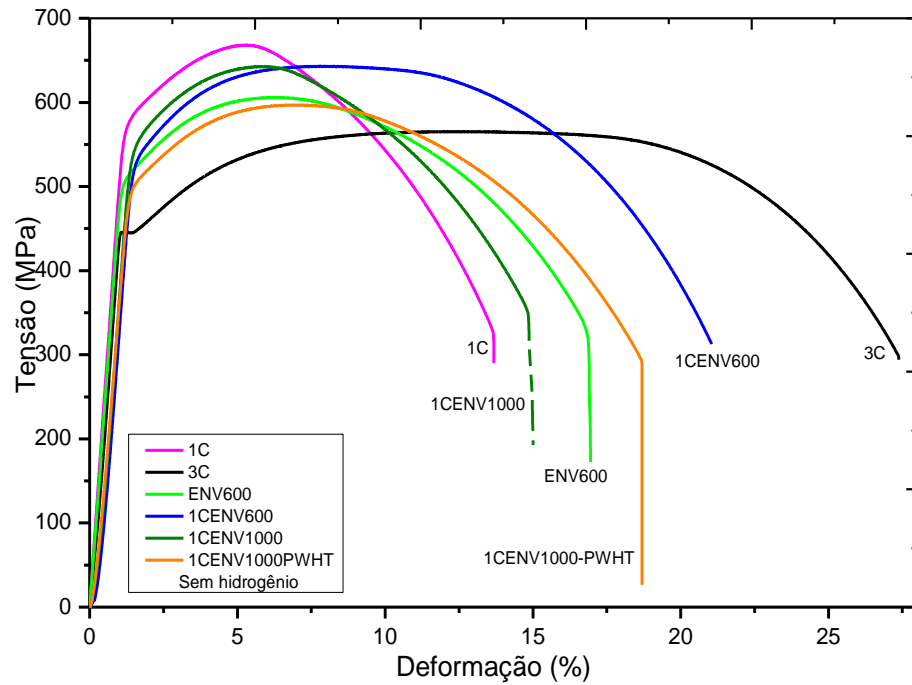


1C.env600°C/1000h



1C.env 600°C/1000h.PWHT

Curvas comparativas TDS na taxa 10°C/min



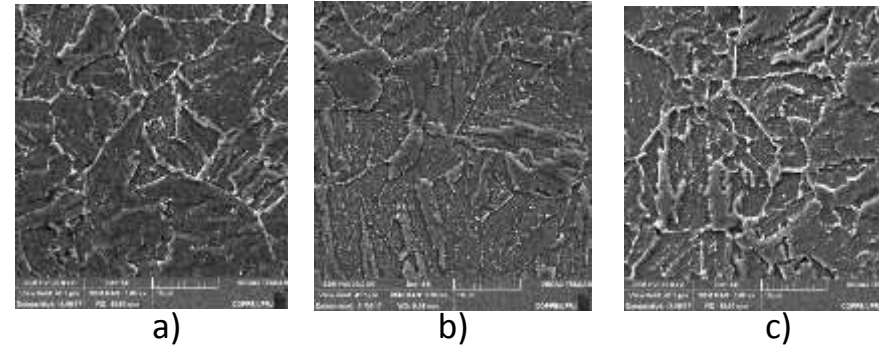
Condições de tratamento térmico	Horas a 600°C Holloman	Não hydrogenado		
		σ_{MAX}	σ_{LE}	$\epsilon(\%)$
ENV600	600	605	503	16,4
1C	2672	667	567	14,1
1CENV600	3272	643	515	20,4
1CENV1000	3672	643	534	14,2
1CENV1000PWHT	6283	597	468	18,0
3C	8016	565	454	26,5

Condições de tratamento térmico	Hydrogenado por 72h			Perda de ductilidade
	σ_{MAX}	σ_{LE}	$\epsilon(\%)$	
ENV600	611	512	8,2	50%
1C	616	540	4,4	68,7%
1CENV600	666	557	12,6	38,2%
1CENV1000	625	538	6,0	57,7%
1CENV1000PWHT	613	516	7,6	57,7%
3C	615	509	10	62,3%

Caracterização microestrutural e termodinâmica da evolução da precipitação no aço 2,25Cr-1Mo-0,25V durante envelhecimento

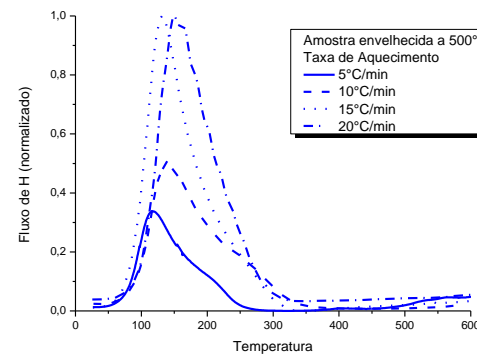


Renata Oliveira aluna DSc

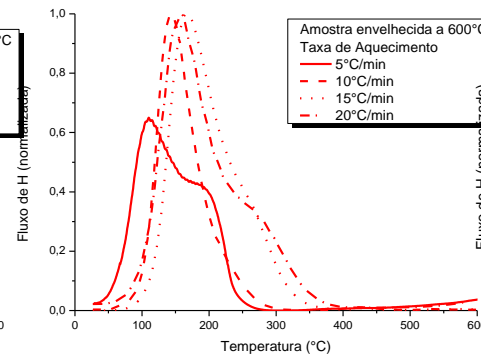


Micrografias das amostras envelhecidas a a) 500°C, b) 600°C e c) 700°C.

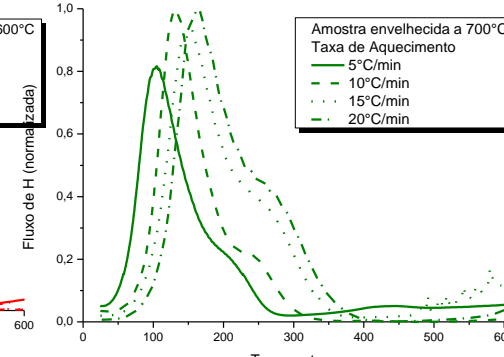
TDS das amostras envelhecidas a: a) 500°C, b) 600°C e c) 700°C.



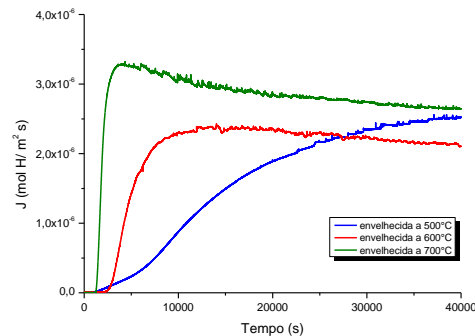
a)



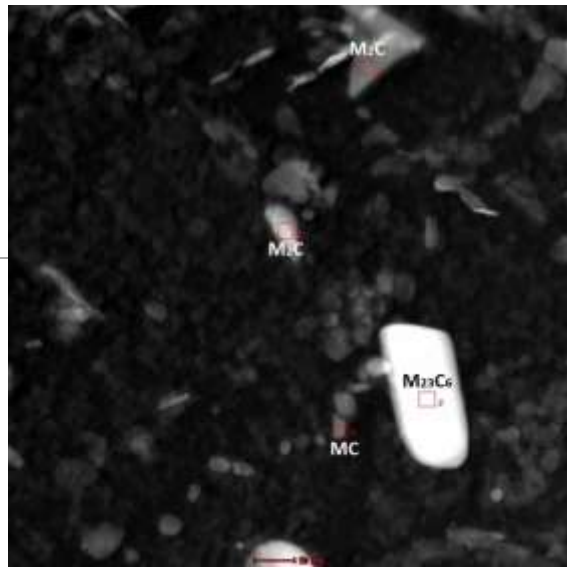
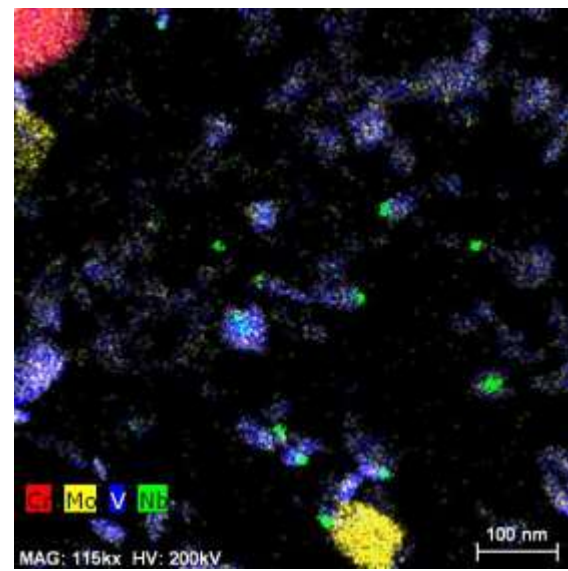
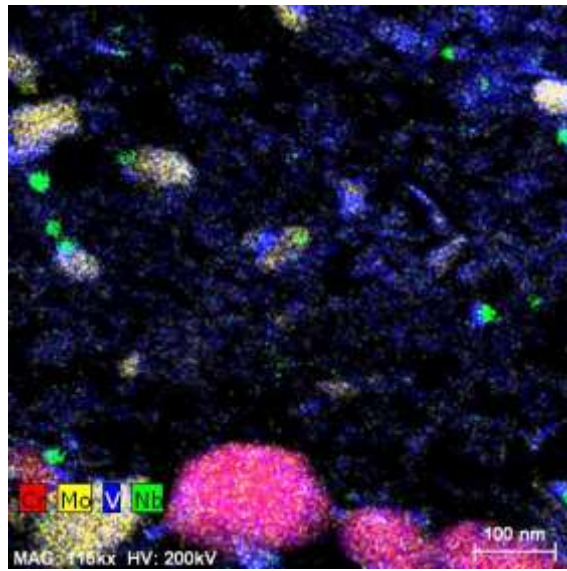
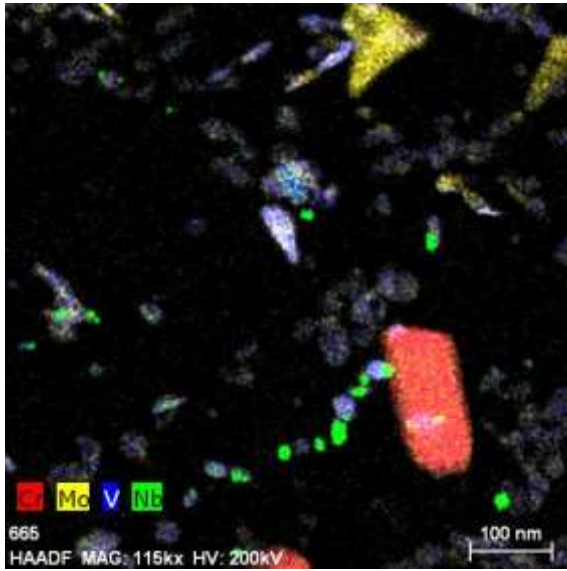
b)



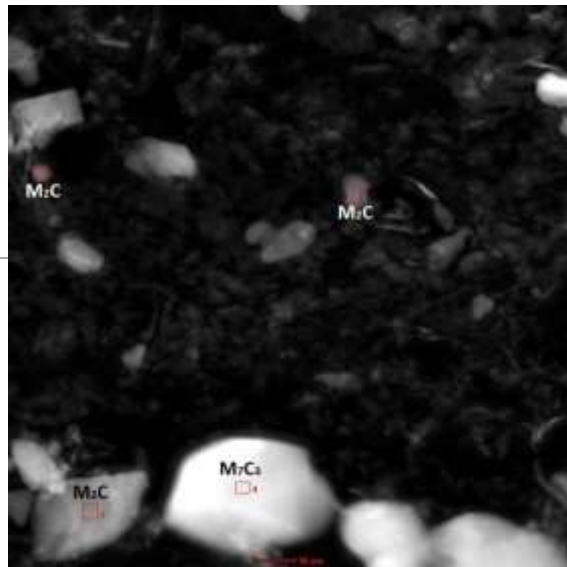
c)



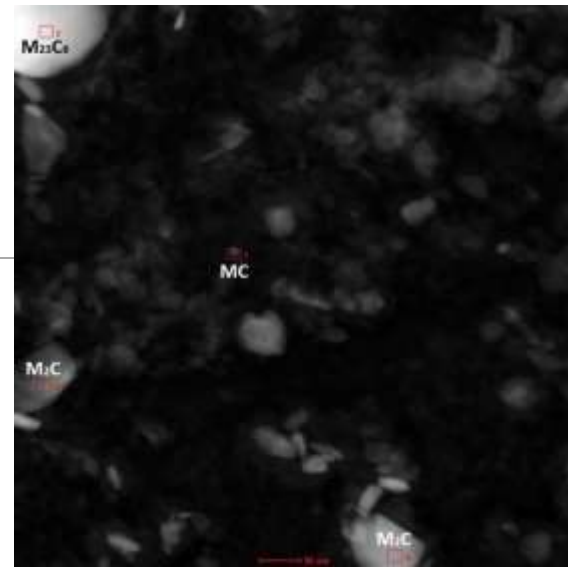
Comparação entre a permeação das amostras envelhecidas a 500°C (azul), 600°C (vermelha) e 700°C (verde).



