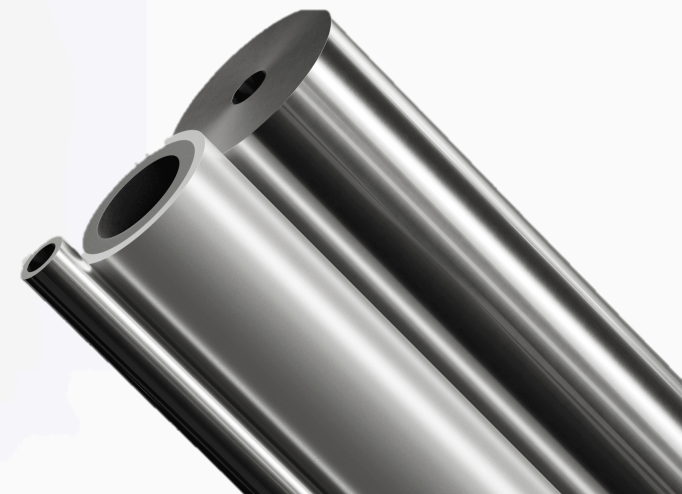


Evaluation of Impact of Cold Deformation on Duplex, UNS S32205, Super Duplex, UNS S32750, and Super Austenitic UNS N08935 Grades for use in Chloride and Sour Environments

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Heat Exchanger

Twisting, U-bending, and Finning

- Better heat transfer efficiency



- API technical report 938-C, 3rd ed.

...testing has shown that the properties of the U-bends without heat treatment are acceptable for refinery services down to bend radiuses of 1.5 times the tube diameter for 25% Cr SDSS grades and at least 3.3 times the tube diameter for 22% Cr DSS.

Cold deformation

- Usually reduce corrosion properties
- Improper heat treatment operations are detrimental to U-bend design

- UNS S32750 has extensive data to chloride stress corrosion cracking and limited data to sulfide stress corrosion cracking (S-SCC)

Background

- Metallic materials in wet H₂S environment are governed by the international standard NACE MR0103:

| Alloy | Hardness Max. | Hardness Conversion |
|------------------------------|-----------------|----------------------|
| DSS S32205 | 28 HRC | HRC = 0.091*HV - 2.4 |
| SDSS S32750 | 32 HRC | HRC = 0.091*HV - 2.4 |
| Highly alloyed austenitic SS | 35 HRC (335 HV) | ASTM E140 |

- DSS tubing are typically produced to ASME 789
- Hardness values typically increase to a degree representative of the cold deformation induced during bending or twisting
- Higher hardness generally have an increased susceptibility to stress corrosion cracking presenting a challenge for the industry

UNS S32205 Seamless Tubes

- 0.750" OD x 0.083" AW (19.05 x 2.10 mm)

| C | Mn | P | S | Ni | Cr | Mo | N | PRE |
|-------|------|-------|-------|-----|------|-----|-----|-----|
| 0.019 | 0.76 | 0.025 | 0.001 | 5.3 | 22.2 | 3.2 | 0.2 | 35 |

UNS S32750 Seamless Tubes

- 0.750" OD x 0.065" AW (19.05 x 1.65 mm)

| C | Mn | P | S | Ni | Cr | Mo | N | PRE |
|-------|------|-------|-------|-----|------|-----|-----|------|
| 0.012 | 0.46 | 0.010 | 0.001 | 6.6 | 25.4 | 3.9 | 0.3 | 42.5 |

UNS N08935 Seamless Tubes

- 1.000" OD x 0.083" AW (25.4 x 2.10 mm)

| C | Mn | P | S | Ni | Cr | Mo | N | PRE |
|-------|-----|-------|-------|----|------|-----|-----|-----|
| ≤0.03 | 0.8 | ≤0.03 | ≤0.02 | 35 | 27.0 | 6.5 | 0.3 | 52 |

$$\text{PRE} = \% \text{Cr} + 3.3 \times \% \text{Mo} + 16 \times \% \text{N}$$



S32750 finned and u-bend samples bent to 1.5D and 2D shown on the right.

