Danos por Hidrogênio em Aços Duplex e Superduplex

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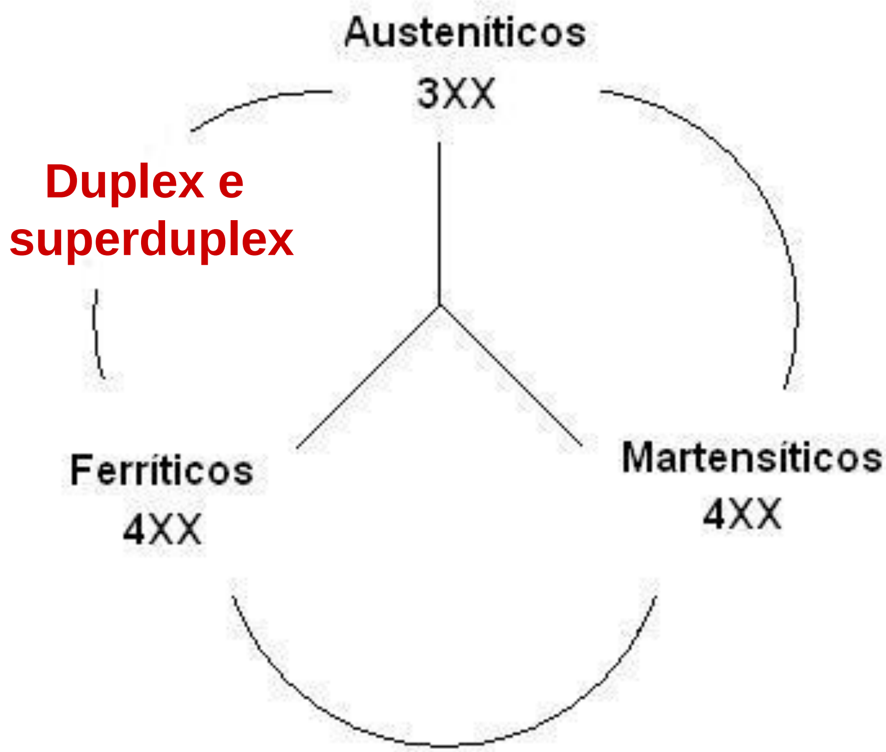
Tipos de aços inoxidáveis

Lean duplex
Duplex
Superduplex
hyperduplex



Outros tipos de aços inox:

- Supermartensíticos
- Superausteníticos
- Superferríticos
- Endurecíveis por precipitação (martensíticos, semi-austeníticos, austeníticos)

PRE ↑

Dureza, L.E, L.R. ↑

CUSTO ↑

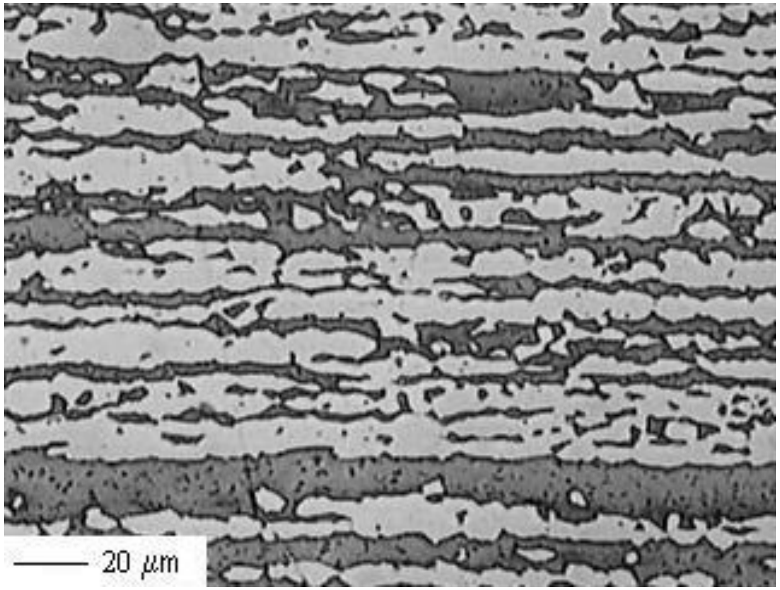
Estabilidade da γ ↑

- **Lean duplex**
- **Duplex**
- **Superduplex**
- **hyperduplex**

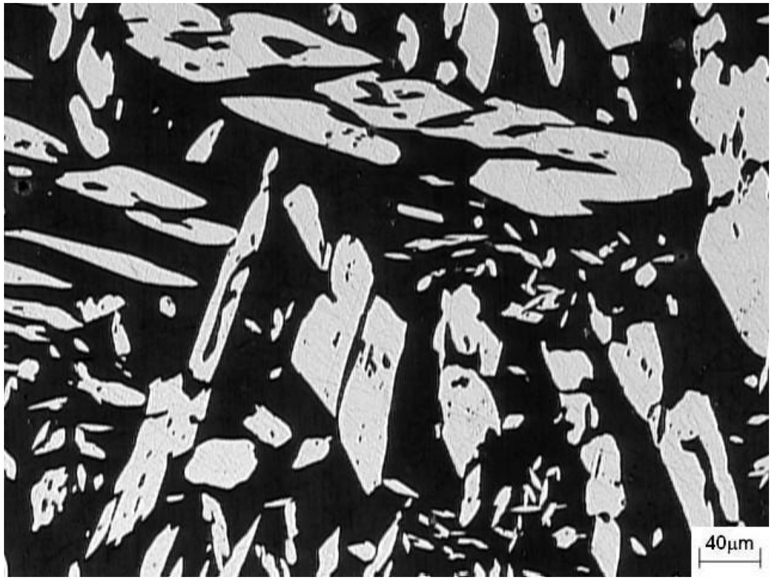
$$PRE = \%Cr + 3{,}3(\%Mo + 0{,}5(\%W)) + 16(\%N)$$

Aços inoxidáveis duplex e superduplex

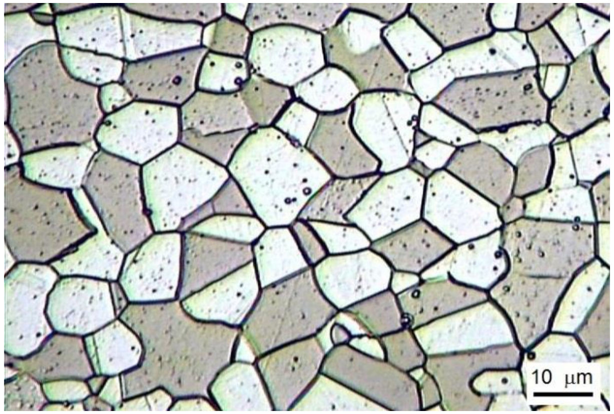
Aços inoxidáveis de microestrutura austeno-ferrítica



Estrutura trabalhada - laminada



Material fundido e solubilizado



Aço produzido por metalurgia do pó - HIP

Fragilização por hidrogênio

Fontes de hidrogênio:

- Processos de fabricação (ex.: soldagem, recobrimento,...)