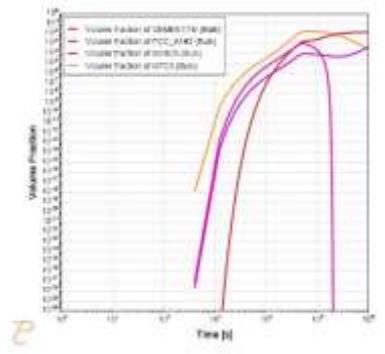
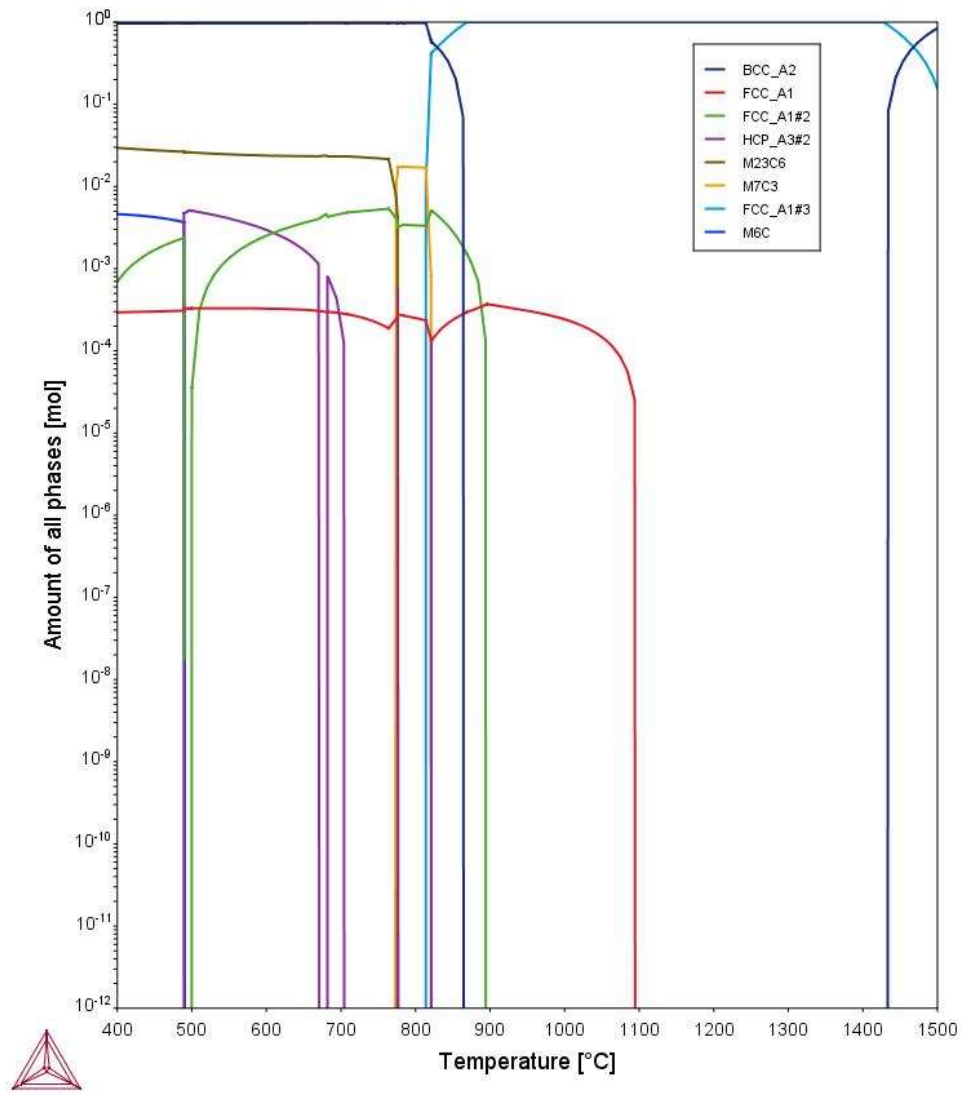
500°C



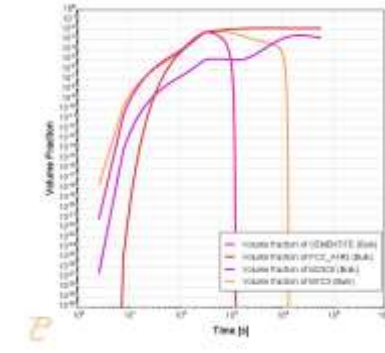
600°C



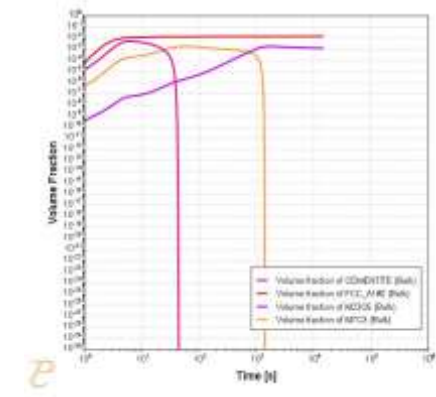
700°C



500°C



600°C



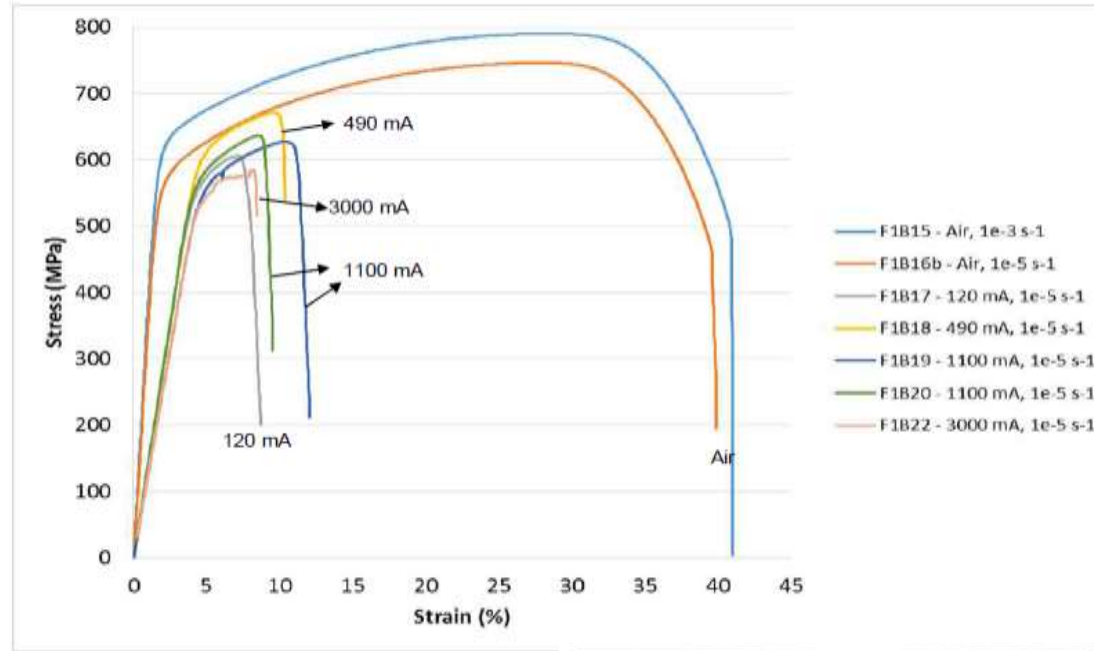
700°C



Hydrogen in superduplex forged

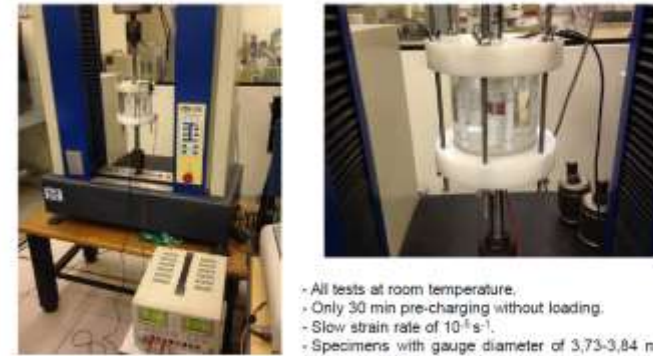
Pedro Cridy
Aluno DSc

Tensile Tests under In-Situ Hydrogen Charging

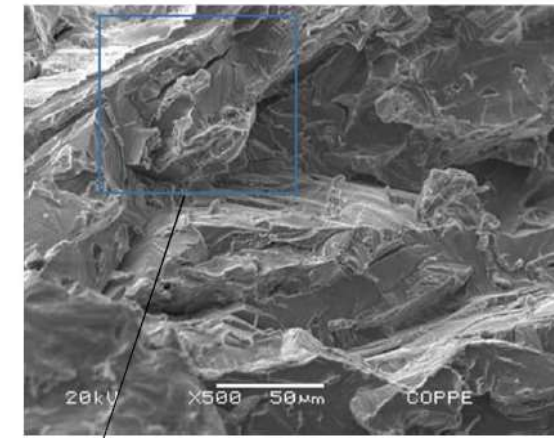
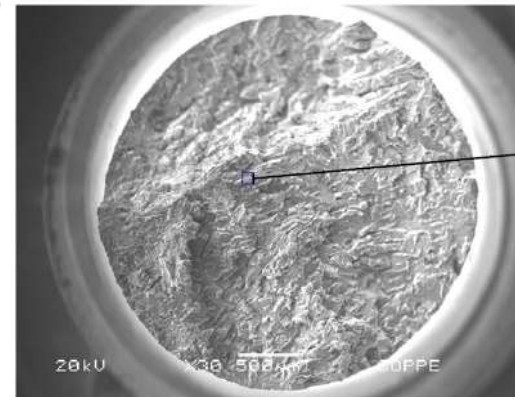


Electrochemical cathodic charging Hydrogen transport by dislocations in SSDS

Tensile Tests under In-Situ Hydrogen Charging



- All tests at room temperature.
- Only 30 min pre-charging without loading.
- Slow strain rate of 10^{-5} s^{-1} .
- Specimens with gauge diameter of 3,73-3,84 mm and gauge length of 16,74-18,01 mm.
- 3.5% NaCl solution with cathodic currents between 120 and 3000 mA – current densities of 0,56-14,9 mA/mm² (560-14900 A/m²) – potentials of -5 up to -19,6 V_{SCE}.

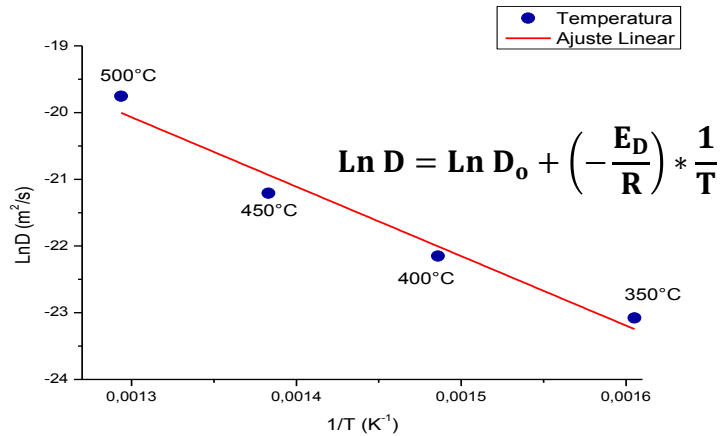




H em aços super duplex HIP

Thais P. Sequeira,
aluna DSc
Technip

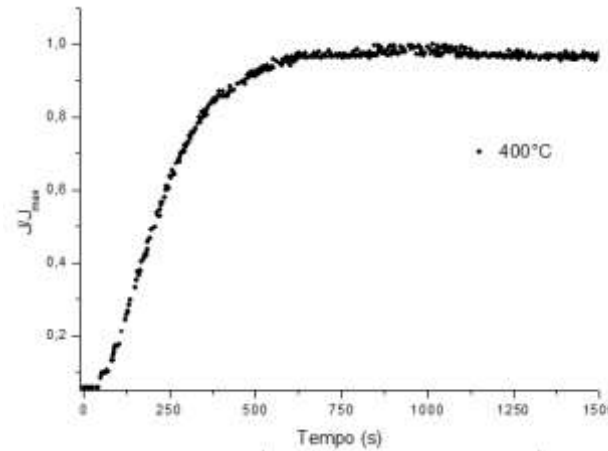
Permeação Gasosa



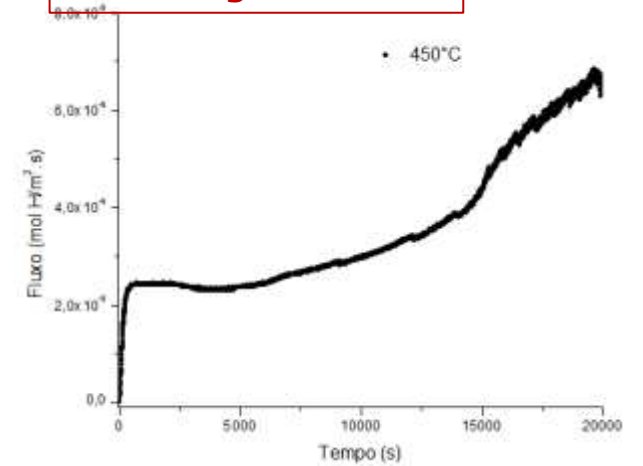
Constante D_0 e E_D - AISD HIP

D_0 (m ² /s)	Energia de Ativação E_D (kJ/mol)
$1,5 * 10^{-3}$	86,4

1° patamar de estado estacionário



Comportamento Bi-sigmoidal



Coeficientes de difusão de Hidrogênio (AISD HIP)

Temperatura (°C)	D_H (m ² /s)
350	$9,5 * 10^{-11}$
400	$2,4 * 10^{-10}$
450	$6,1 * 10^{-10}$
500	$2,6 * 10^{-9}$

