Hydrogen Induced Stress Cracking (HISC) in duplex stainless steel caused by cathodic protection

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FTUI Metalurgi dan material

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Metalurgi 80

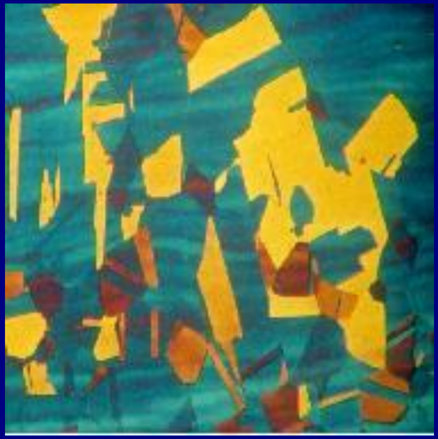
Deepwater field

Total Angola - Dalia Field lay-out + SPS / SURF

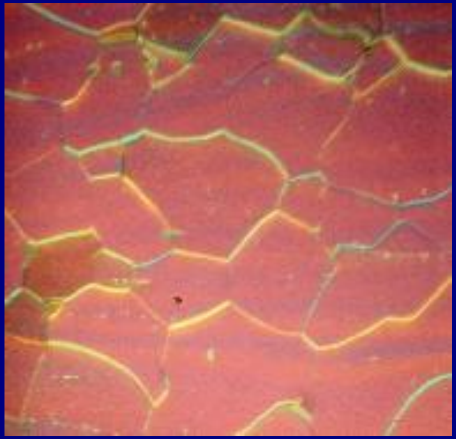
What is Duplex Stainless

- An equal percentage of ferrite and austenite is essential for the microstructure to the welded joint in SAF2507
- It is essential for UNS S32750 weld chemistry and HAZ to have a correct balance of ferrite and austenite optimum similar to the parent metal.
  - Austenite produces a toughness in the alloy
  - Ferrite helps provide rigidity and strength
  - UNS S32750 is alloyed so that both phases have the same corrosion resistance
  - By combining the best properties of both phases the alloy UNS S32750 develops excellent stress corrosion resistance essential for this service