- Em serviço:

- Proteção catódica (carregamento catódico) – Apesar de ser bastante resistente à corrosão, alguns equipamentos com partes feitas em aços duplex/superduplex são protegidos catodicamente, e experimentam carregamento de hidrogênio que pode ser crítico se o potencial de proteção for exagerado.

- Processos corrosivos (o hidrogênio pode ser gerado por processos corrosivos – reação catódica).

- H_2S (“corrosão sob tensão por sulfetos” – SSC)

A.A. El Yazgi, D. Hardie, Stress corrosion cracking of duplex and superduplex stainless steels in sour enviroments, Corrosion Science 40(6) (1998) 909-930.

When, as in a sour environment, H_2S comes into contact with water, it dissociates to form a weak acid according to the reactions:

$$H_2S \rightarrow HS^- + H^+ \tag{1}$$

$$H_2S \rightarrow 2H^+ + S^{2-} \tag{2}$$

and hence, a corrosion reaction takes place between these ions and steel resulting in the formation of ferrous ion at the anoxic sites and the reduction of hydrogen ion at the cathodic sites on the steel surface:

$$Fe \rightarrow Fe^{++} + 2e^- \text{ (at the anoxic site)} \tag{3}$$

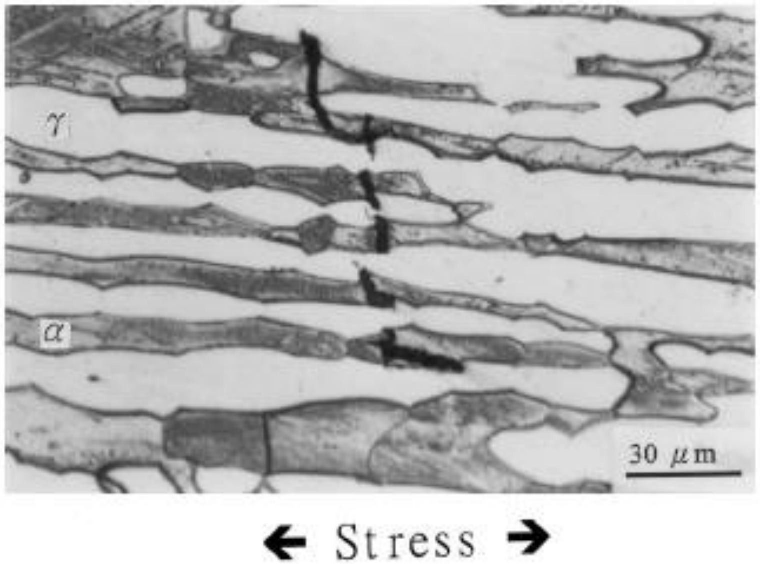
$$2H^+ + 2e^- \rightarrow 2H \text{ and } 2H \rightarrow H_2 \text{ (at the cathodic site)} \tag{4}$$

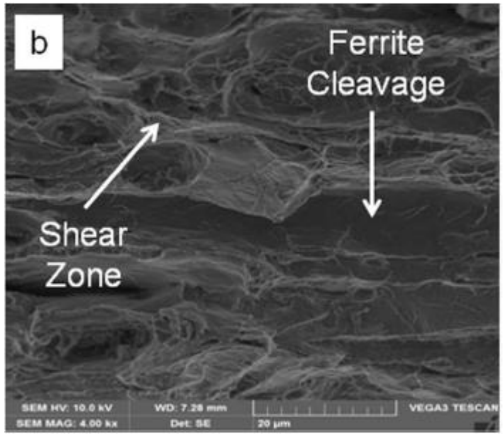
Thus the overall reaction can be represented as:

$$Fe + H_2S(aq) \rightarrow FeS + 2H \tag{5}$$

The recombination of atomic to produce molecular hydrogen is inhibited by the presence of the dissociated hydrogen sulphide, and this results in a greater hydrogen fugacity, which facilitates penetration of hydrogen into the steel, hence intensifying any embrittlement effects.

Aços duplex e superduplex podem sofrer fragilização por hidrogênio. Neste caso, a fase ferrita é a mais susceptível e a austenita pode conferir um efeito de barreira à propagação de trincas.