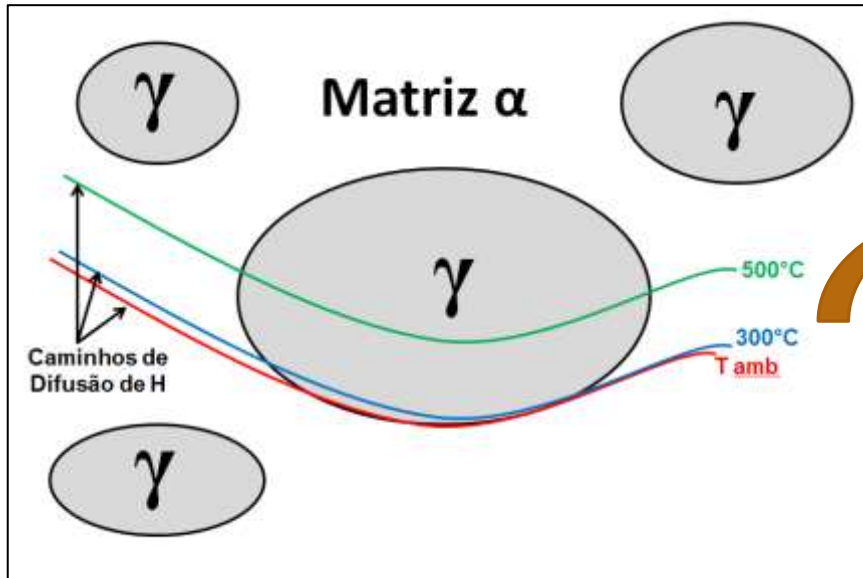
D aumenta com T

AISD HIP
 ↓ H difusível (alta E_D)
 ↑ Tolerância à fragilização por H

Aços Bifásicos → Difusão influenciada por ambas as fases

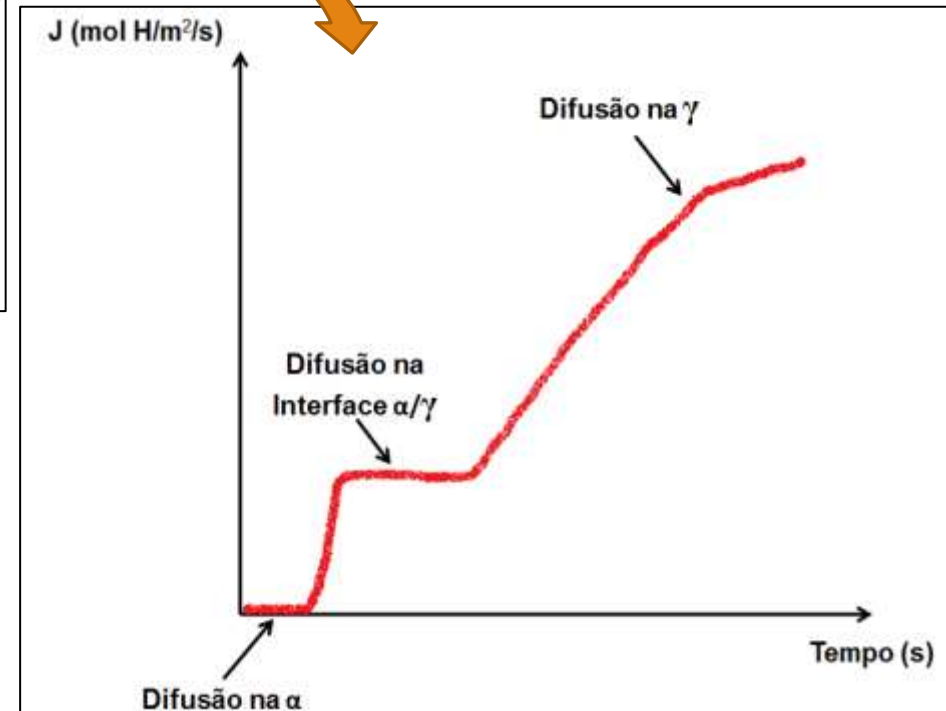
$$D_{\alpha} \gg \gg D_{\gamma}$$

$$\text{Solubilidade}_{\alpha} \ll \ll \text{Solubilidade}_{\gamma}$$

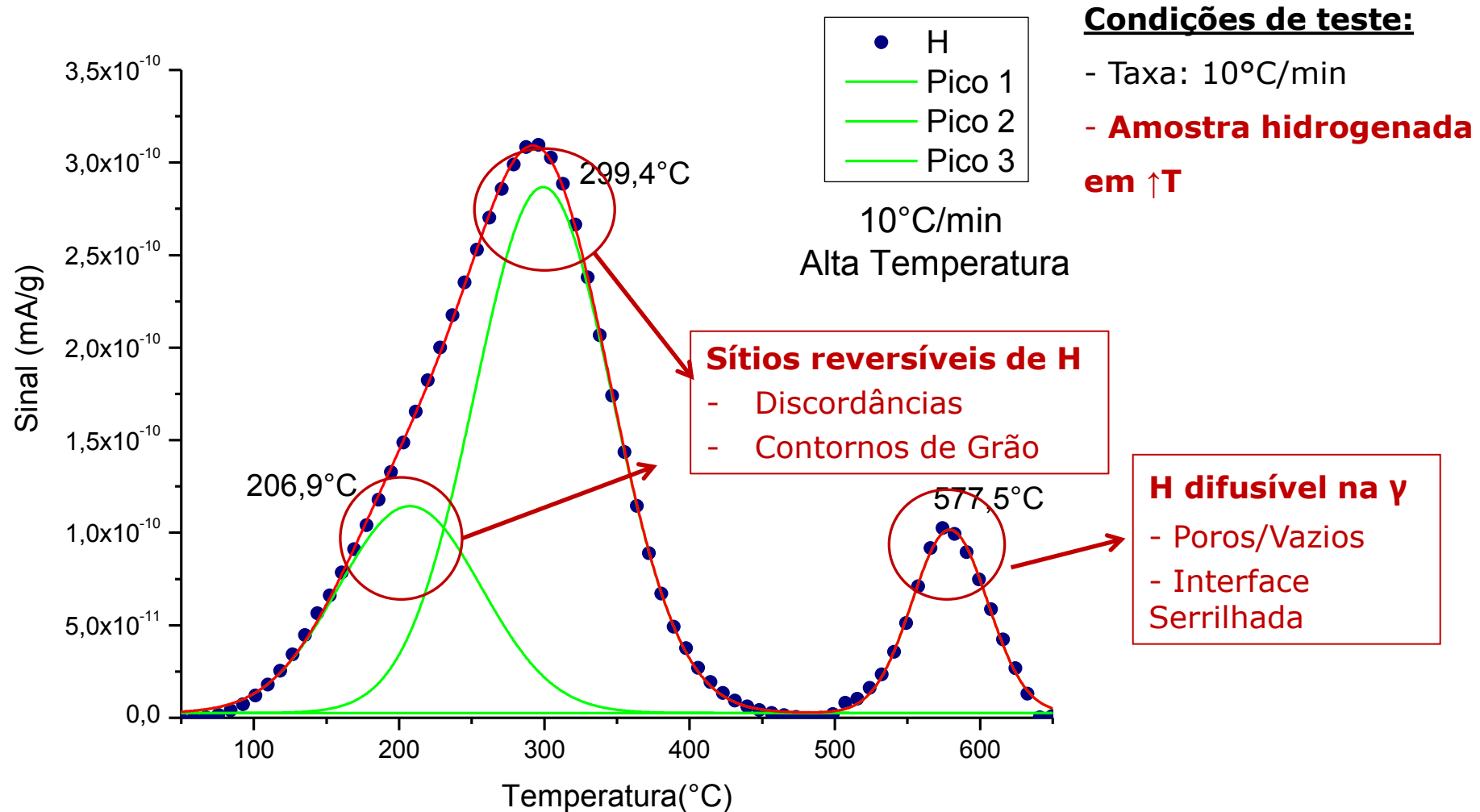


Difusão de Hidrogênio pela Austenita

- AISD HIP: significante apenas em elevadas temperaturas (a partir de 450°C)
- Baixas temperaturas → Difusão começa na α e continua na interface α/γ



Espectroscopia de Dessorção Térmica - TDS

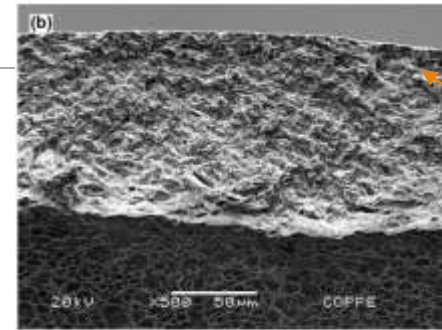
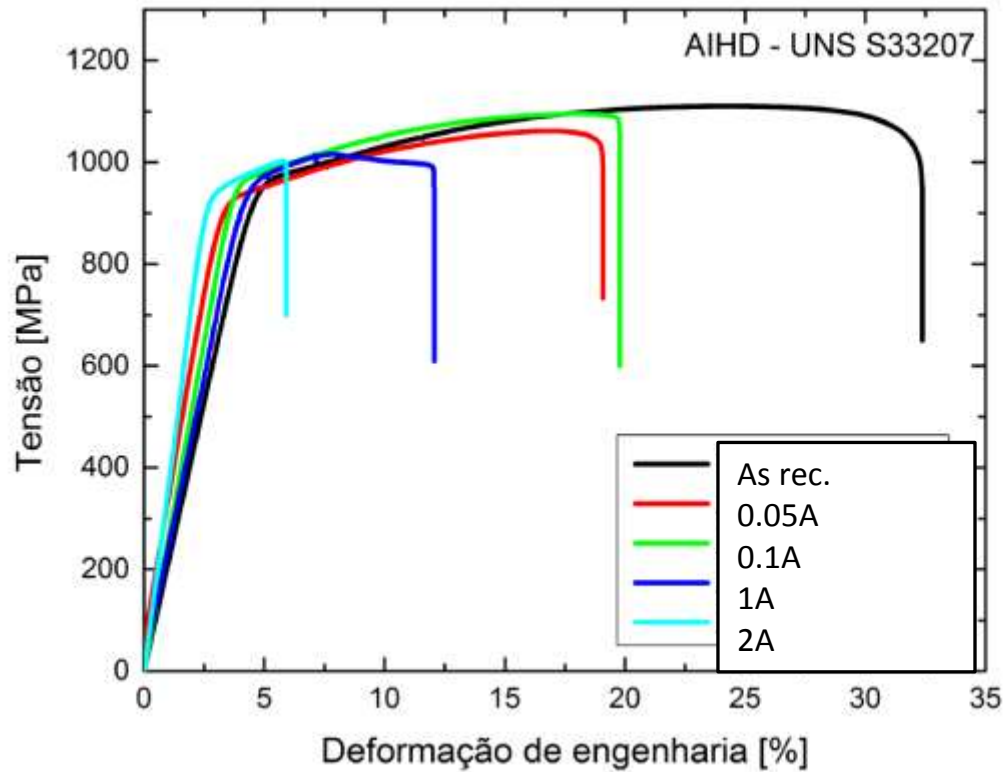




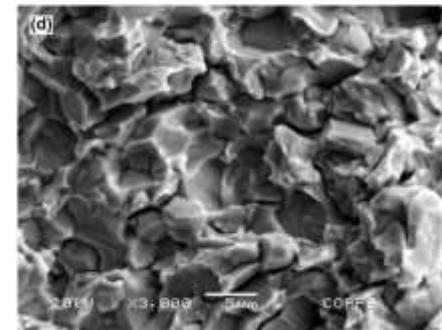


Filipe Salvio
aluno DSc
SubSea 7

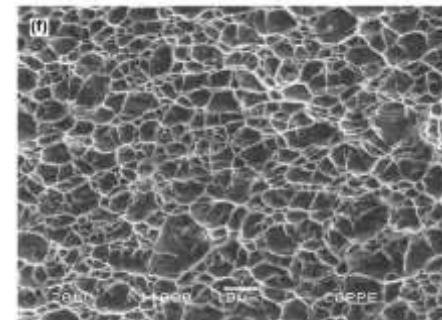
Hydrogenation under elastic stress (75 % yield strength) (150h)



hydrogenation surface



Near surface



middle



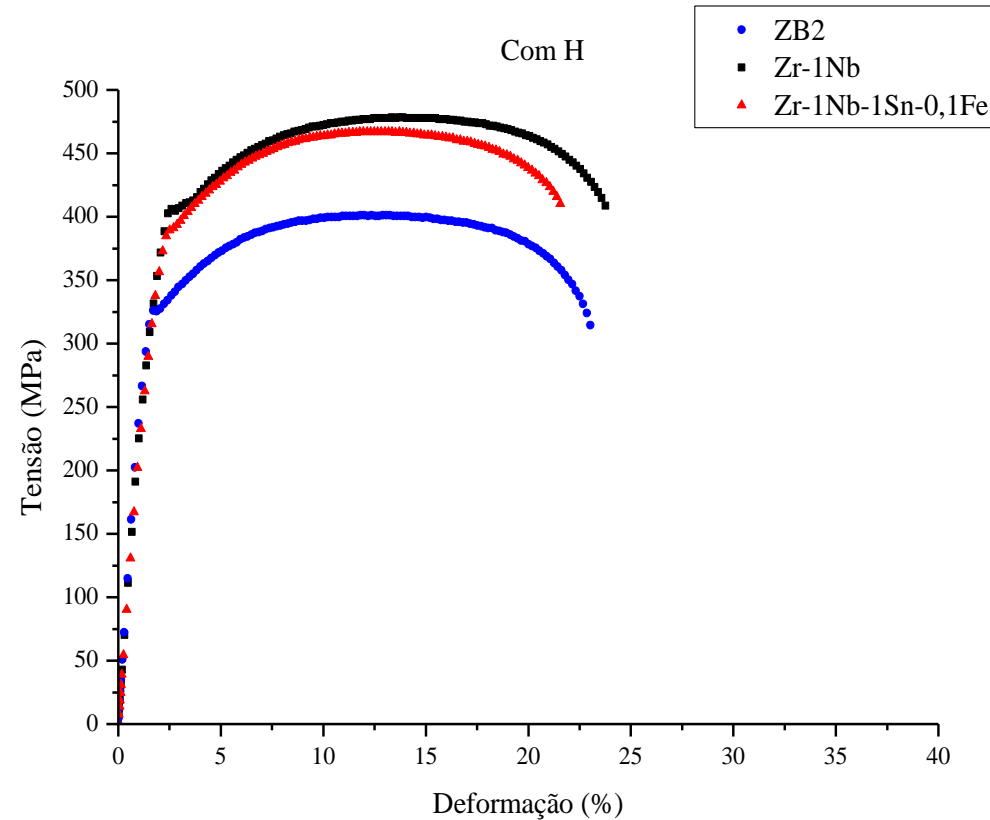
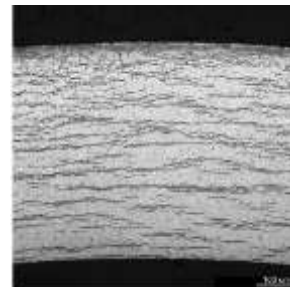
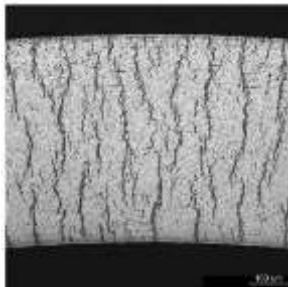
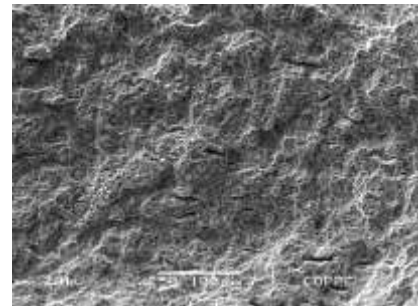
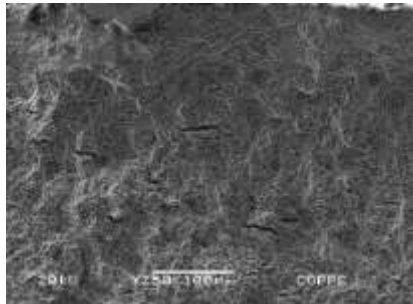


Ligas de Zr para aplicações nucleares

Leandro Martins – Aluno DSc
Engenheiro Metalúrgico

Tração com H

- Liga Zr-1Nb – maior ductilidade média e resistência à tração
- Perda de ductilidade:
 - ZB-2 – 36,2%
 - Zr-1Nb-1Sn-0,1Fe – 4,7%
 - Zr-1Nb – 1,6%



Propriedades Mecânicas com hidrogênio			
Liga	σ_{LE} (MPa)	σ_{LR} (MPa)	Alongamento (%)
ZB-2	328 ± 4	410 ± 12	22 ± 0
Zr-1Nb	403 ± 9	479 ± 2	25 ± 4
Zr-1Nb-1Sn-0,1Fe	405 ± 23	479 ± 17	19 ± 0