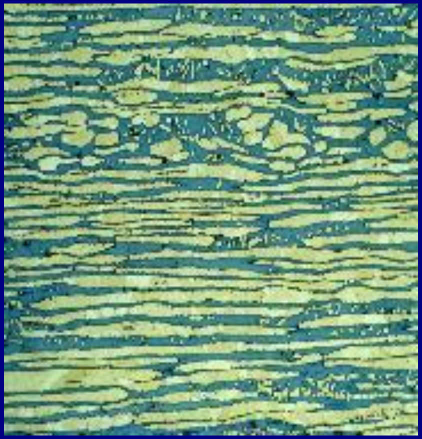
Austenite



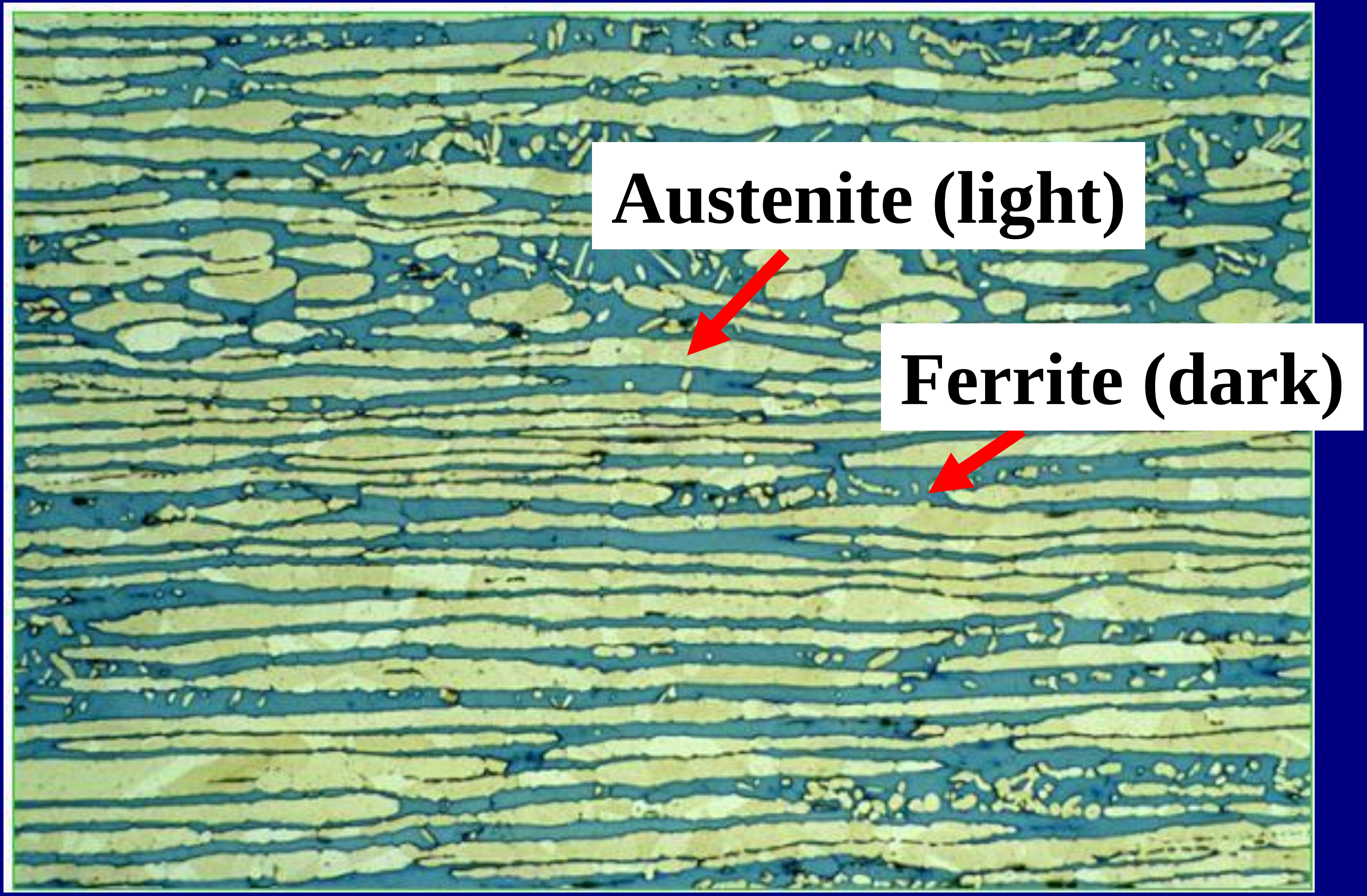
Ferrite



Duplex



Duplex Microstructure



Duplex Stainless Family

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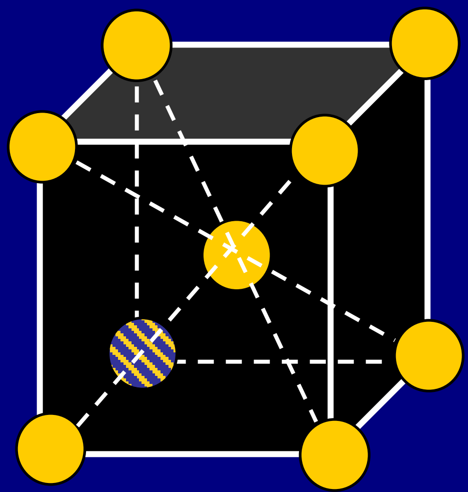
Alloy	C max	Si max	Mn max	P max	S max	Cr	Ni	Mo	Others
UNS S32101	0.030	1.0	5.0	0.04	0.03	21.5	1.5	0.3	PREN > 22
UNS S32304	0.030	1.0	2.0	0.035	0.015	22.5	4.5	0.3	Cu=0.3 N=0.1 PREN > 24
UNS S32205	0.030	1.0	2.0	0.030	0.015	22	5	3.2	N = 0.18 PREN > 35
UNS S32750	0.030	0.8	1.2	0.035	0.015	25	7	4	N = 0.3 PREN > 42
UNS S33207	0.030	0.8	1.5	0.035	0.010	32	7	3.5	N = 0.5 PREN > 50
UNS S32707	0.030	0.5	1.5	0.035	0.010	27	6.5	4.8	N=0.4 Co=1.0 PREN > 48