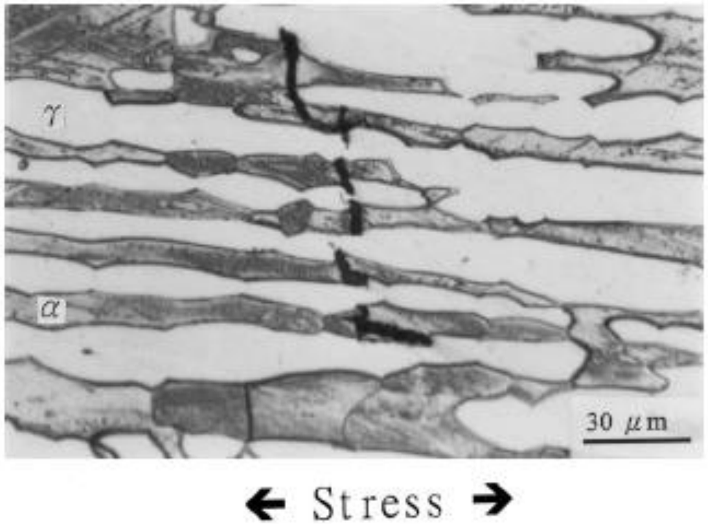


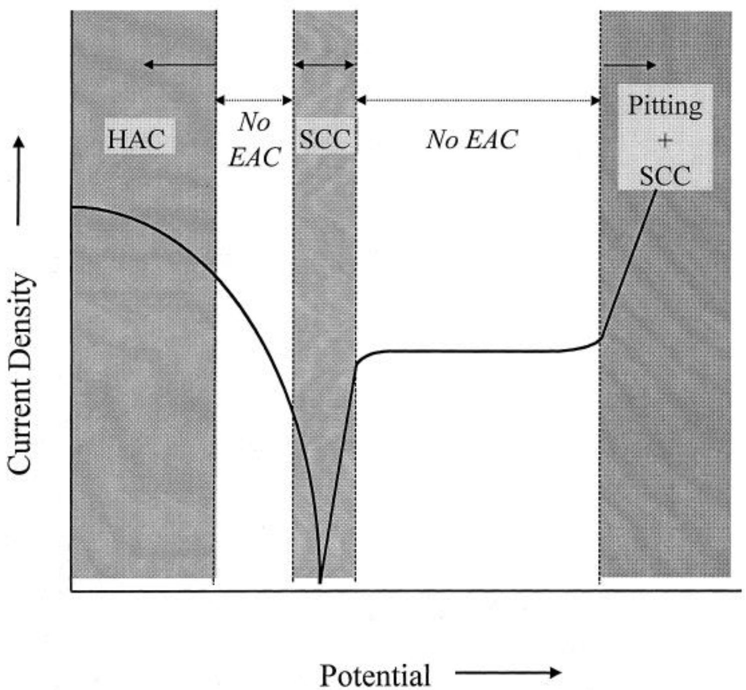


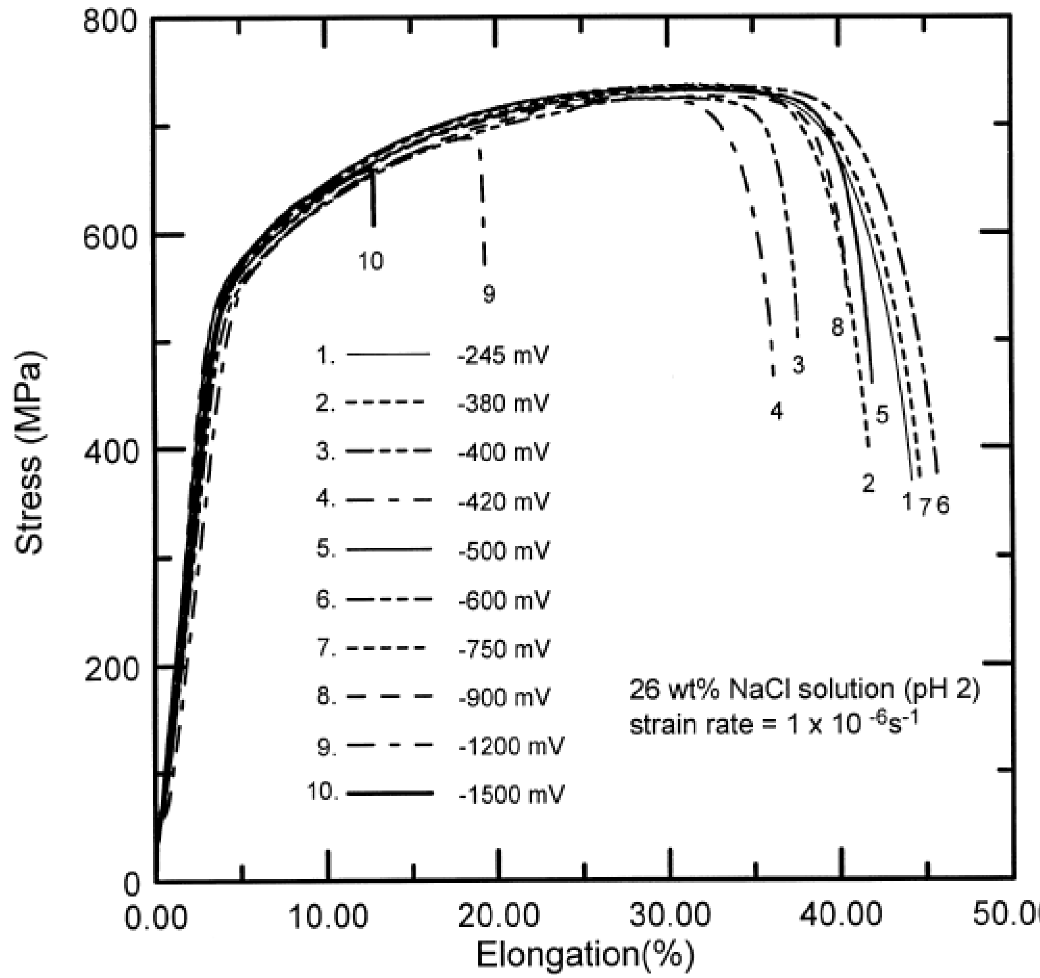
Cristian Pohl Meinhardt et al., Mat Sci. Eng. A 706 (2017) 48-56.

Trincas sob tensão induzidas por hidrogênio (HISC) geralmente se propagam diretamente por clivagem na ferrita. A trinca pode ser parada pela austenita ou propagar por ela, dependendo do tamanho da trinca e nível de tensão.

W.T. Tsai, S. L. Chou, Environmentally assisted cracking behavior of duplex stainless steel in concentrated sodium chloride solution, Corrosion Science 42 (2000) pp.1742-1762.

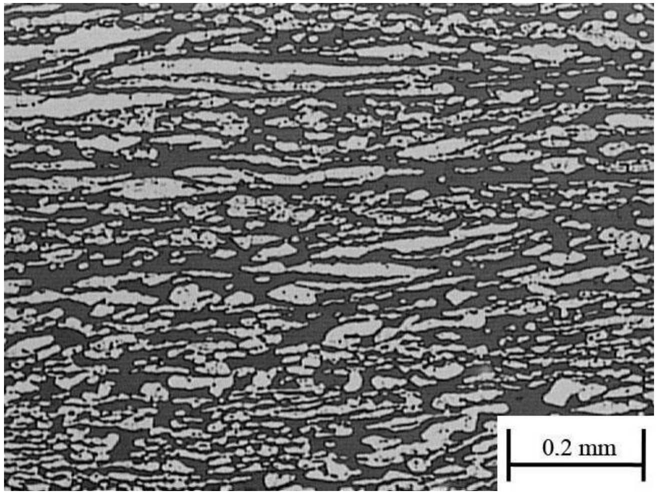




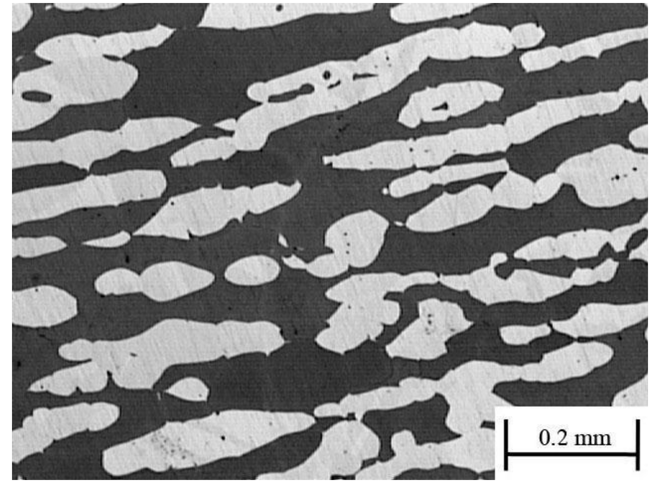


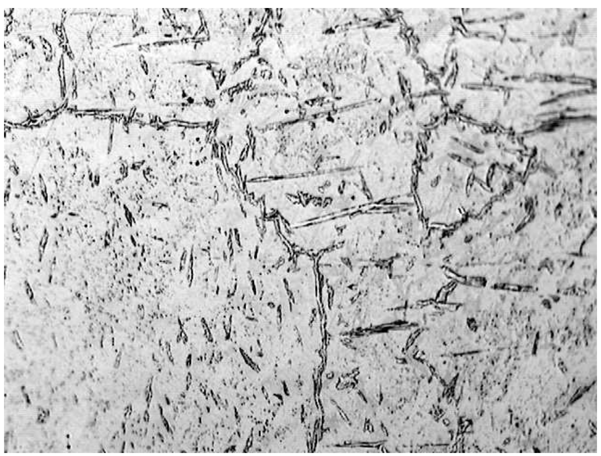
Solução salina (26%NaCl)