Cold bending of heat exchanger tubing

BEND SCHEDULE

| Bend Dies Radii | 1.125" | 1.500" | 2.250" |
|------------------|--------|--------|--------|
| Final Bend Radii | 1.5D | 2D | 3D |

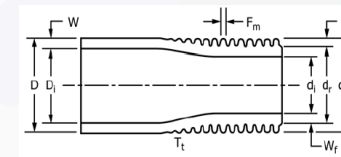
No heat treatment after bending

TUBE FINNING

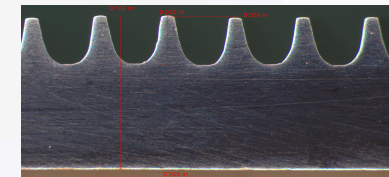
Integrally finned tubes were manufactured according to ASTM A1012.

28 fins per inch (FPI):

- S32205:** 0.035" fin height (FH)
0.065" wall under fin thickness (WUF)
- S32750:** 0.035" fin height (FH)
0.045" wall under fin thickness (WUF)



Schematic of fin configuration showing the tube maintains original OD after finning operation.



Finning configuration dimensions demonstrating fin height, wall thickness under fin and tube OD for S32205 duplex tube sample.

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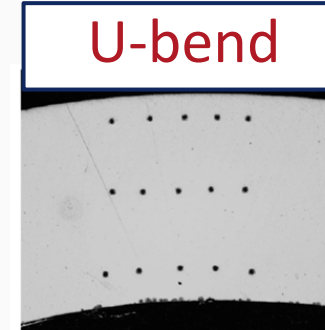
Hardness Testing

2022

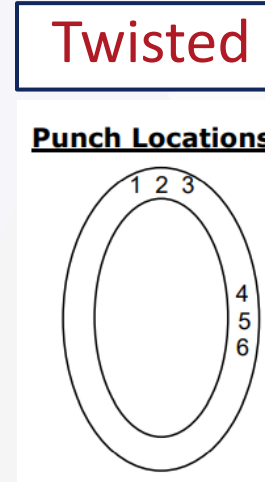
- Vickers scale with a load of 500 g

As Bent

- sub-surface OD (Tension)
- Mid-wall (Neutral)
- sub-surface ID (Compression)

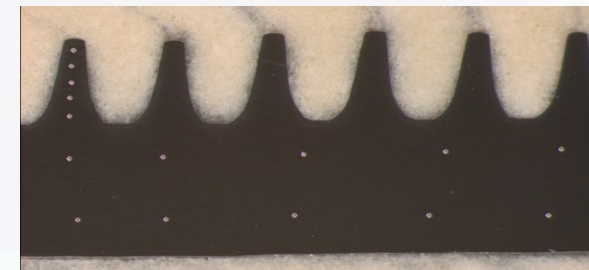


Micro-hardness
indentation



As Finned

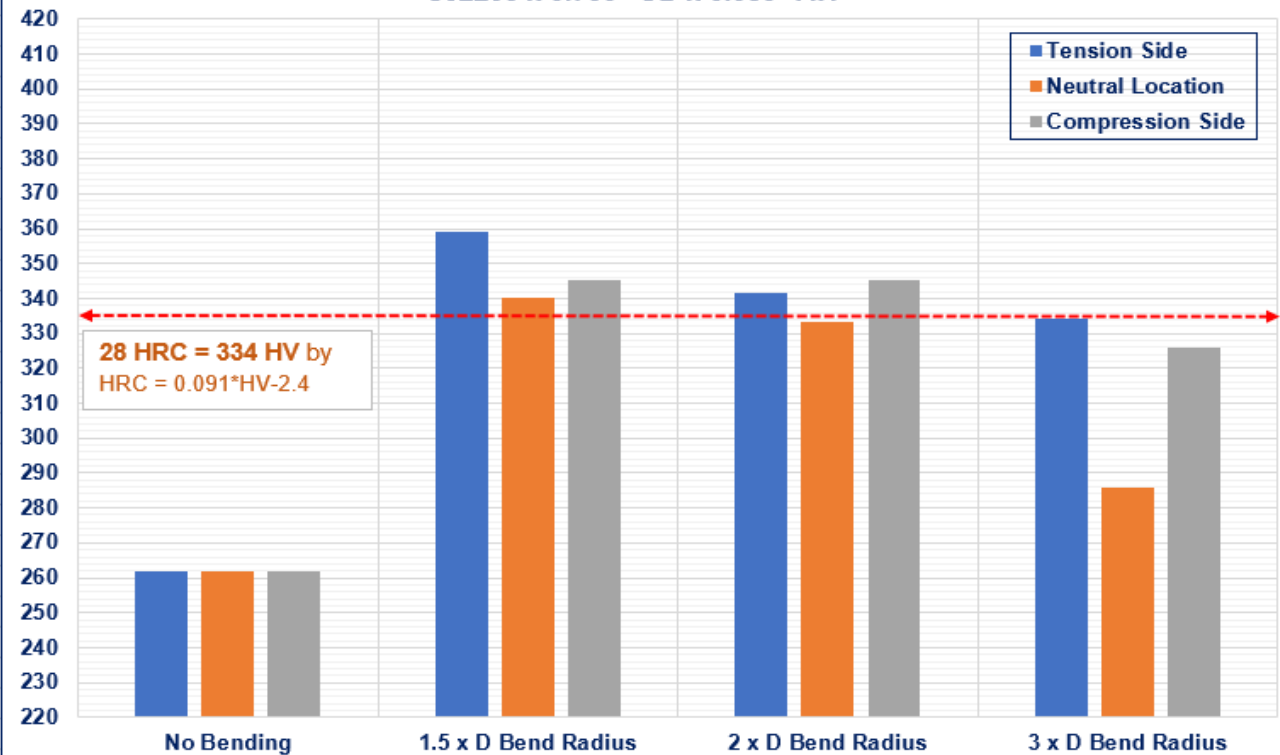
- S32205 and S32750 tube were cut longitudinally
- Fin tip, mid-section of the base tube, and ID of the base tube