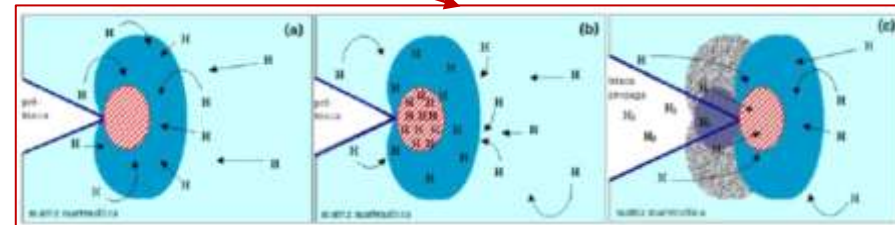
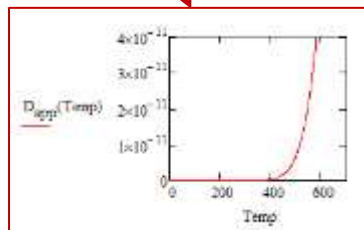
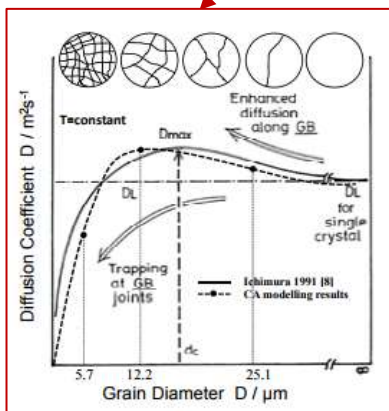
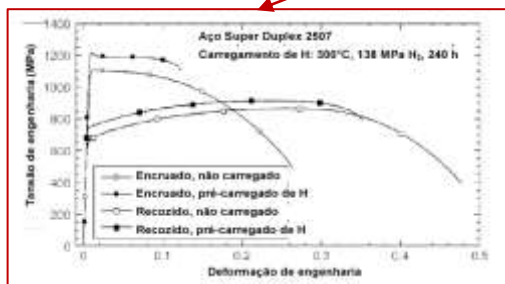


Mario Castro
Technip/FMC

- HE close related to H diffusion:

$$\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2}$$

Second Fick's Law

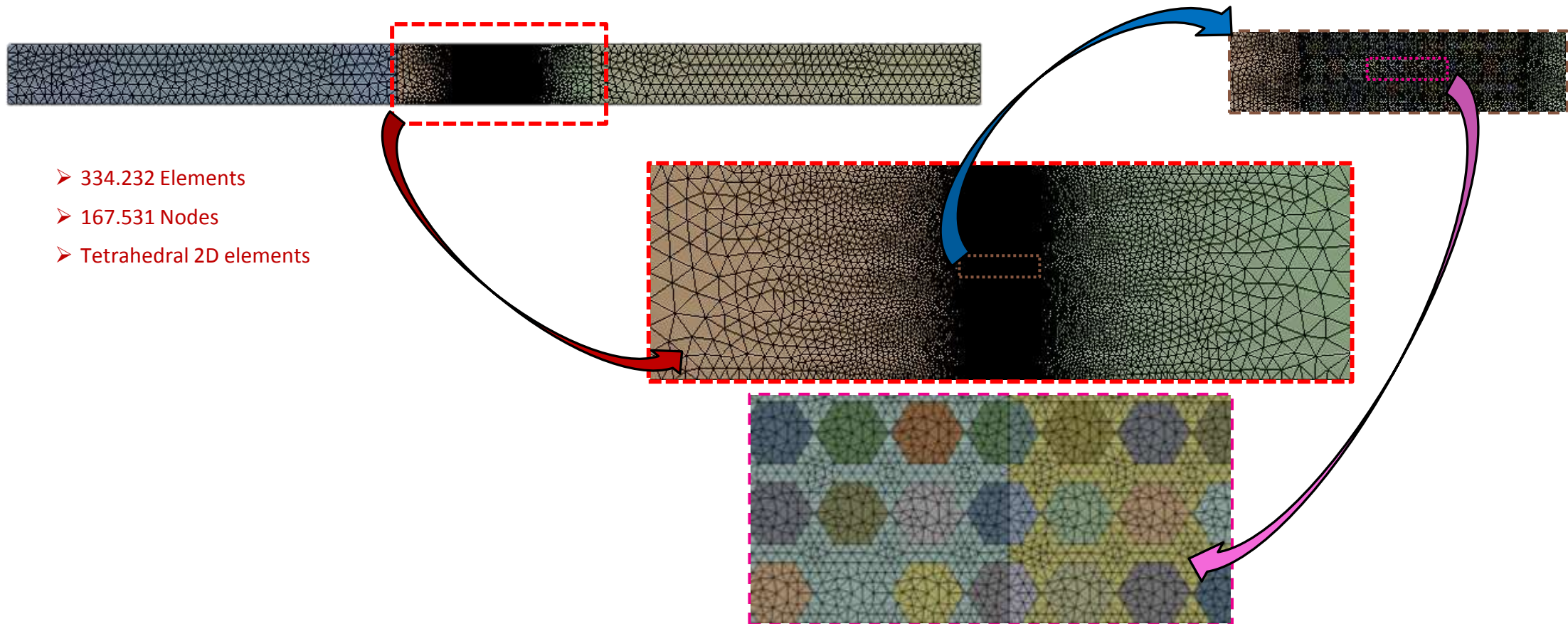


$$\frac{\partial C_L}{\partial t} - D_L \nabla^2 C_L + \nabla \cdot \left(\frac{D_L C_L V_H}{3RT} \nabla \sigma_{kk} \right) + \alpha \theta_T \frac{\partial N_T}{\partial \epsilon_p} \frac{\partial \epsilon^p}{\partial t} = 0$$

5. Role of Phases Anisotropy

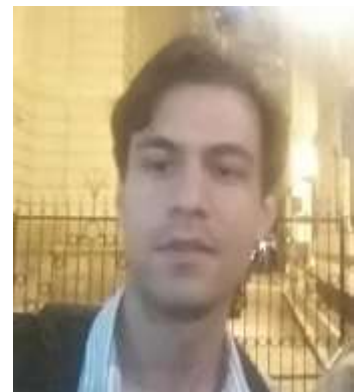
- FEA simulation: Aims to investigate preliminarily small anisotropy between two commercial inox materials:

➤ Mesh:

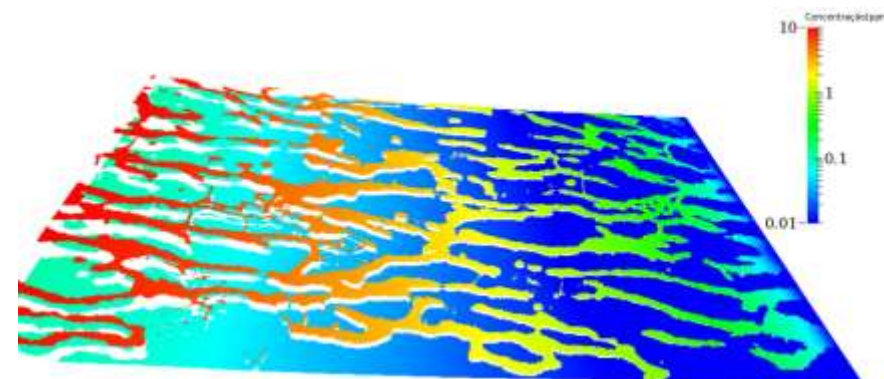
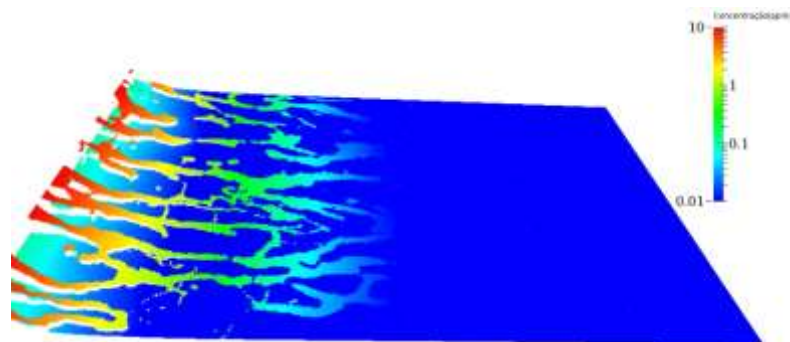
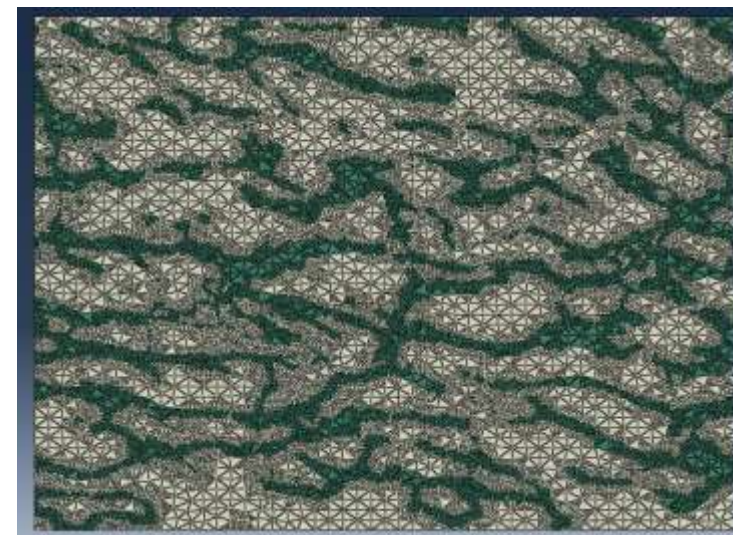




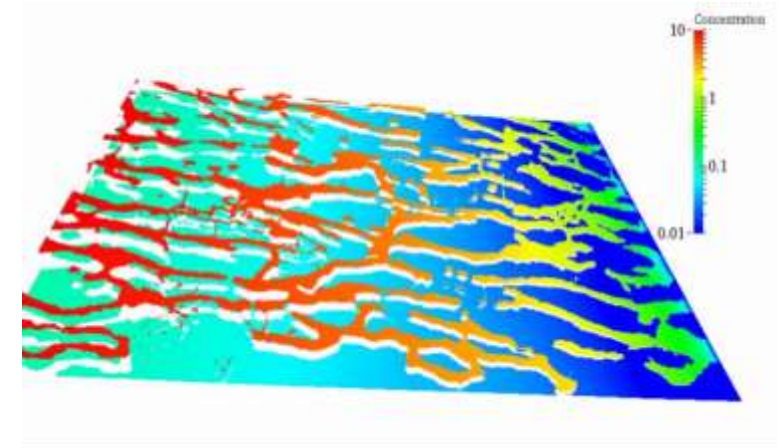
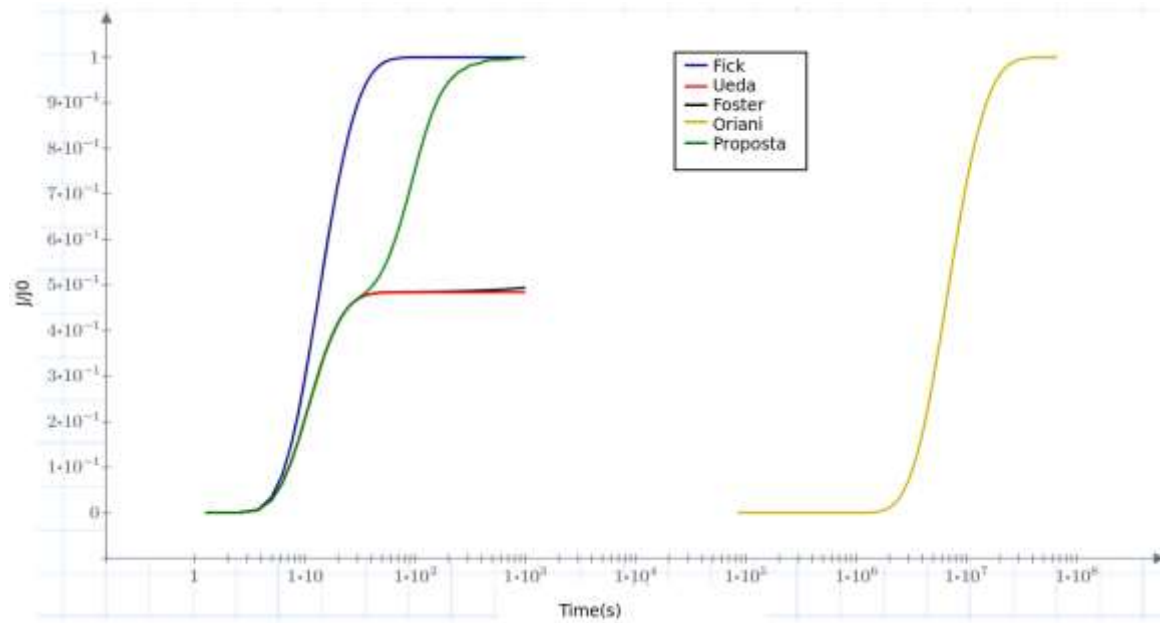
Cálculo por Elementos Finitos da difusibilidade do H em ligas multifásicas



Léo Roberto Costa
Aluno DSc
Engenheiro Metalúrgico



Modelos e resultados







Simulação da interação H- interfaces

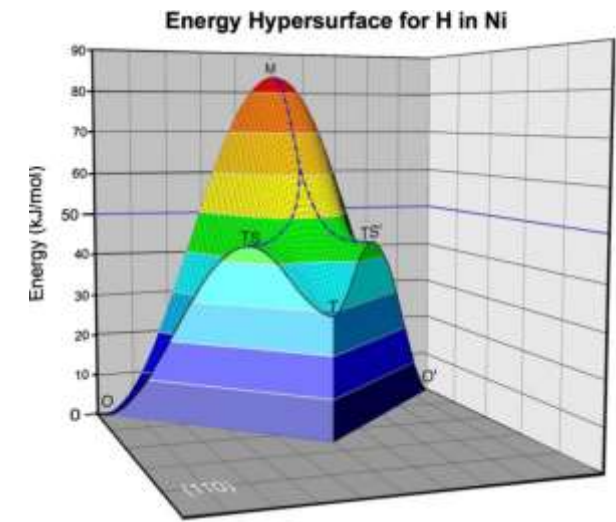
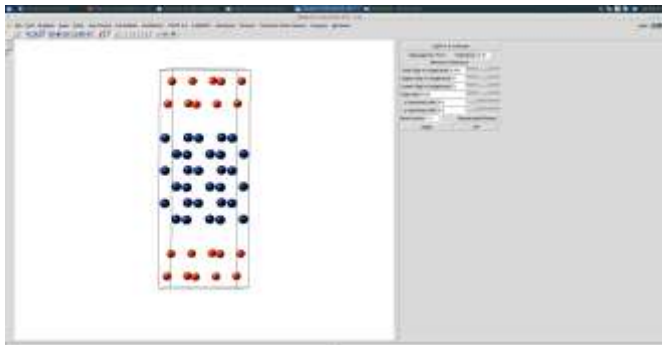
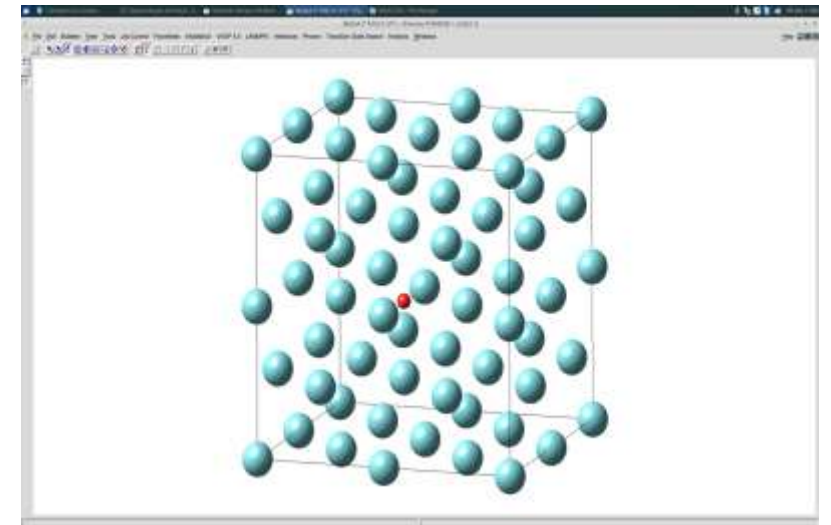
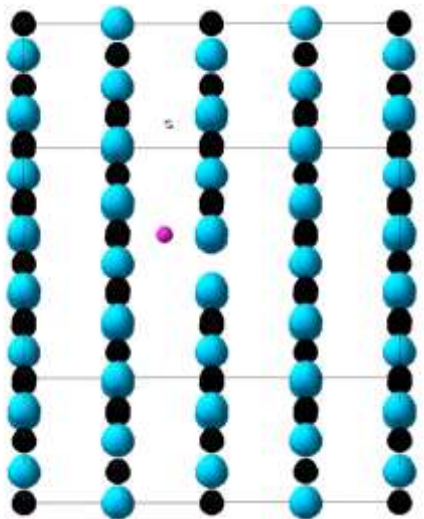