Influência da Microestrutura



X





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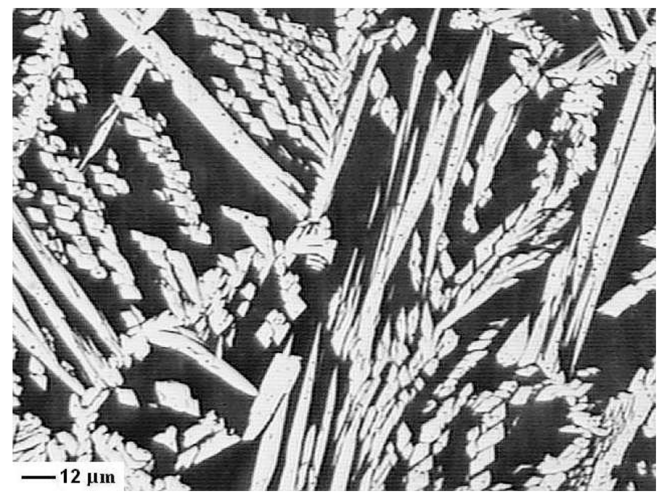


Fases σ, χ, α’

Estabilidade da austenita (ε, α’)

DNV – Recomeended Practice – F112

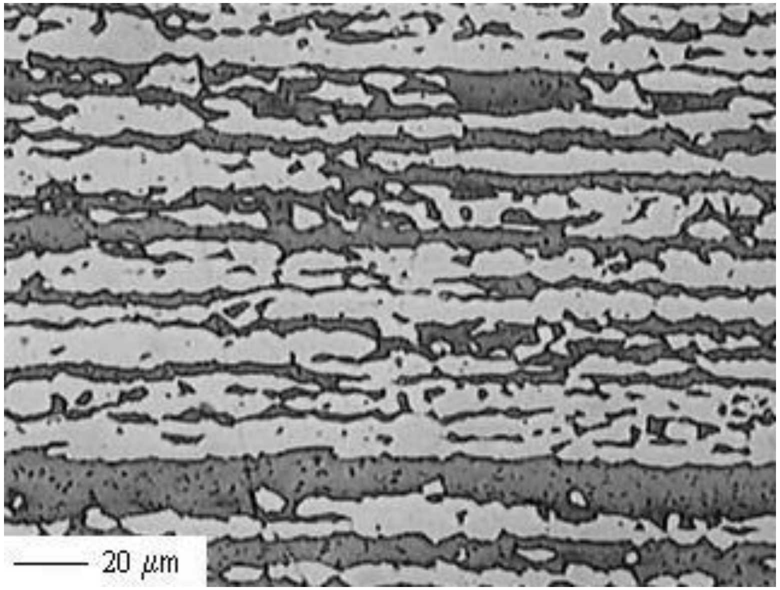
Design of duplex stainless steel subsea equipment exposed to cathodic protection

- Preocupação com a trinca induzida por hidrogênio (Hydrogen Induced Stress Cracking - HISC)

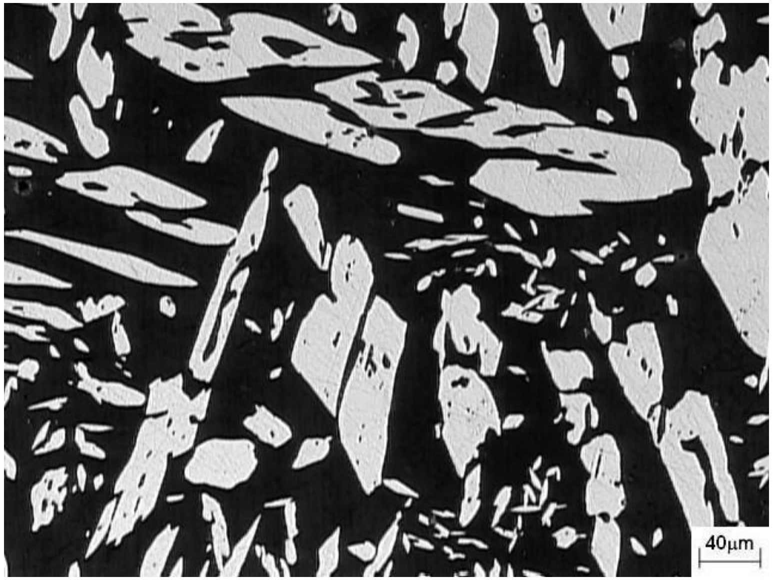
- Há indicações de que materiais de grãos grosseiros são mais susceptíveis à HISC do que materiais de grãos finos.

- Para algumas aplicações onde há risco de HISC pode ser interessante a especificação de um valor mínimo de espaçamento entre as ilhas de austenita. Um valor sugerido seria 30μm.

- Dificuldade: medir o espaçamento entre as ilhas de austenita em juntas soldadas ou estruturas fundidas