$$PREN = \%\,Cr + 3.3 \times (\%\,Mo + 0.5 \times \%\,W) + 16 \times \%\,N$$

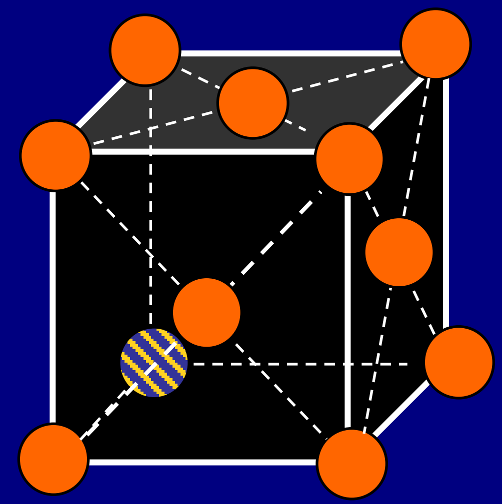
Crystal Structures

Ferrite



Body Centered Cubic

Austenite



Face Centered Cubic

Add Nickel

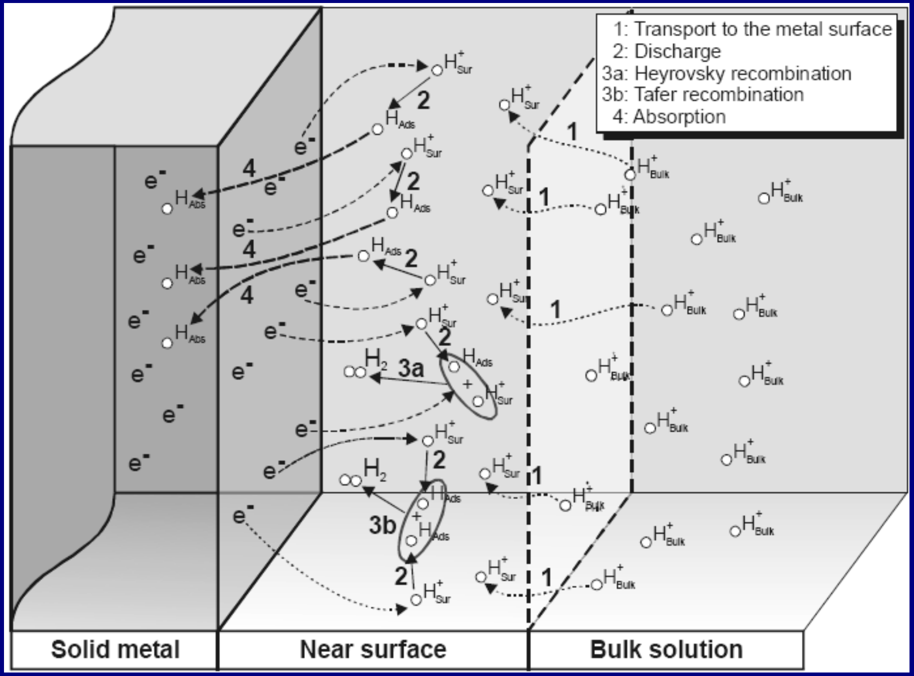
Hydrogen formation and evolution

Cathodic reactions:

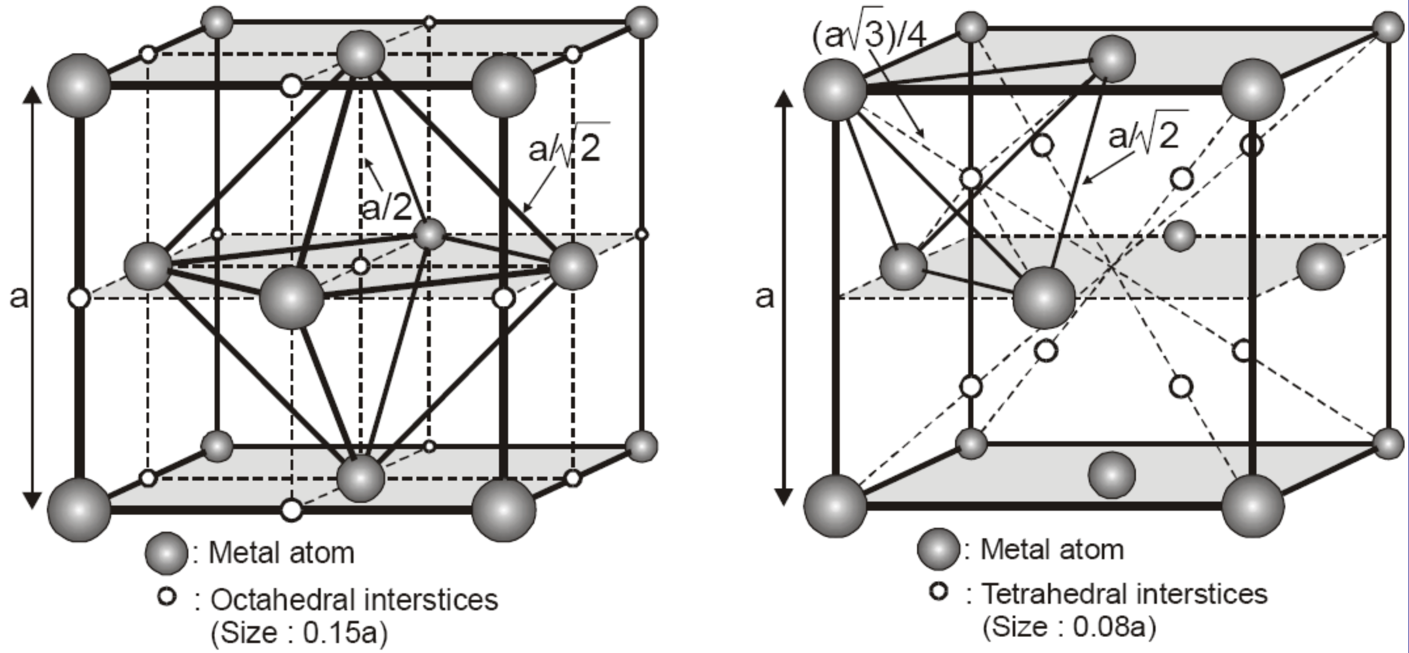
$H2O \rightarrow H^{+} + OH^{-}$
$H^{+} + e \rightarrow H_{(ads)}$