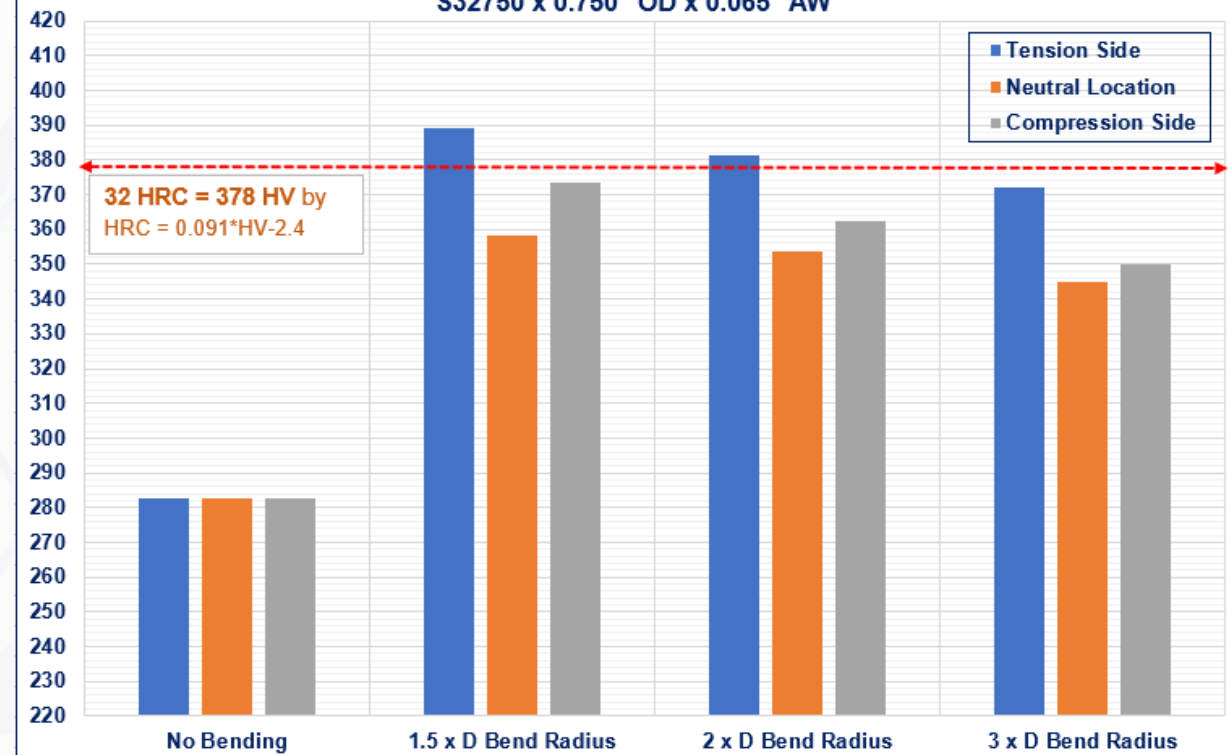
Microhardness indentation of the as finned tube samples.