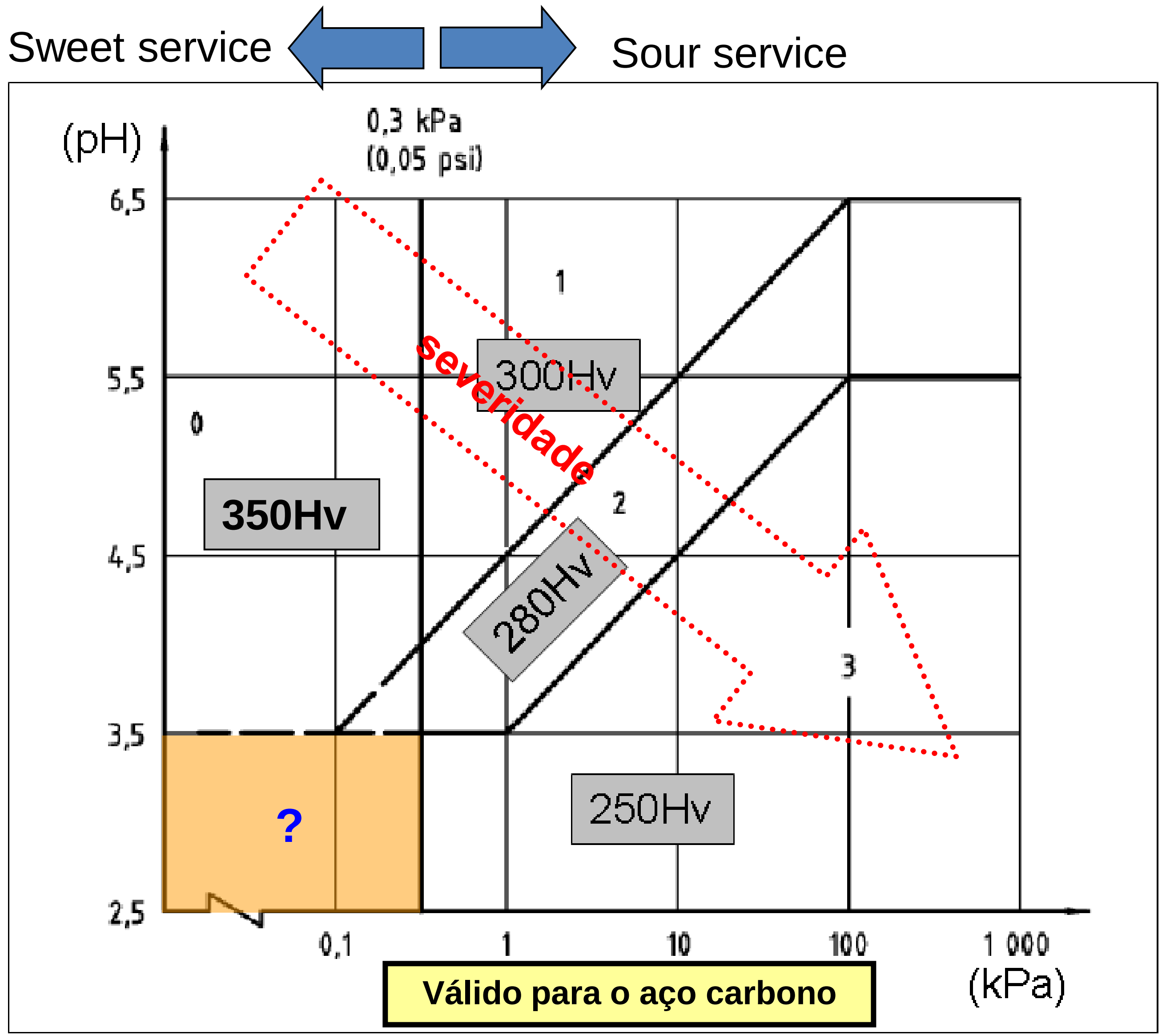
Fácil



Não tão fácil

Corrosão por tensão por sulfetos

NACE MR-0175/ISO15156-2 - Petroleum and Natural Gas Industries - Materials for Use in H_2S-containing Environments in Oil and Gas Production



- Acredita-se que uma das formas de se evitar a corrosão sob tensão por sulfetos em diversos materiais seja pelo controle da dureza.
- Para algumas aplicações o duplex ou superduplex é encruado para atingir a resistência mecânica necessária. (Exemplo: tubos de produção 125 ksi)
- Para aplicações em ambiente “sour” o limite de durezas do duplex/superduplex deformado a frio é 36 HRC.

Norma ISO 15156-3

Table A.25 — Environmental and materials limits for duplex stainless steels used as downhole tubular components and as packers and other subsurface equipment

Materials type	Temperature max. °C (°F)	Partial pressure H_2S p_{H_2S} max. kPa (psi)	Chloride conc. max. mg/l	pH	Sulfur-resistant?	Remarks
$30 \leqslant F_{PREN} \leqslant 40$, Mo $\geqslant 1,5$ %	See "Remarks" column	2 (0,3)	See "Remarks" column	See "Remarks" column	NDS[a]	Any combination of temperature, chloride concentration and *in situ* pH occurring in production environments is acceptable.
$40 < F_{PREN} \leqslant 45$	See "Remarks" column	20 (3)	120 000	See "Remarks" column	NDS[a]	Any combination of temperature and *in situ* pH occurring in production environments is acceptable. Chloride limits have been found to be strongly dependent upon yield strength and the level of cold work.

For these applications, these materials shall

— be in the solution-annealed, liquid-quenched, and cold-worked condition;

— have a ferrite content (volume fraction) of between 35 % and 65 %; and

— have a maximum hardness of 36 HRC.

Será que 36 HRC é o suficiente ?

NOTE Higher values of F_{PREN} provide higher corrosion resistance, however they also lead to increased risk of sigma- and alpha- prime phase formation, in the materials' ferrite phase, during manufacture, depending on product thickness and achievable quench rate. The ranges of F_{PREN} quoted are typical of those found to minimize the problem of sigma- and alpha- prime phase formation.

[a] No data submitted to ascertain whether these materials are acceptable for service in the presence of elemental sulfur in the environment.

Norma ISO 13628-15

Table 10 — Hardness limitations to avoid hydrogen embrittlement under cathodic protection

Material	Maximum hardness
Carbon and low-alloy steels for general applications (excluding bolting; see Table 6)	350 HV/35 HRC/330 HB
Martensitic and supermartensitic stainless steels	325 HV/33 HRC/329 HB[a]
Ferritic-austenitic stainless steels	Hardness has not been shown to be a determining factor in the sensitivity to hydrogen-induced stress cracking under cathodic protection, hence no hardness limit is specified. However, compliance with ISO 15156-3 is recommended.
Austenitic stainless steels	For these materials, hydrogen embrittlement is not considered an issue under cathodic protection, hence no hardness limit is specified.
Nickel alloys	See ISO 15156-3.

[a] Based on 325 HV, hardness conversion to HRC based on ASTM E140, conversion HRC to HBW based on tests by Foroni Metals relationship HRC = 43,796 × ln(HBW) – 220,86.

[b] Heat treatment and weld procedures should be designed to avoid microstructural defects such as sigma-phase in duplex stainless steels and delta phase in age-hardened nickel alloys.

- O ganho de resistência por envelhecimento a 475ºC é também considerado prejudicial para aplicações sob proteção catódica.

R.N. Gunn

13.5 Cathodically protected bolts

During the mid-1990s, a few failures of cathodically protected 25%Cr duplex bolts (S32550) were reported on one of BP's North Sea platforms.[3] The microstructure comprised about 70% ferrite, with the strength of the bolts achieved by ageing at about 500°C, rather than by cold work. As described in Section 3.4.1, this heat treatment leads to the precipitation of alpha prime, which produces a dramatic drop in resistance to embrittlement in the slow strain rate test, especially with 70% ferrite.[7] It is for this reason that the high strength bolting grade should be achieved by cold work and not by ageing, while maintaining a 50/50 phase balance.