Hydrogen evolution

$M + H_{(ads)} \rightarrow MH_{(ads)}$
$MH_{(ads)} + MH_{(ads)} \rightarrow 2M + H_2$

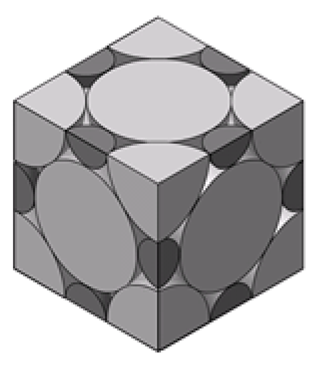


Hydrogen interstitial in austenite

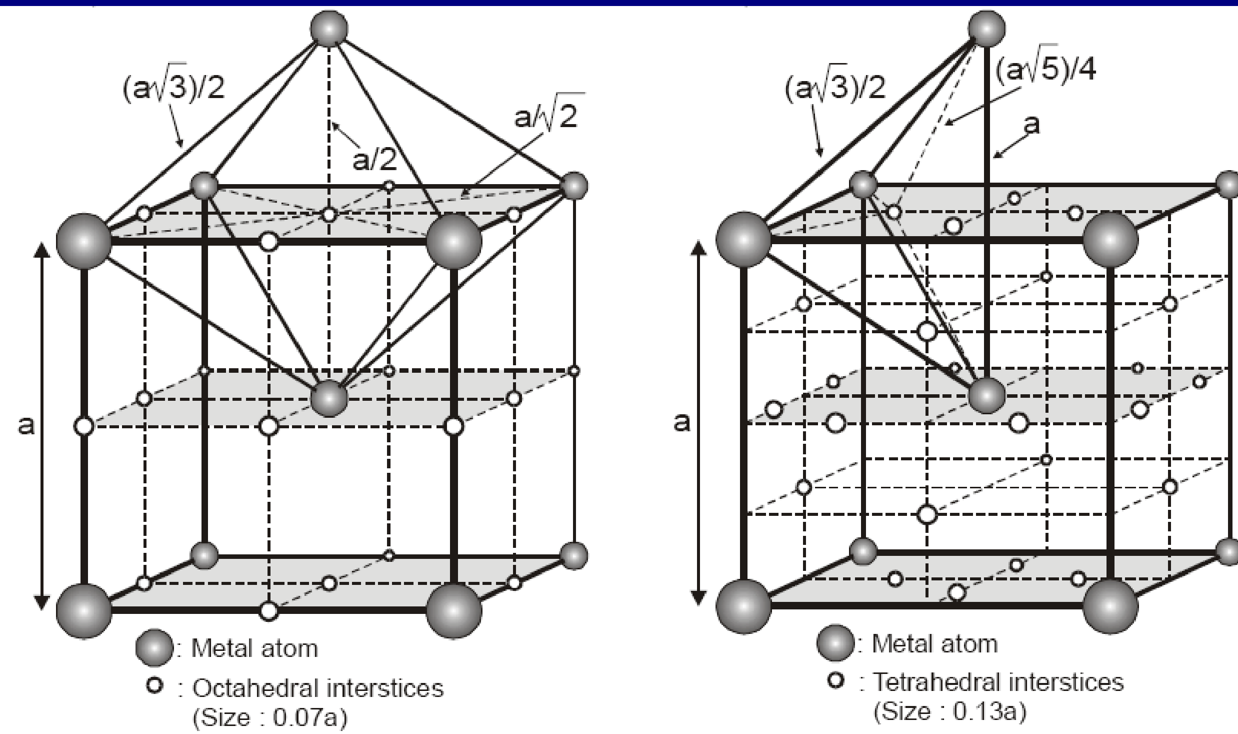


a) γ-Iron system (Octahedral interstices)   b) γ-Iron system (Tetrahedral interstices)

$$\textit{Packing Density} = \frac{4 \times \left(\frac{4}{3}\pi r^3\right)}{\left(\sqrt{2} \times r\right)^3} = \frac{\pi}{3\sqrt{2}} \approx 74\%$$



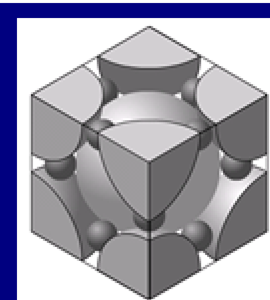
Hydrogen interstitial in ferrite



c) α-Iron system (Octahedral interstices)

d) α-Iron system (Tetrahedral interstices)

$$Packing\ Density = \frac{2 \times \left(\frac{4}{3}\pi r^3\right)}{\left(\frac{4}{\sqrt{3}} r\right)^3} = \frac{\sqrt{3} \times \pi}{8} \approx 68\%$$