FIG. 2. (Color online) Energy hypersurface of H diffusing in nickel between octahedral interstitial sites. Note the pronounced local minimum at the tetrahedral site (T) and two transition states (TS and TS') along the path from O to O'. The dashed-dotted line is the energy divide.

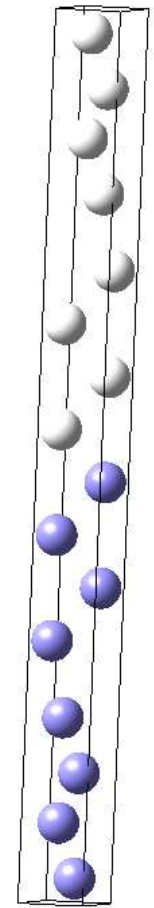
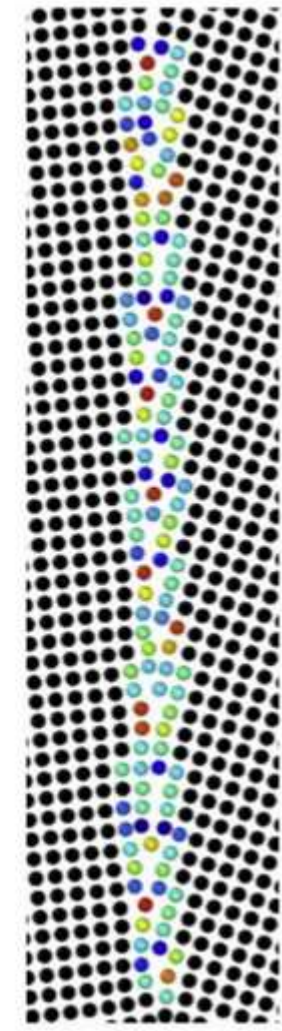
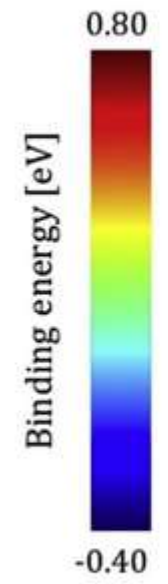
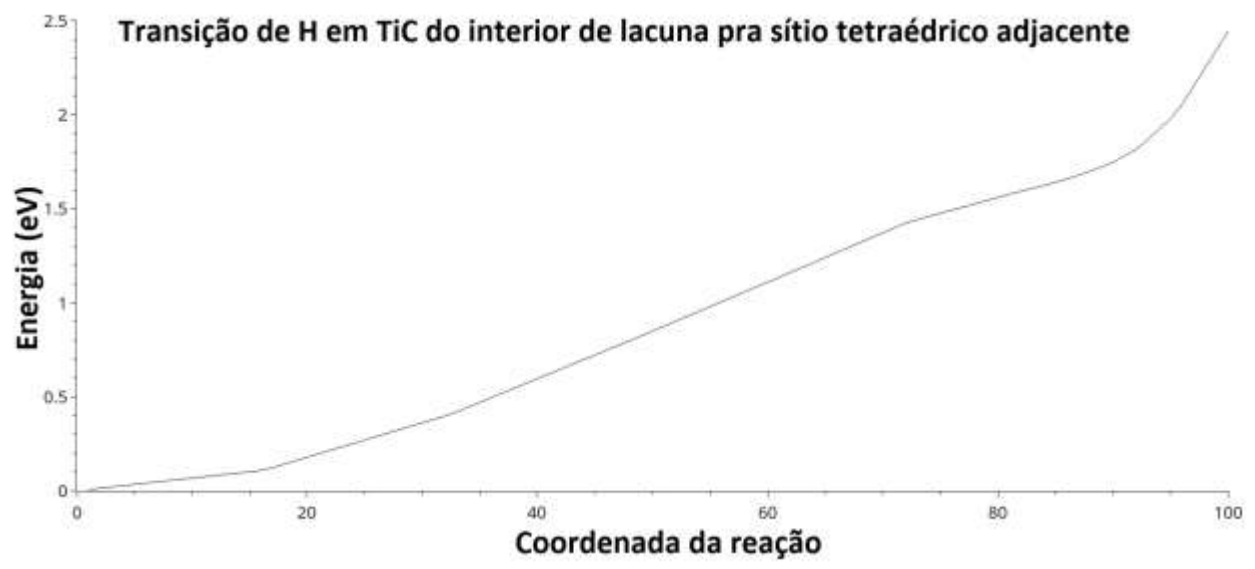
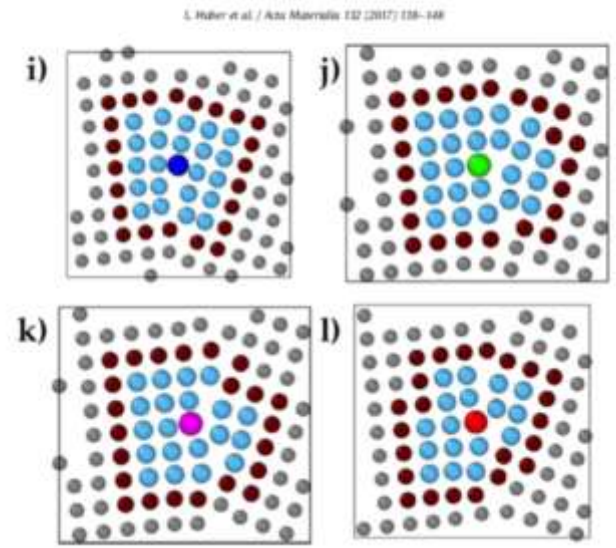
PHYSICAL REVIEW B 77, 134305 (2008)

Amanda Ventura Castilho
Aluna DSc do PENT





Hidrogênio em sítio intersticial próximo a lacuna de carbono em TiC
 rosa: H
 preto: C
 azul : Ti



interface (110) matriz (branco), (110)
 martensita (roxo)

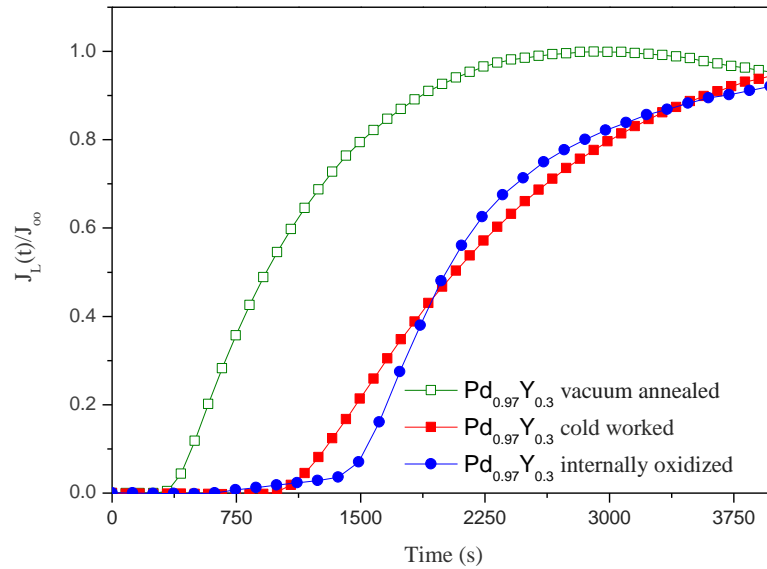
Segregação de Mg em contornos de alumínio
 Noguebouer et al, **Acta Materialia 132 (2017)**
 138-148



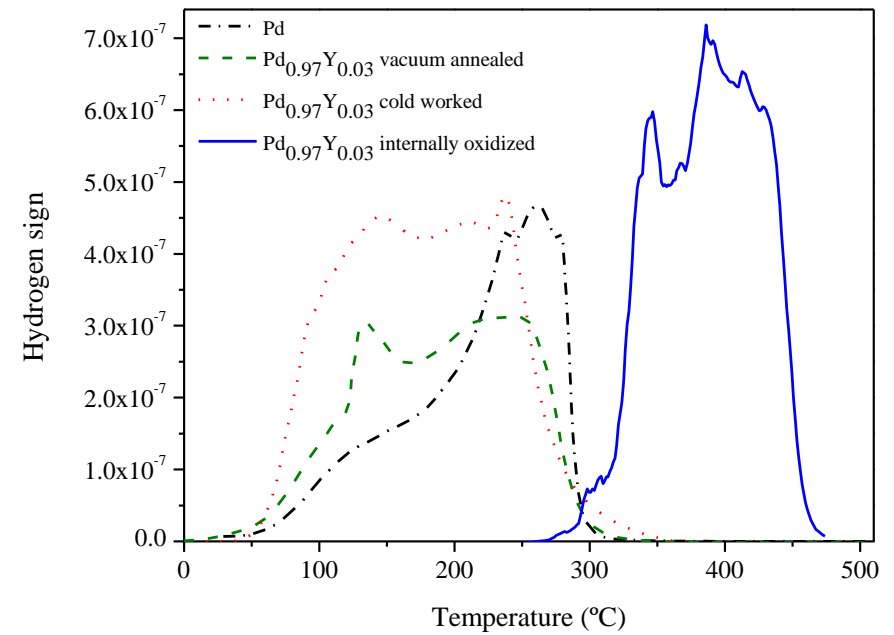


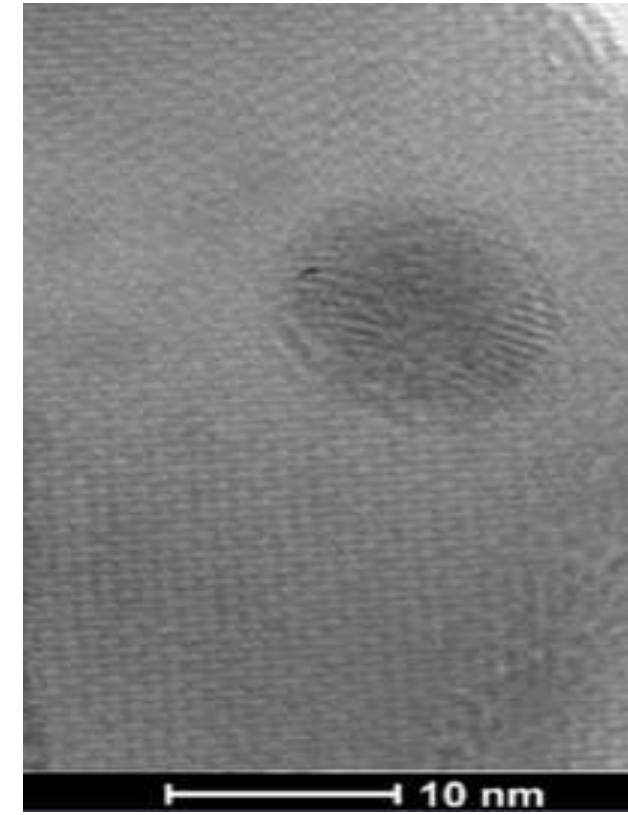
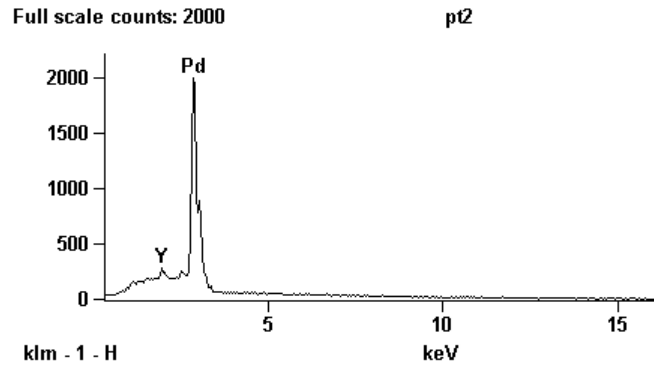
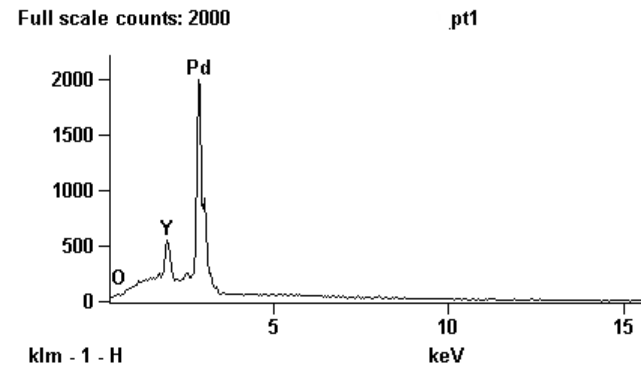
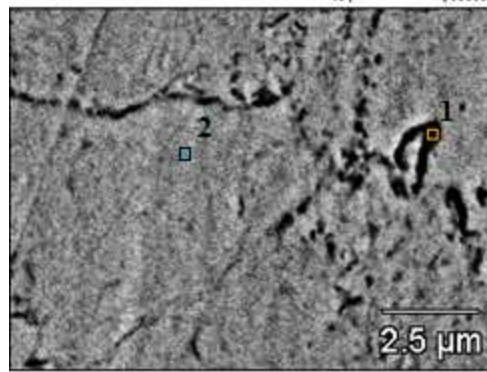
Permeação do H em aços e ligas de Ni com óxidos nanometricos

Tabatta Regina Martins
Aluna DSc do PENT



Teste de permeação e TDS no Pd-Y





MEV e MET do Pd₂YO₃ na matriz de Pd





Chemomechanical effect of Hydrogen in 13Cr SS jul 2017

- Debora Molter Aluna DSc

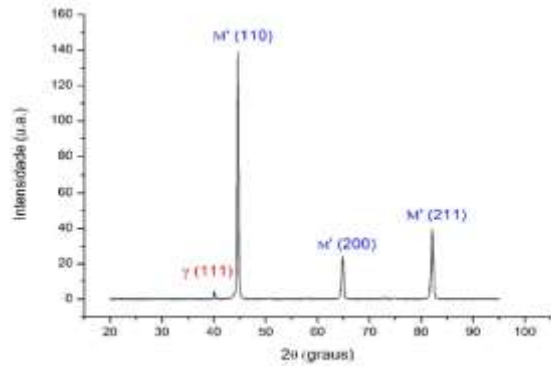
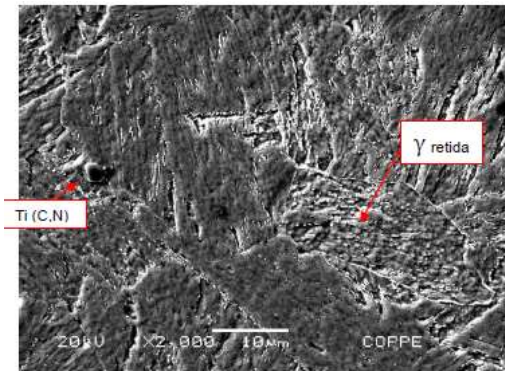


Figura 35 - Difratograma do AISM como recebido.