3 Francis R: Conf proc *Duplex Stainless Steels '94*, Glasgow, TWI, 1994, Vol. 3, paper KIV.

Norma ISO 15156-3

Table A.24 — Environmental and materials limits for duplex stainless steels used for any equipment or component

Materials type/ individual alloy UNS number	Temperature max. °C (°F)	Partial pressure H_2S p_{H_2S} max. kPa (psi)	Chloride conc. max. mg/l	pH	Sulfur-resistant?	Remarks
$30 \leqslant F_{PREN} \leqslant 40$, Mo $\geqslant$ 1,5 %	232 (450)	10 (1,5)	See "Remarks" column	See "Remarks" column	NDS[a]	Any combination of chloride concentration and *in situ* pH occurring in production environments is acceptable
S31803 (HIP)	232 (450)	10 (1,5)	See "Remarks" column	See "Remarks" column	No	
$40 < F_{PREN} \leqslant 45$	232 (450)	20 (3)	See "Remarks" column	See "Remarks" column	NDS[a]	
$30 \leqslant F_{PREN} \leqslant 40$ Mo $\geqslant$ 1,5 %	See "Remarks" column	See "Remarks" column	50	See "Remarks" column	NDS[a]	These materials have been used without restrictions on temperature, p_{H_2S} or *in situ* pH in production environments. No limits on individual parameters are set but some combinations of the values of these parameters might not be acceptable.
$40 < F_{PREN} \leqslant 45$	See "Remarks" column	See "Remarks" column		See "Remarks" column	NDS[a]	

Wrought and cast duplex stainless steels shall

— be solution-annealed and liquid-quenched,

— have a ferrite content (volume fraction) of between 35 % and 65 %, and

— not have undergone ageing heat-treatments.

Hot isostatic pressure-produced (HIP) [15] duplex stainless steel UNS S31803 ($30 \leqslant F_{PREN} \leqslant 40$, Mo $\geqslant$ 1,5 %) shall have a maximum hardness of 25 HRC and shall

— be in the solution-annealed and water-quenched condition,

— have a ferrite content (volume fraction) of between 35 % and 65 %, and

— not have undergone ageing heat-treatments.

NOTE Higher values of F_{PREN} provide higher corrosion resistance, however they also lead to increased risk of sigma- and alpha-prime phase formation, in the materials' ferrite phase, during manufacture, depending on product thickness and achievable quench rate. The ranges of F_{PREN} quoted are typical of those found to minimize the problem of sigma- and alpha- prime phase formation.

[a] No data submitted to ascertain whether these materials are acceptable for service in the presence of elemental sulfur in the environment.

Pesquisa na base SCOPUS:

"Duplex Stainless Steel" AND "Failure":

- 235 artigos em periódicos
- 104 artigos de conferência
- 7 Reviews
- 4 Capítulos de Livro
- Outros - 11

"Duplex Stainless Steel" AND "hydrogen embrittlement":

- 120 artigos em periódicos
- 60 artigos de conferência
- 4 Reviews

Journal of Alloys and Compounds 720 (2017) 451–459

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

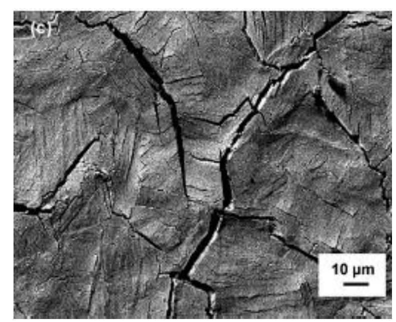
Mechanisms of hydrogen trapping in austenitic, duplex, and super martensitic stainless steels

R. Silverstein*, D. Eliezer

Department of Material Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel

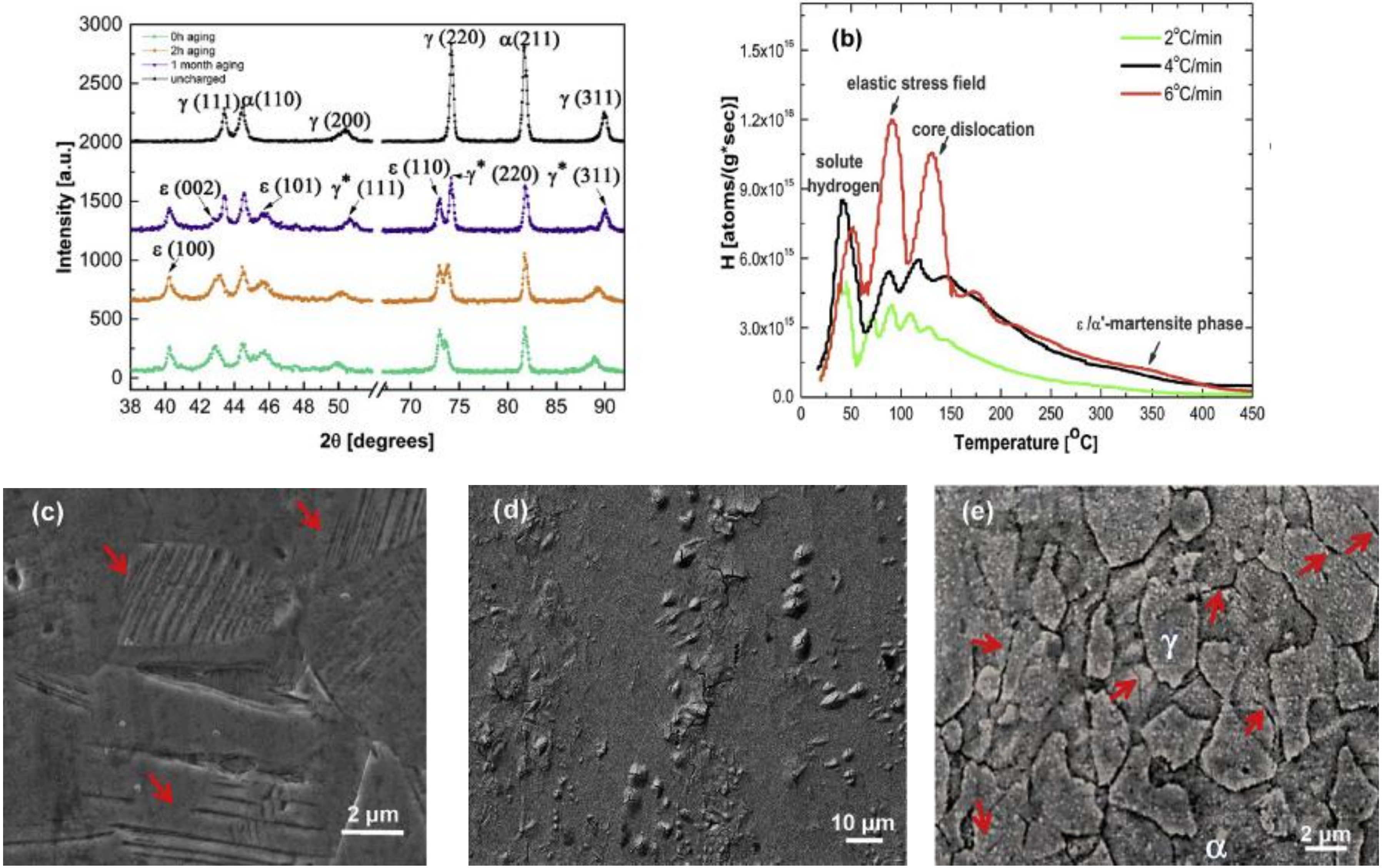
Segundo este autor, o hidrogênio carregado catodicamente nas amostras provoca a transformação de fase da austenita conforme:

$$\gamma \rightarrow \varepsilon\ (\mathrm{hc})\ \text{- - - - - - -}\rightarrow \alpha'\ (\mathrm{ccc})$$



Isso foi observado nos aços duplex, austeníticos e supermartensíticos.