Size references

Sizes:

Fe atomic diameter: 2.80 Å
Mo atomic diameter: 2.90 Å
Ni atomic diameter: 2.70 Å
H atomic diameter: 0.50 Å

BCC unit size: 2.87 Å
FCC unit size: 11.85 Å

Ferrite tetrahedral interstice: 0.37 Å
Austenite octahedral interstice: 1.177 Å

Austenite spacing in bars microstructure

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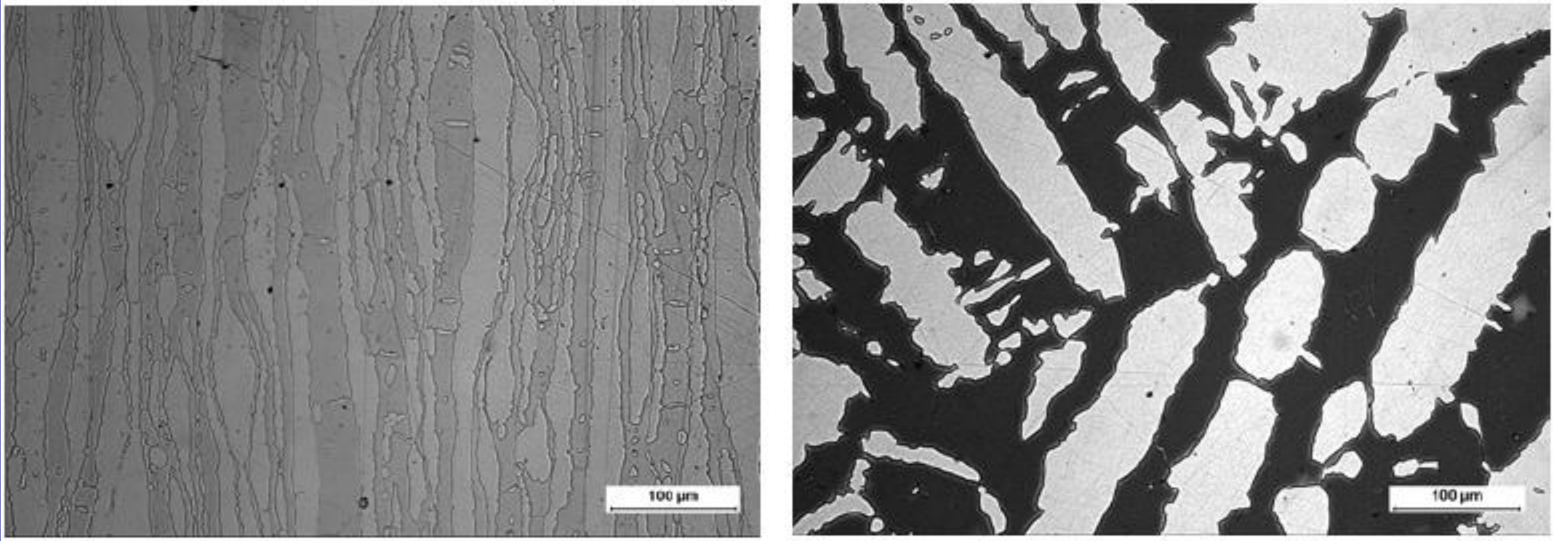

FIGURE 3 – Left, the microstructure of extruded tube (sample 1, 90 % $R_{p0.2\%}$) and right, the microstructure of the large diameter bar (sample 2, 84 % of $R_{p0.2\%}$). The samples are etched in Murakami, which makes the austenite appear white and the ferrite tanned.

Tests at super duplex bars

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Test conditions:

- Bar and extruded material of SAF2507 – UNS S32750
- Small test bars and extruded tube with austenite spacing 15–16 µm
- Large test bars with austenite spacing between 32-51 µm
- Pre-charged at 20 mA/cm2 in 10% H2SO4 with 30 mg/l As2O3 as cathodic poison for 24 hours.
- Testing time 500 hours or until failure with constant load relative to yield strength.
- Polarized to -1050 mV SCE at 4^{o}C in artificial sea water 3.5% NaCl
- Testing specimen: standard tensile specimen with total length of 100 mm, gauge length: 25.4 mm diameter 3 mm.
- Constant load testing, exposure time 500 hrs, or until failure