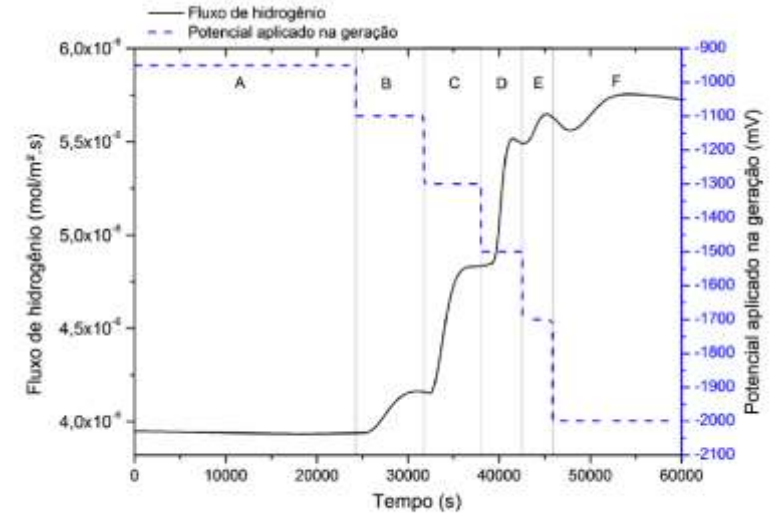
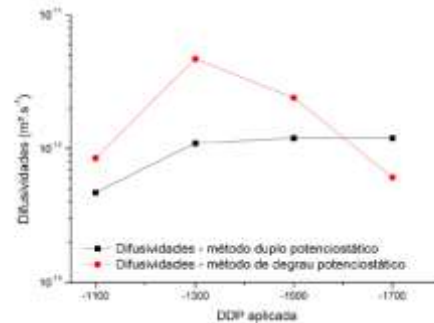
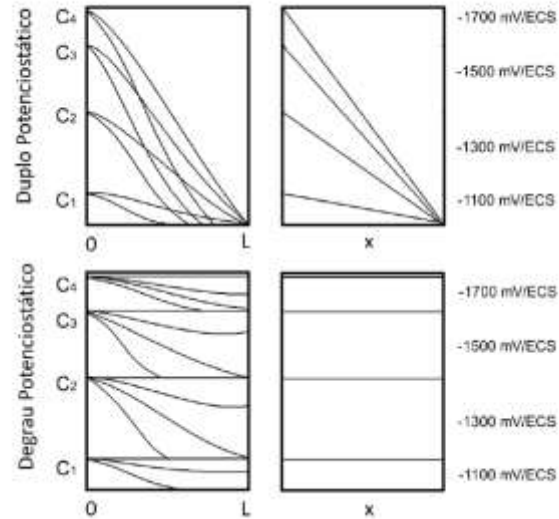


Figura 37 - Curva de permeação de hidrogênio pelo método duplo potenciostático.

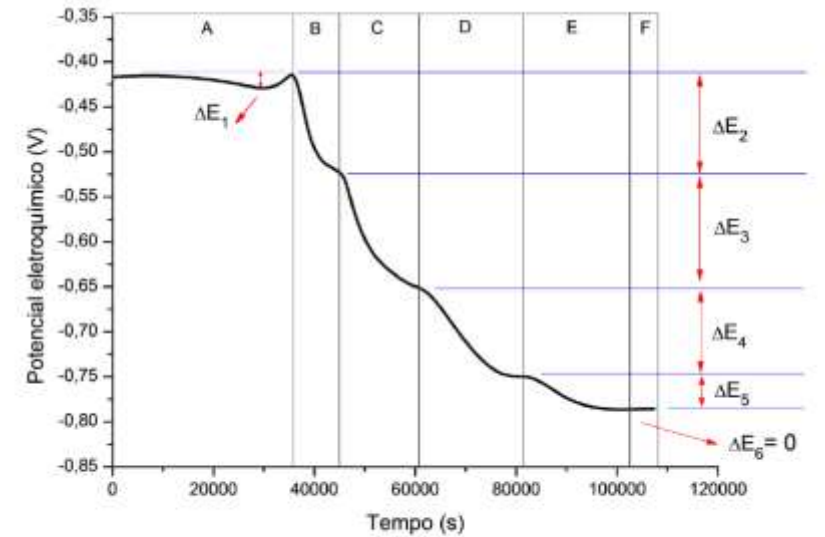


Figura 39 - Curva de permeação de hidrogênio pelo método de degrau potenciostático.

From chemomechanical

$$\left. \frac{\partial \gamma}{\partial \mu_i} \right|_{V,T,A,n_m} = - \left. \frac{\partial n_i}{\partial A} \right|_{V,T,\mu_i,n_m}$$

$$d\gamma = -\Gamma_i d\mu_i$$

$$\mu_{i,f} = \mu_{i,f}^0 + 2W \frac{\Gamma_i}{\Gamma_{sat}} + RT \ln \frac{\Gamma_i}{\Gamma_{sat} - \Gamma_i}$$

$$d\gamma = -\Gamma_i \frac{d\mu_{i,f}}{d\Gamma_i} d\Gamma_i = - \left[2W \frac{\Gamma_i}{\Gamma_{sat}} + RT \frac{\Gamma_{sat}}{(\Gamma_{sat} - \Gamma_i)} \right] d\Gamma_i$$

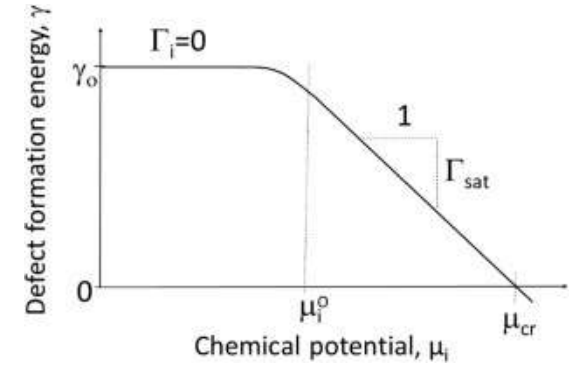
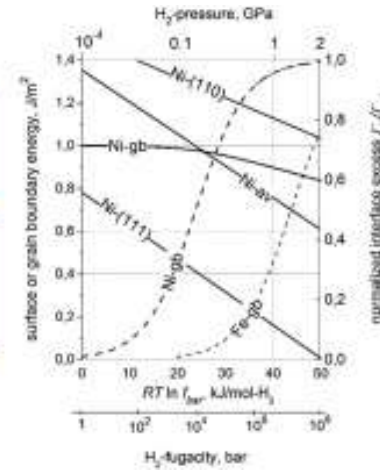
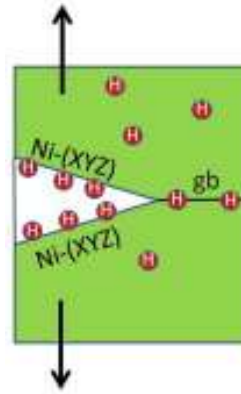
Integrating Eq. (4) gives

$$\gamma = \gamma_0 - \Gamma_{sat} \left[W \left(\frac{\Gamma_i}{\Gamma_{sat}} \right)^2 + RT \ln \frac{\Gamma_{sat}}{(\Gamma_{sat} - \Gamma_i)} \right]$$

$$\mu_g^0 + RT \ln p_{bar} = 2\mu_{H,s}^0 + 4W \frac{\Gamma_H}{\Gamma_{sat}} + 2RT \ln \frac{\Gamma_H}{\Gamma_{sat} - \Gamma_H}$$

Acta Materialia 99 (2015) 87-98

Reiner Kirchheim^{a,b,c,*}, Brian Somerday^{c,d}, Petros Sofronis^{c,e}



	in crystal	at grain boundary	at interface
without hydrogen			
with slow hydrogen			
with fast hydrogen			

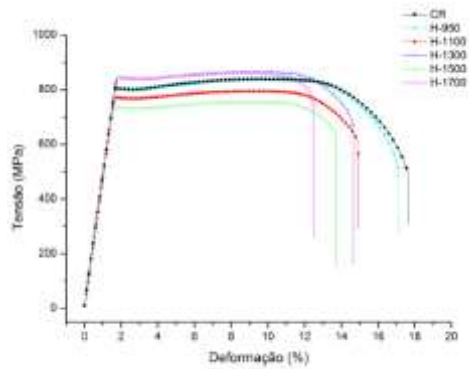


Figura 45 – Curvas tensão x deformação de engenharia.

MSc- Debora Molter

Chemomechanical effect of Hydrogen in 13Cr SS

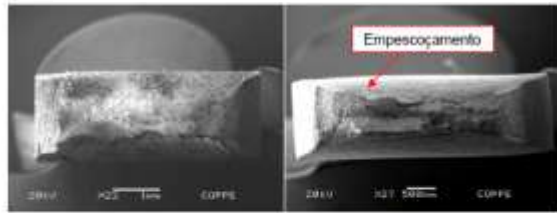
jul 2017

Tabela 10 – Valores de difusividade, solubilidade e permeabilidade obtidos para cada DDP aplicada no ensaio duplo potenciostático.

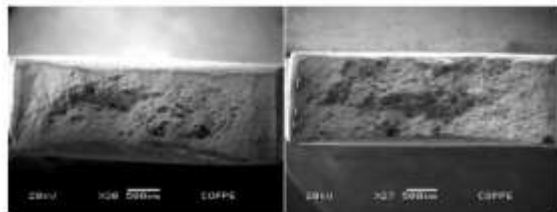
Região (DDP aplicada em mV/ECS)	Difusividade (m ² /s)	Solubilidade (mol _H /m ³)	Permeabilidade (mol _H /m·s)
Região A (- 950)	-	-	-
Região B (- 1100)	4,7 x 10 ⁻¹³	62,6	2,9 x 10 ⁻¹¹
Região C (- 1300)	1,1 x 10 ⁻¹²	88,0	9,9 x 10 ⁻¹¹
Região D (- 1500)	1,2 x 10 ⁻¹²	77,6	9,4 x 10 ⁻¹¹
Região E (- 1700)	1,2 x 10 ⁻¹²	15,7	1,8 x 10 ⁻¹¹
Região F (- 2000)	3,7 x 10 ⁻¹³	64,4	3,3 x 10 ⁻¹¹

Tabela 20 - Valores calculados de W.

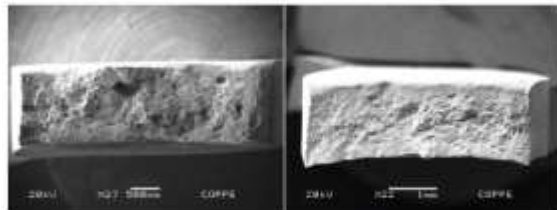
DDP aplicada (mV/ECS)	Δμ (kJ/mol)	W (kJ/mol)
-1100	10,61	35,9
-1300	23,15	22,9
-1500	32,80	66,4
-1700	36,67	saturação



a) Como recebido b) -950 mV/ECS



c) -1100 mV/ECS d) -1300 mV/ECS



e) -1500 mV/ECS f) -1700 mV/ECS

Figura 48 – Fractografias mostrando o grau de empescoamento para cada corpo de prova.

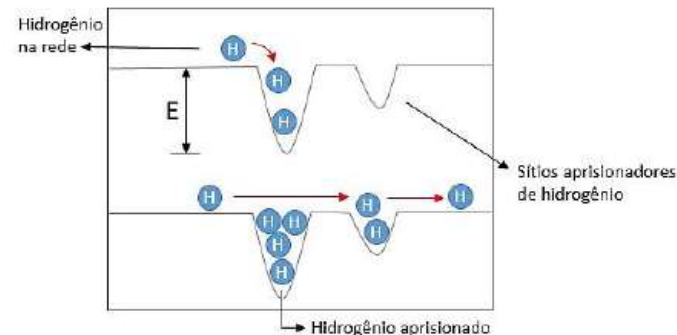


Figura 38 - Difusão do hidrogênio em função do preenchimento dos sítios aprisionadores.

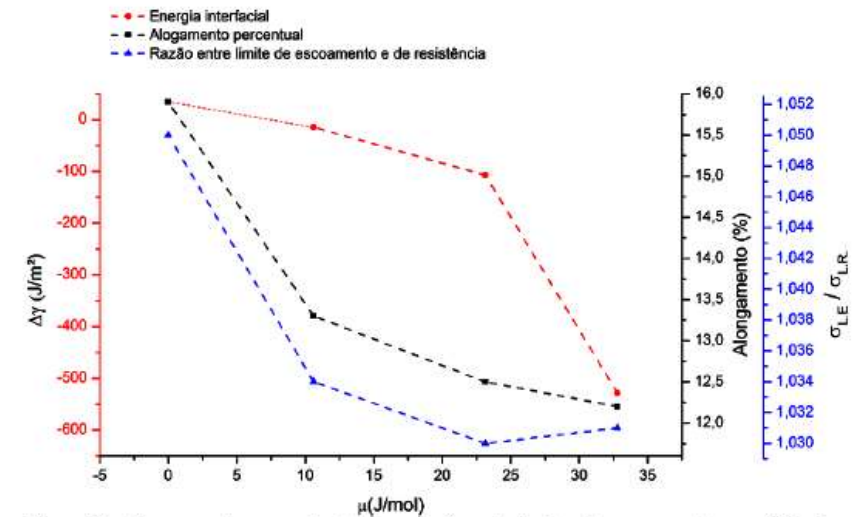


Figura 57 – Alongamento percentual do aço, razão entre limites de escoamento e resistência e energia interfacial em função do potencial químico de hidrogênio.