TDS



0h aging
2h aging
1 month aging
uncharged
γ (111) α(110)
γ (200)
γ (220) α(211)
γ (311)
ε (002)
ε (101)
γ* (111)
ε (110)
γ* (220)
γ* (311)
ε (100)
Intensity [a.u.]
2θ [degrees]
(b)
2°C/min
4°C/min
6°C/min
elastic stress field
core dislocation
solute hydrogen
ε /α'-martensite phase
H [atoms/(g*sec)]
Temperature [°C]
(c)
2 μm
(d)
10 μm
(e)
γ
α
2 μm

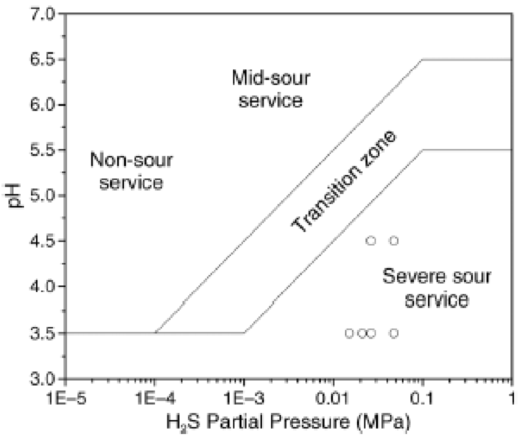
Evaluation of the Susceptibility of a Superduplex Stainless Steel Welded Joint to Sulfide Stress Corrosion by Slow Strain Rate Tensile Tests in Sour Solutions

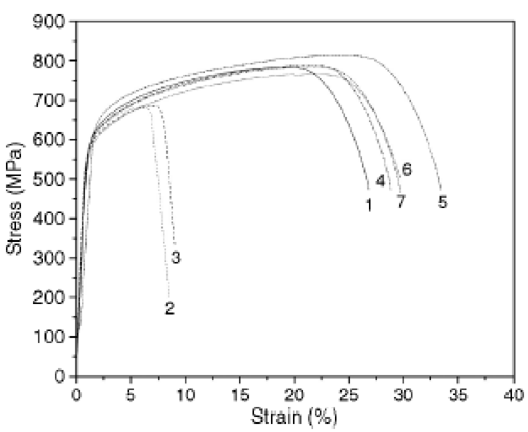
CORROSION—Vol. 68, No. 1

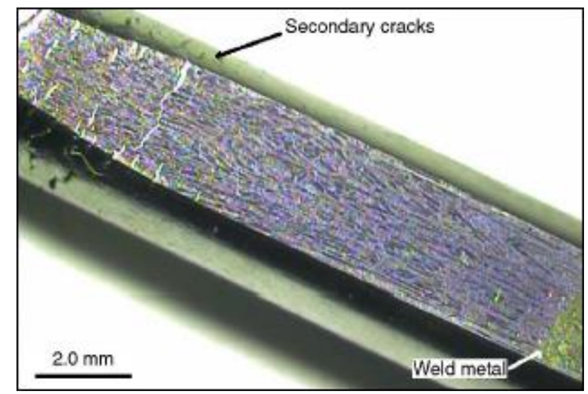
CORROSION—JANUARY 2012

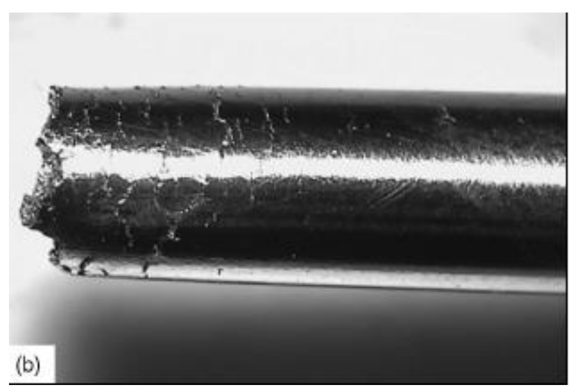
V.G. Silva,* S.S.M. Tavares,‡,* I.P. Baptista,** and J.R. de Oliveira**

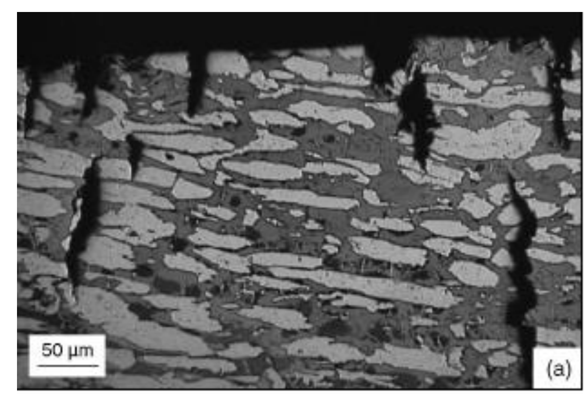
Condição	pH_2S(psia)	P (psia) total mistura	pH	Temperatura (°C)	
1 (inerte)	-	-	-	80	120000
2	6,75	135	3,5		
3	3,75	75	3,5		
4	3	60	3,5		
5	2,15	45	3,5		
6	3,75	75	4,5		
7	6,75	135	4,5		