Cracks at super duplex bars

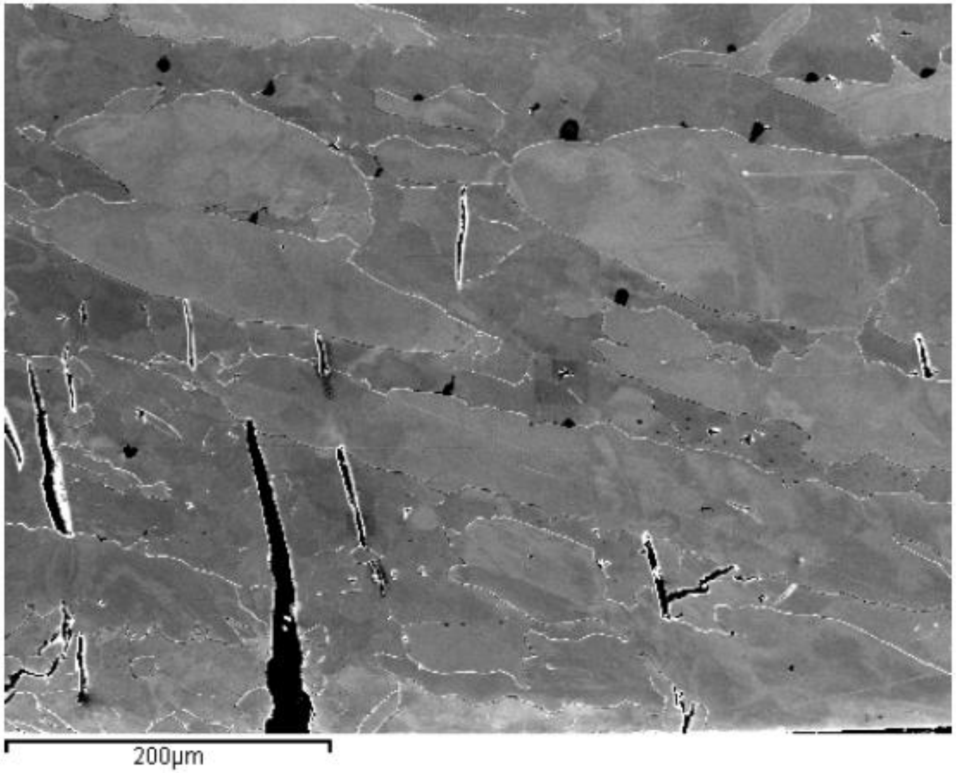


FIGURE 2 – The microstructure of the large dimension bar specimen that failed at 93% of $R_{p0.2\%}$(4°C). The surface of the specimen is at the base of the picture.