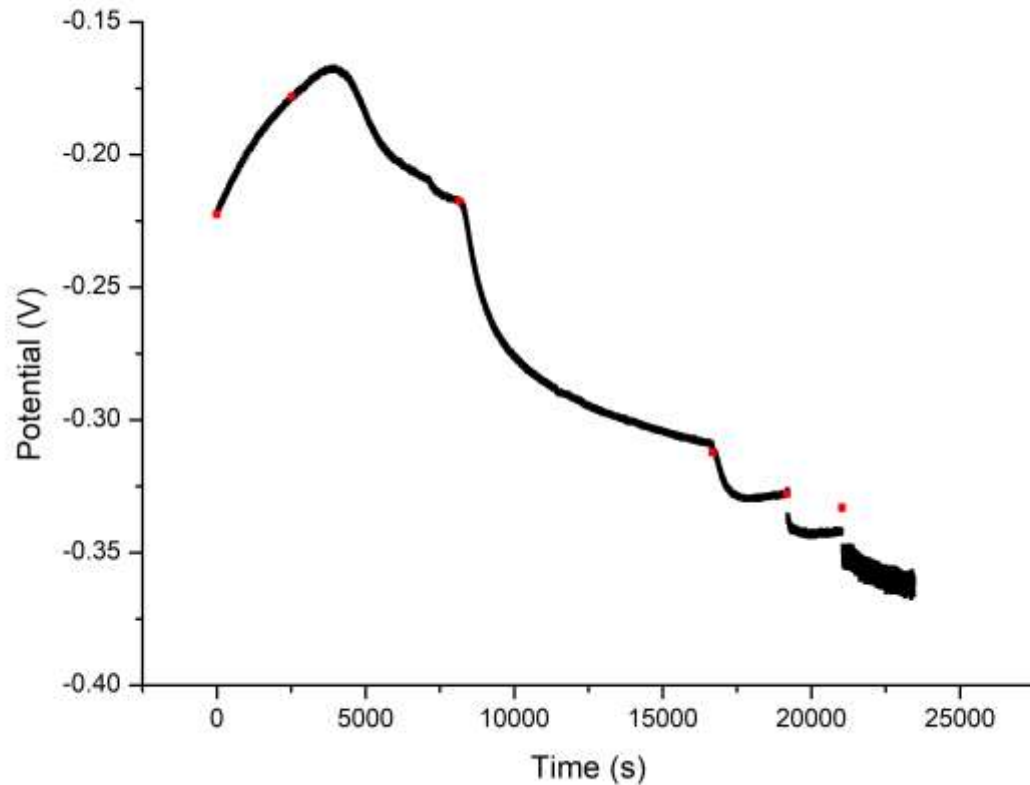
Ligia Yassuda de Mattos
MSc. Metalurgia Física



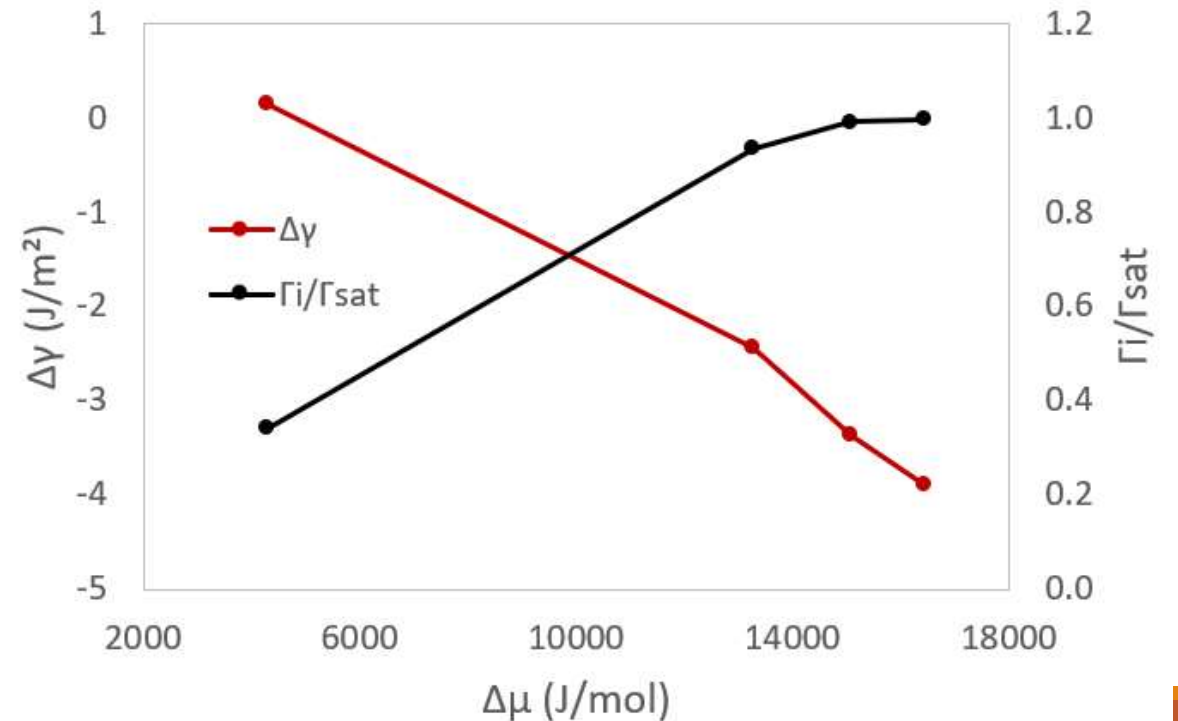
Teoria Mecanoquímica de Fragilização pelo Hidrogênio

Material: Aço X60

Permeação eletroquímica



Diminuição da energia de superfície

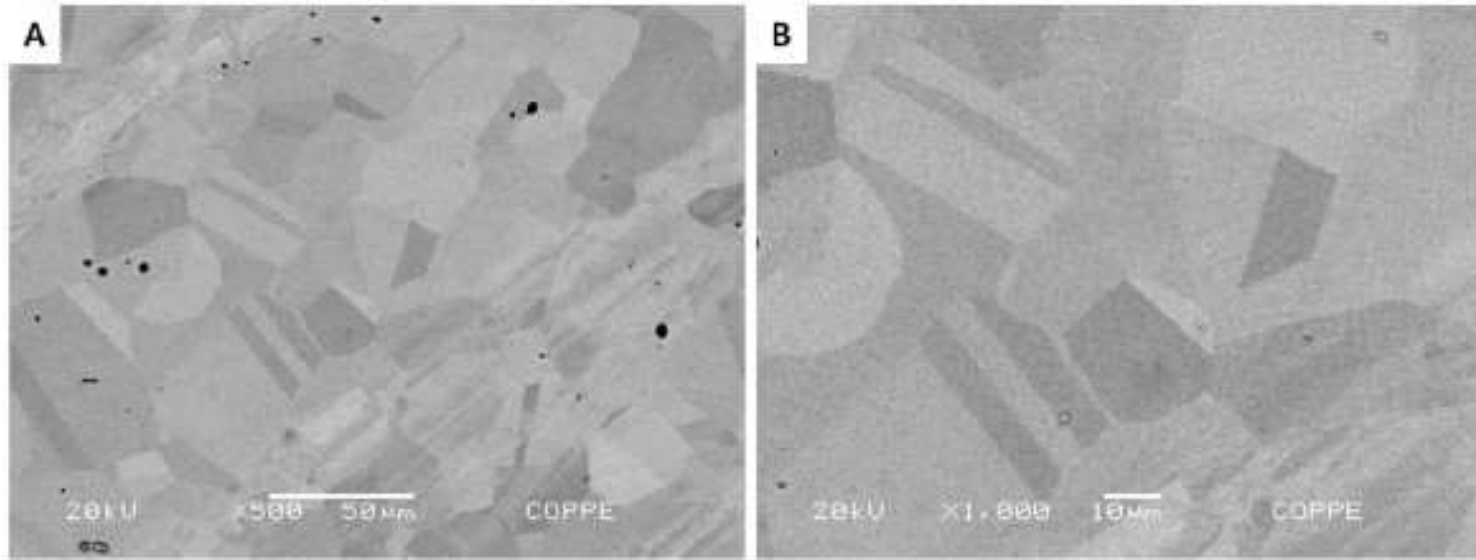




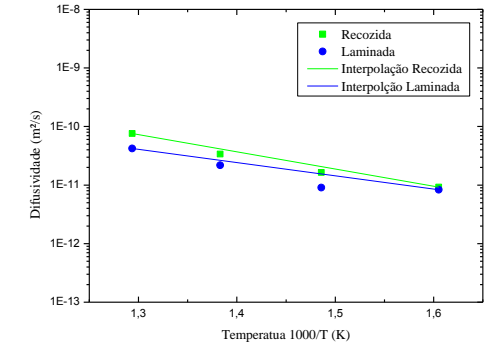
Desenvolvimento de ligas de alta entropia a base de Fe-Mn-Ni resistentes à fragilização pelo hidrogênio

Sara Corrêa Marques

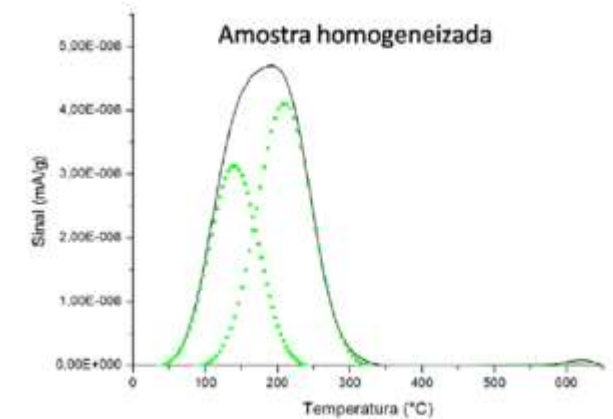
Mestrado: Engenharia Metalúrgica e de Materiais (COPPE/UFRJ)



MEV, referente a uma amostra de composição $Mn_{40}Ni_{30}Fe_{22}Co_6Cr_2$. A: aumento de 500x. B: Aumento de 1000x.



Difusividade do H na liga HEA em função da T Jardel Belo MSc 2017

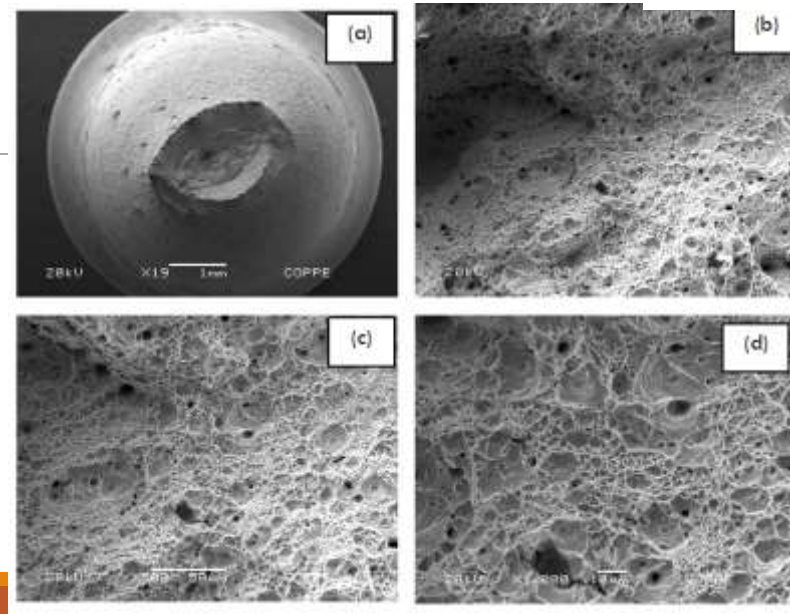
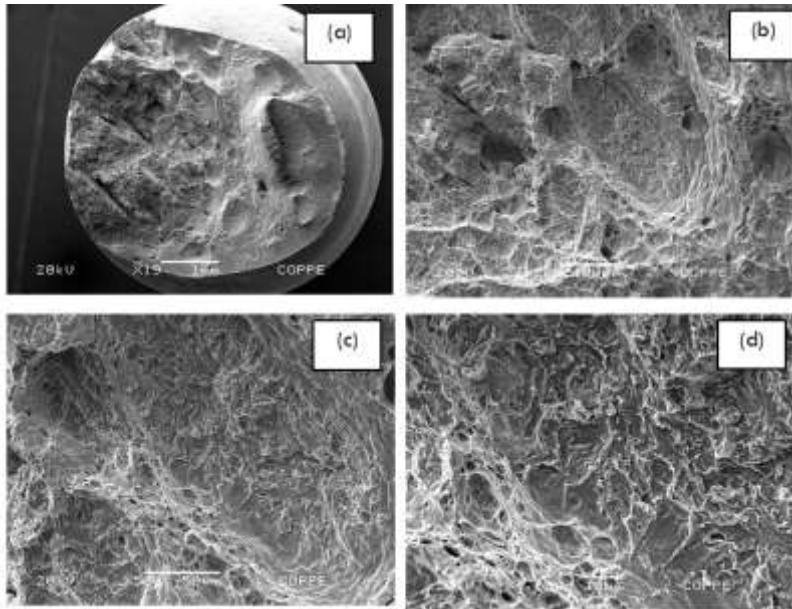
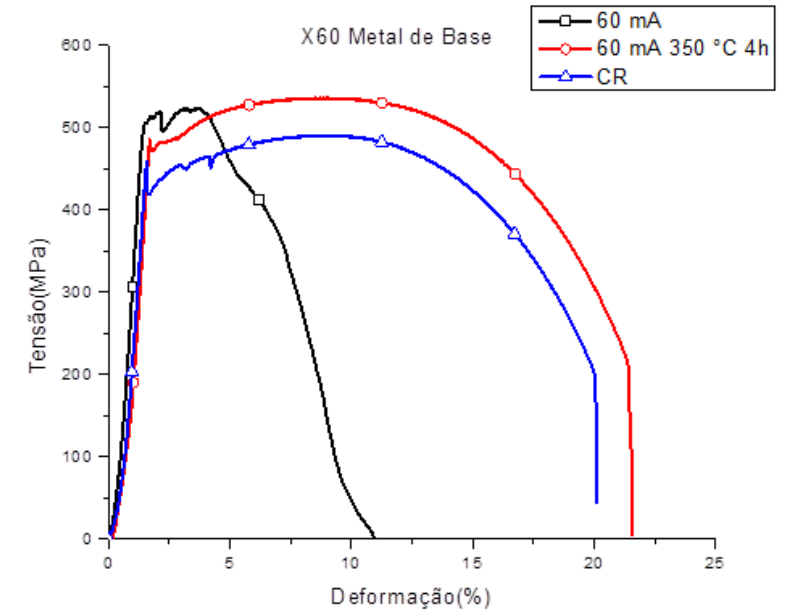