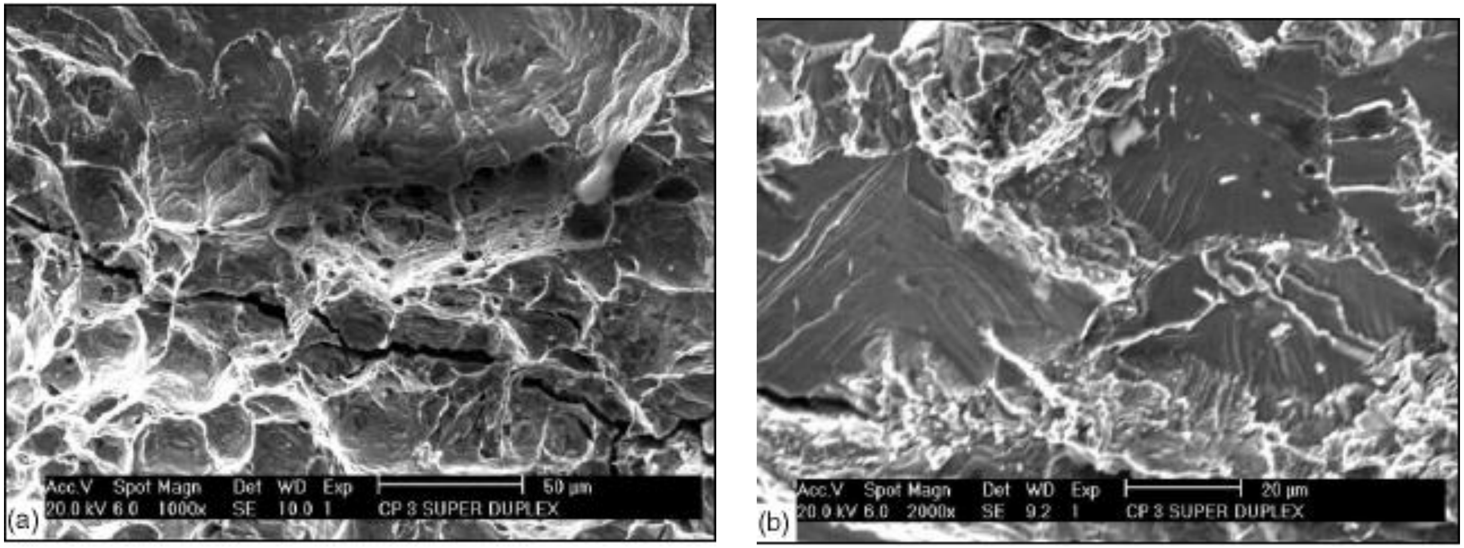




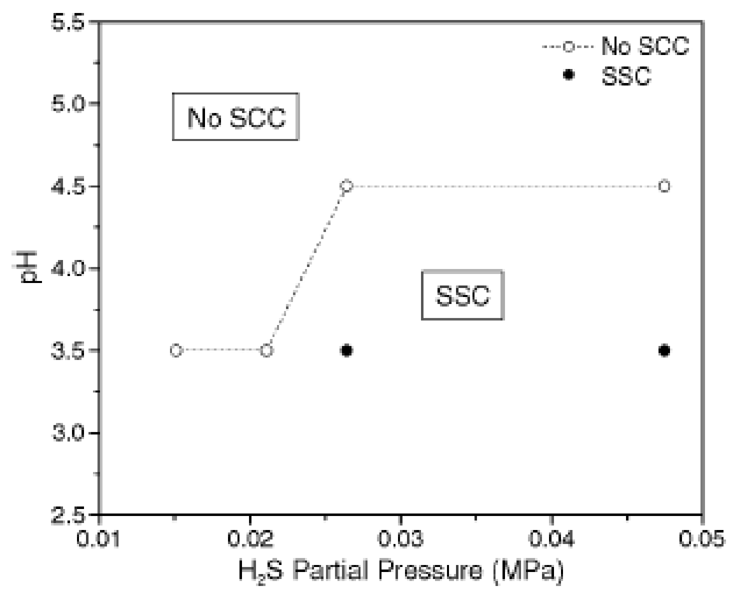




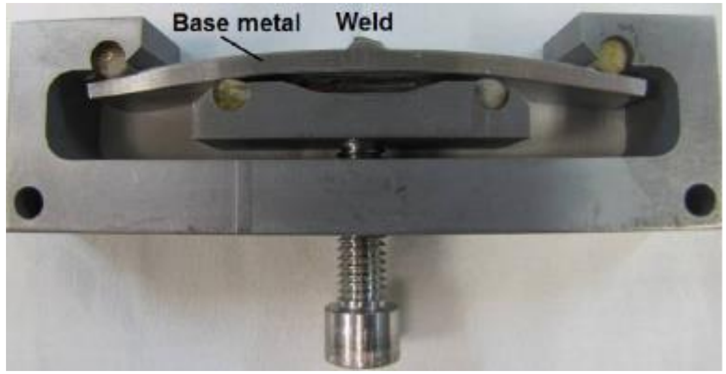
Superfície de fratura – condição 2



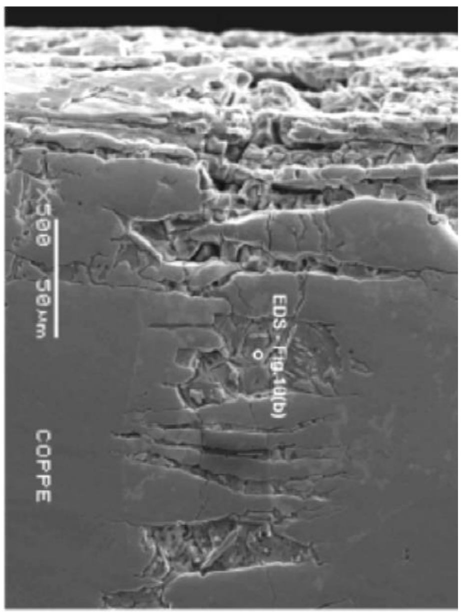
Mapa de utilização

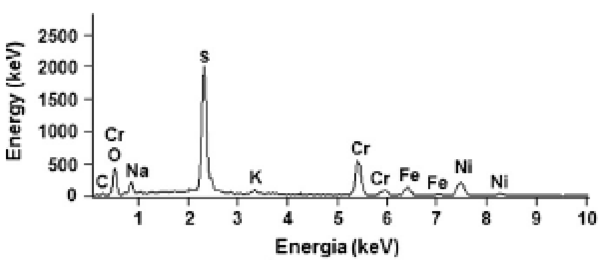


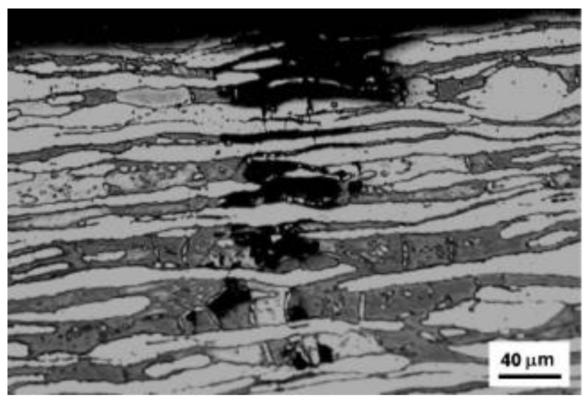
Ensaio de 4 pontos

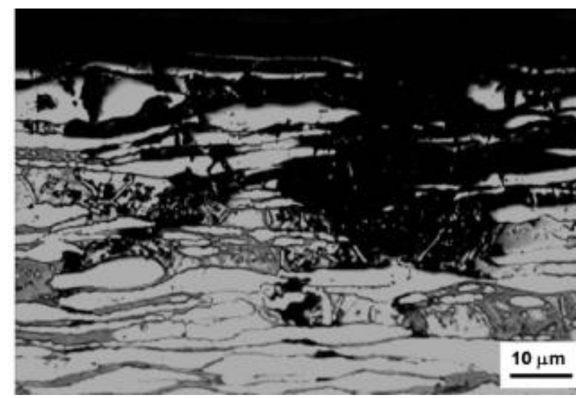


30 psia H_2S









Dissolução preferencial da ferrita

Obrigado !

ssmtavares@id.uff.br