Austenite spacing in HIP'ed and forged materials microstructure

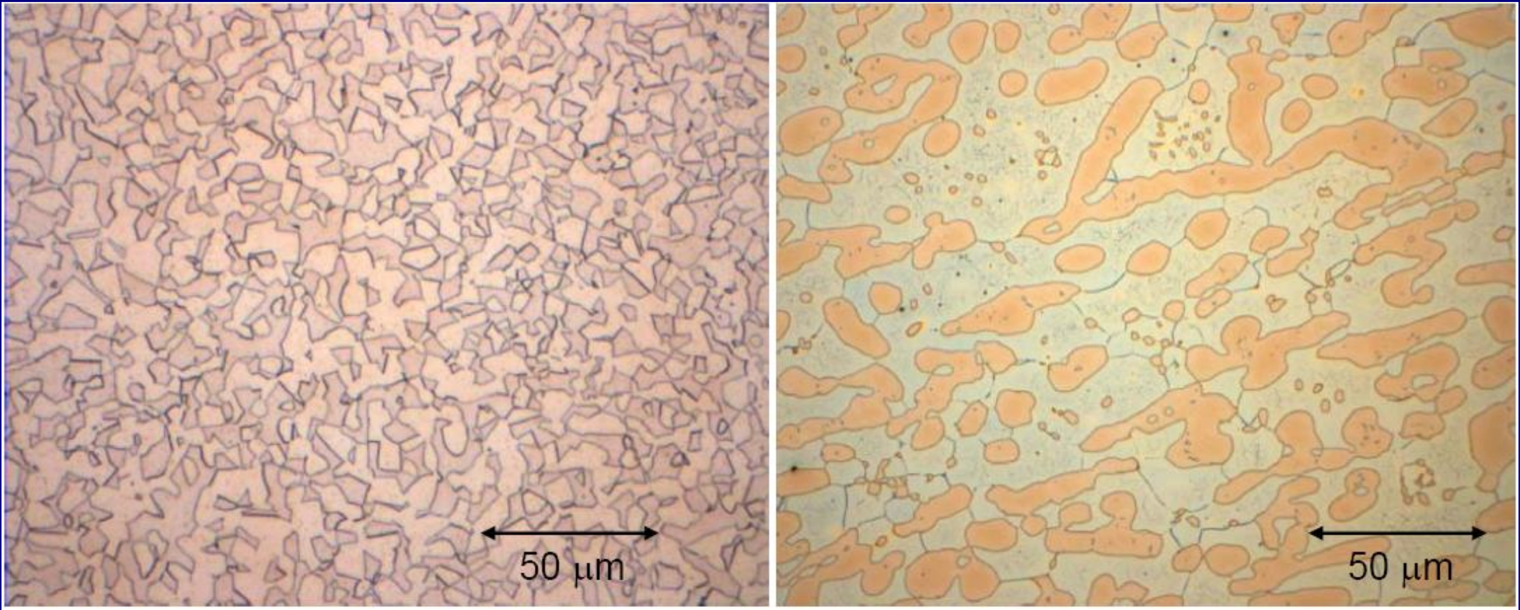


FIGURE 1 - Microstructure of materials: (a) HIP SDSS 32760 and (b) forged SDSS 32760 (M X200).

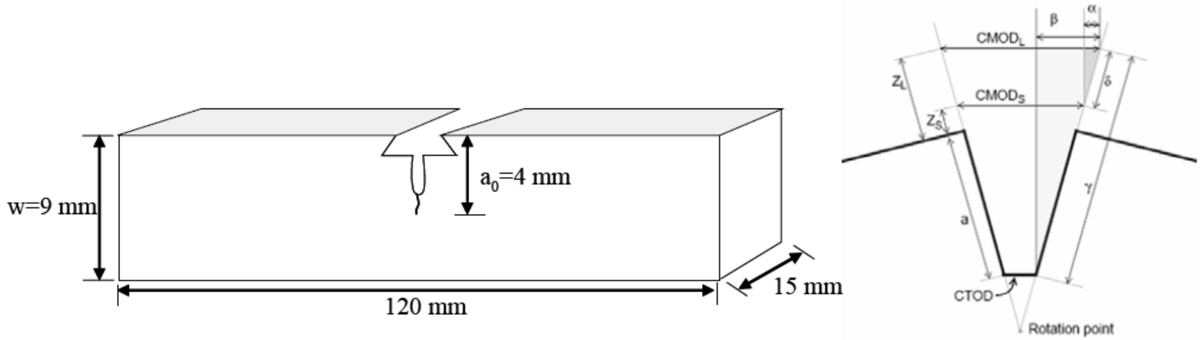
Grain size: 12.7 µm

Grain size: 47.9 – 50.9 µm

Tests at superduplex HIP'ed and forged materials

HIP'ed materials from UNS S31803, UNS S32550 and UNS S32760
Forged materials from UNS S32760
HIP material austenite spacing average 12.7 – 14.6 µm
Forged material austenite spacing average 47.9-50.9 µm
Test temperature: 4^{o}C in artificial sea water 3.5% NaCl
Polarized to -1050 mV SCE
Single edge notch bend testing with crack tip opening displacement, exposure time 30 days.

Crack tip opening displacement (CTOD) test



(a) (b)

FIGURE 2 - SENB sample dimensions and notch/fatigue pre-crack geometry (a), relationship between measured CMOD and CTOD (b).

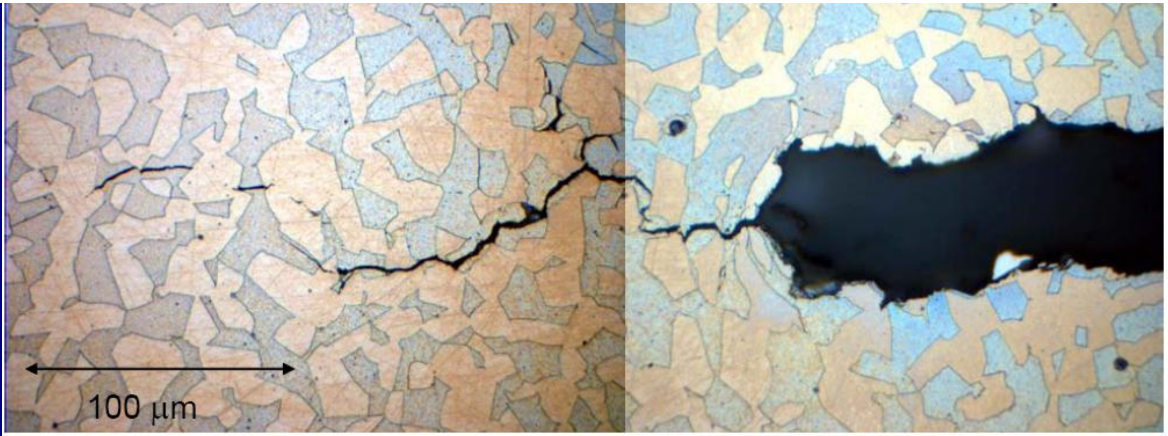


FIGURE 3 - Specimen 32-3(M) SDSS UNS S32760 CTOD=0.08 (Mx500): Crack extends 160 µm from end of fatigue pre-crack, region of cracked ferrite phase extends 280 µm from end of fatigue pre-crack.