TDS referente à liga de alta entropia de composição $Mn_{40}Ni_{30}Fe_{22}Co_6Cr_2$



Estudo e simulação numérica do ensaio de flexão quatro pontos no aço inoxidável Super 13

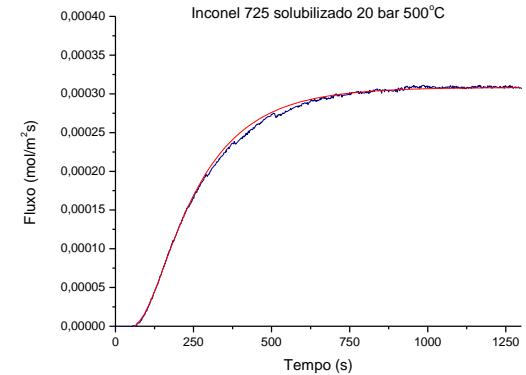
Carlos Henrique da Fonseca Marques
Aluno MSc





Permeação Gasosa de Hidrogênio Inconel 725

Érica Wirth Aluna tcc/MSc

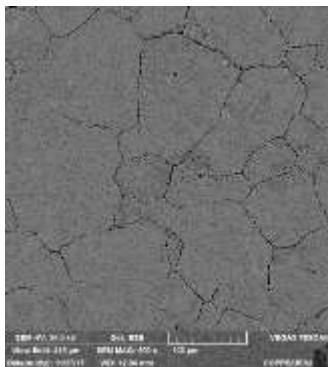


Solubilizado



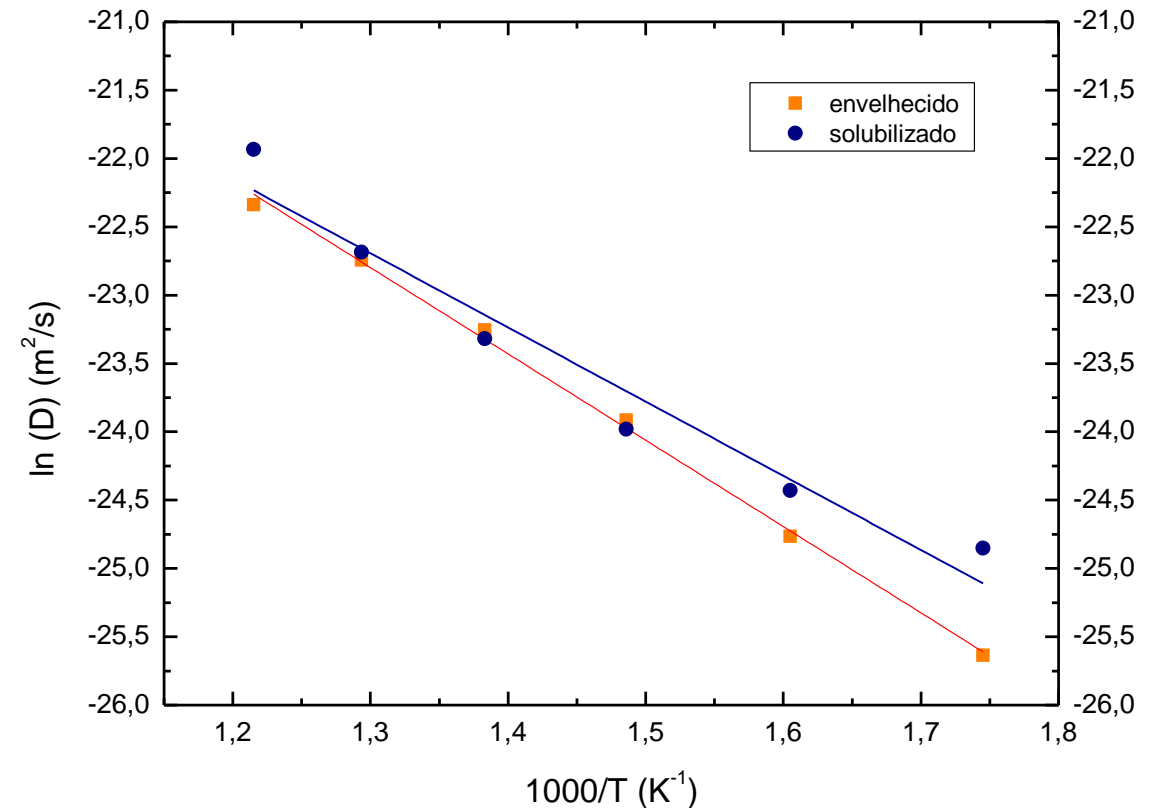
(T = 25°C)
 $D = 1,86 \times 10^{-15} \text{ m}^2/\text{s}$

Envelhecido



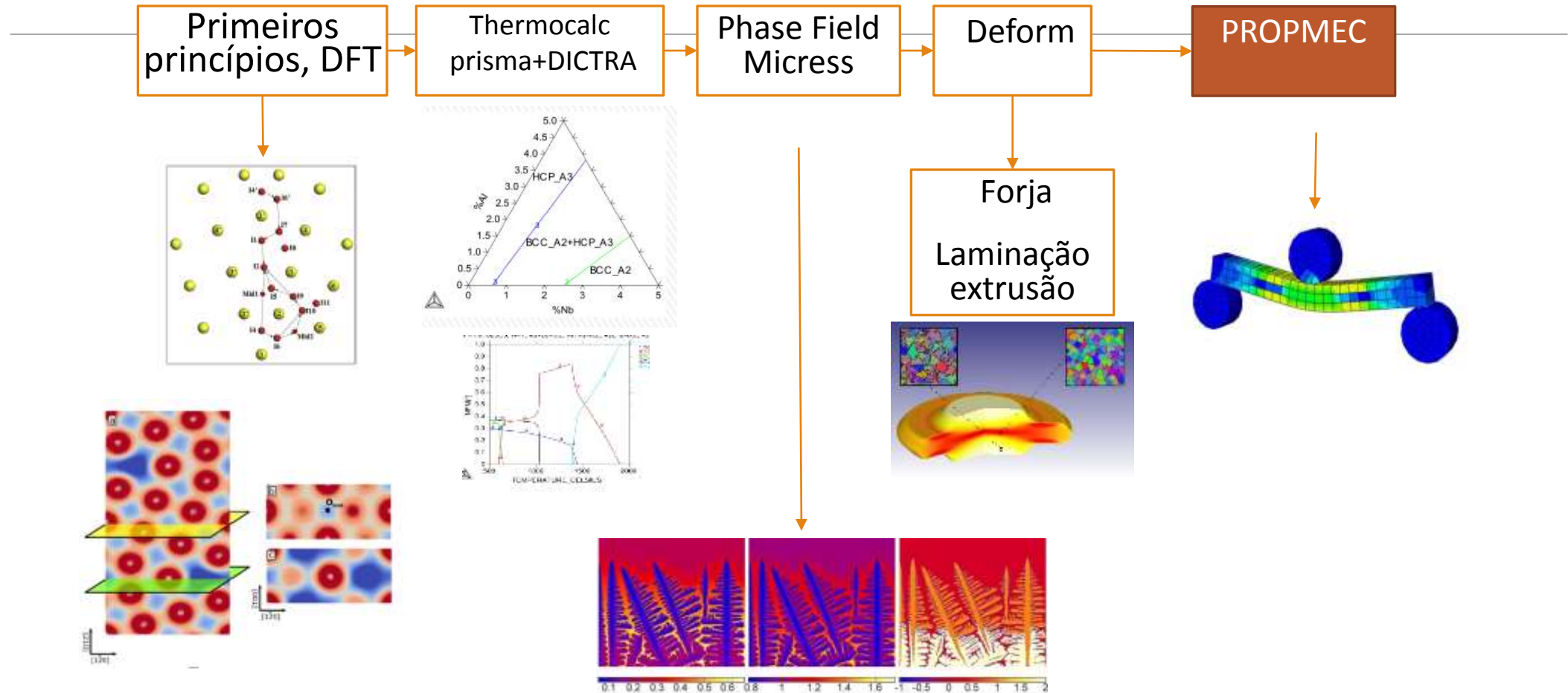
(T = 25°C)
 $D = 3,69 \times 10^{-16} \text{ m}^2/\text{s}$

Difusividade - Inconel 725



Multi-scale Simulation

(Propmec Lab. PEMM-COPPE/UFRJ)



Requisitos: Mecânica quântica + Metalurgia física e mecânica + Solidificação + kUS\$

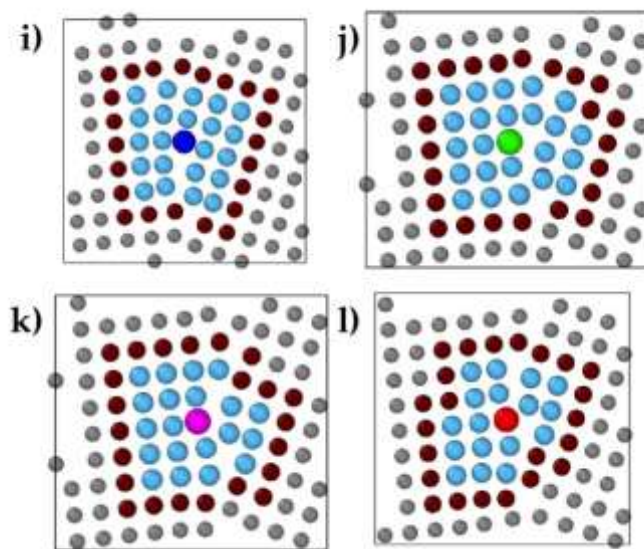


Full length article

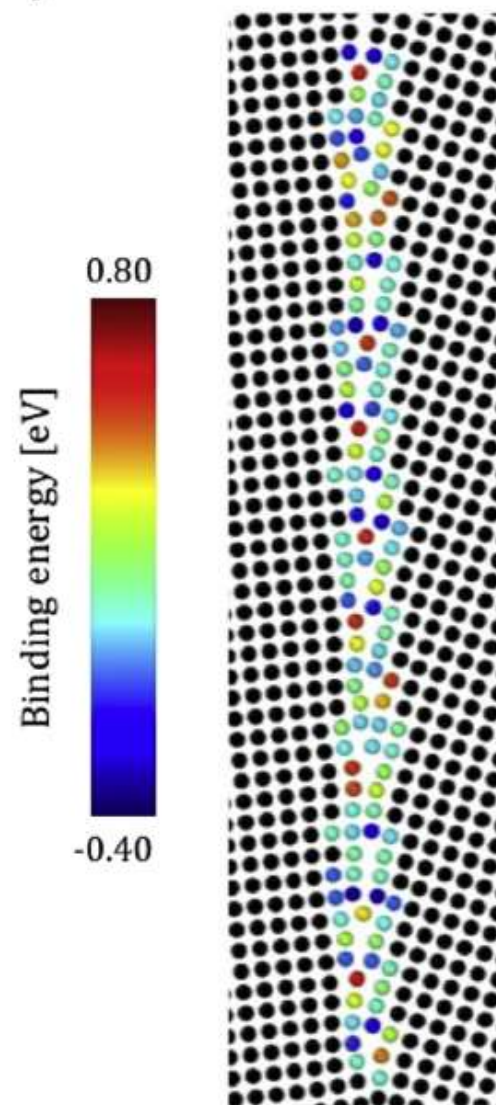
Ab initio modelling of solute segregation energies to a general grain boundary

Liam Huber^{a,*}, Blazej Grabowski^a, Matthias Militzer^b, Jörg Neugebauer^a, Jörg Rottler^c^a Max-Planck-Institut für Eisenforschung GmbH, D-40237, Düsseldorf, Germany^b Centre for Metallurgical Process Engineering, The University of British Columbia, 309-6350 Stews Road, Vancouver, BC, V6T 1Z4, Canada^c Department of Physics and Astronomy, The University of British Columbia, 6224 Agricultural Rd., Vancouver, BC, V6T 1Z1, Canada

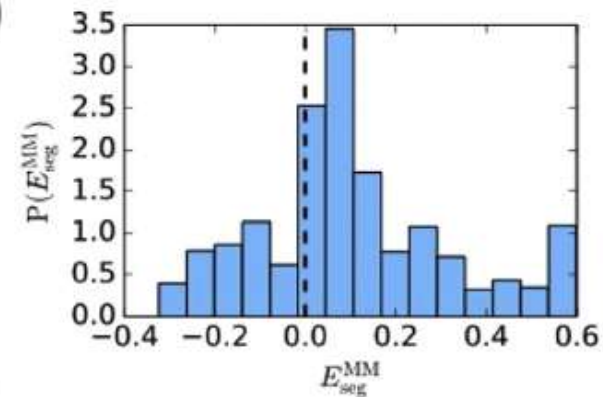
L. Huber et al. / Acta Materialia 132 (2017) 138–148



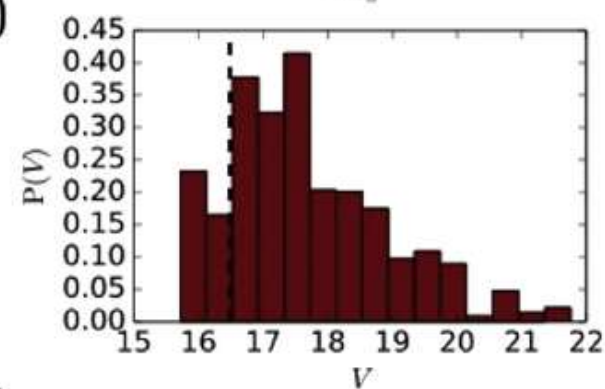
a)



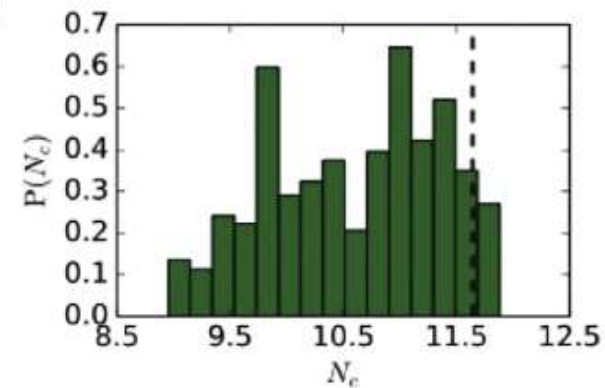
b)



c)



d)



Apoio financeiro