Results and conclusion

Results:

1. Large bars with austenite spacing between 38-45 µm failed
2. No failure was detected for materials with austenite spacing 15–16 µm
3. COTD 0.06-0.08 mm for HIP materials and COTD 0.016-0.03 mm for forged materials.

Conclusion

1. The importance of product form and austenite spacing is significant
2. DNV limit of allowable stress max. 80% of yield strength with max. austenite spacing 30 µm is a little bit too conservative that 90% of yield strength is acceptable.
3. For coarser austenite spacing, allowable stress max. 80% of yield strength is reasonable.

Recommended practice:

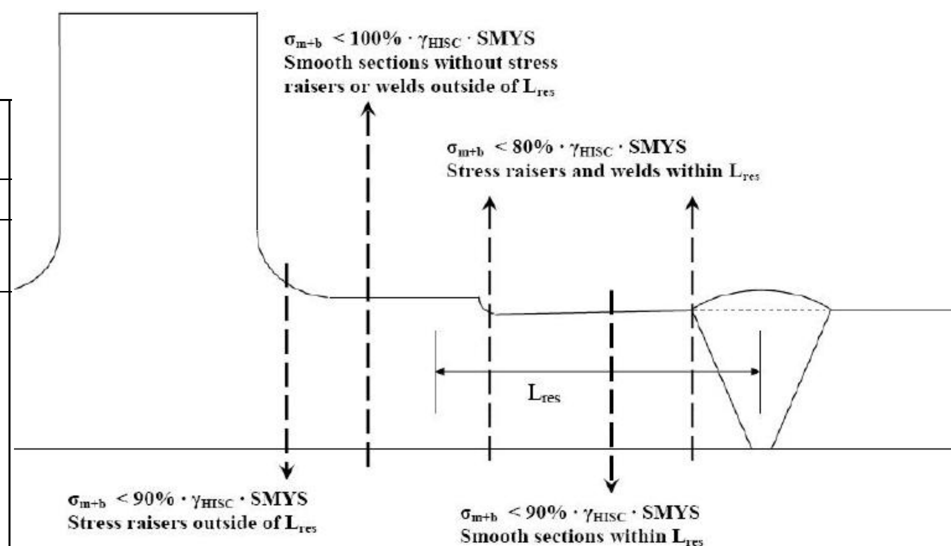
DNV-RP-F112 – October 2008

Allowable SMYS factor

Table D1 Allowable SMYS factor for duplex stainless steel
(See also Figure 2)

	α	*Area considered*	*Details*
Membrane stress (α_m)	80%	Everywhere	D303
Membrane plus bending stress (α_{m+b})	100%	Smooth sections without stress raiser or welds – outside of L_{res}	D304
	90%	Smooth sections within L_{res}	
	90%	Weld toes attachments (see C403) and stress raisers - outside of L_{res}	
	80%	Weld toes and stress raisers – within L_{res}	

Note:
The value for SMYS at elevated temperatures shall be adjusted for temperature effects, see B100.



$$\sigma_m < \alpha_m * \gamma_{HISC} * SMYS$$

$$\sigma_{m+b} < \alpha_{m+b} * \gamma_{HISC} * SMYS$$

Table D2 HISC material quality factor
(See also C300)

Material	γ_{HISC}	*Details*
Fine austenite spacing	100%	D305
Coarse austenite spacing	85%	

Recommended practice:

DNV-RP-F112 – October 2008

Scope:

This is a recommended practice covers all components made from duplex stainless steel that are installed subsea and are exposed to cathodic protection

Material requirement of duplex/super duplex Stainless steel according to DNV-RP-F112

- Material should be solution annealed and water quenched.
- Material categorized as fine austenite spacing
    - HIP materials
    - Weld metal. HAZ follows the base material.
    - Tube and pipe produce by extrusion, seamless rolling or drawing in all dimensions and wall thickness.
    - Rolled plates with wall thickness < 25 mm
- Materials that do not fall into the category above should be considered have coarse austenite spacing (> 30 µm) unless physical measurement of the austenite spacing indicate otherwise.
- Metallographic and material tests:
    - Metallographic characterization of microstructure – ferrite content, inter-metallic phase, austenite spacing.
    - Corrosion test according to ASTM G48
    - Impact test at an appropriate temperature.

References

References:

1. Recommended Practice DNV-RP-F112, “ Design of Duplex stainless steel subsea application equipment exposed to cathodic protection” – October 2008
2. Gro Ostensesn Lauvstad Roy Johnsen ,Bard Nyhus – Sintef , Norway
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5. Ekkarut Viyanit, M.Eng Helmut Schmidt Universitat – Hamburg, Germany, “Numerical Simulation of Hydrogen Assisted Cracking in Supermartensitic Stainless Steel Welds”, Doktor-Ingenieurs dissertation, 2005.