Microhardness Results – U bends

Vickers Hardness (HV_{0.5}) by the Bend Radii and Location
S32205 x 0.750" OD x 0.083" AW



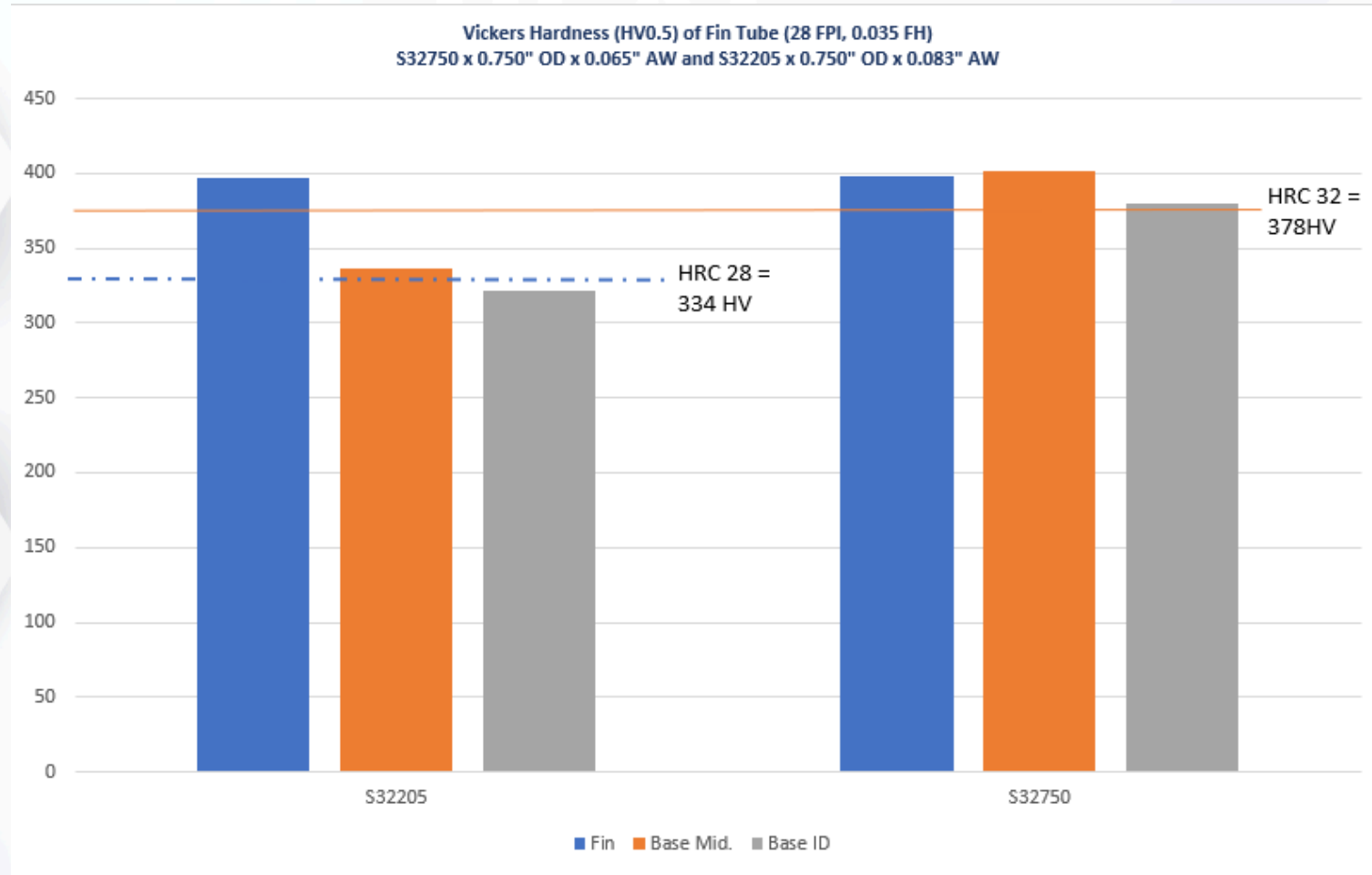
Vickers Hardness (HV_{0.5}) by the Bend Radii and Location
S32750 x 0.750" OD x 0.065" AW



Dashed red line indicates 28HRC reference line for sour services per NACE MR0103 and CSCC per ASME 789

Dashed red line indicates 32HRC reference line for sour services per NACE MR0103 and CSCC per ASME 789

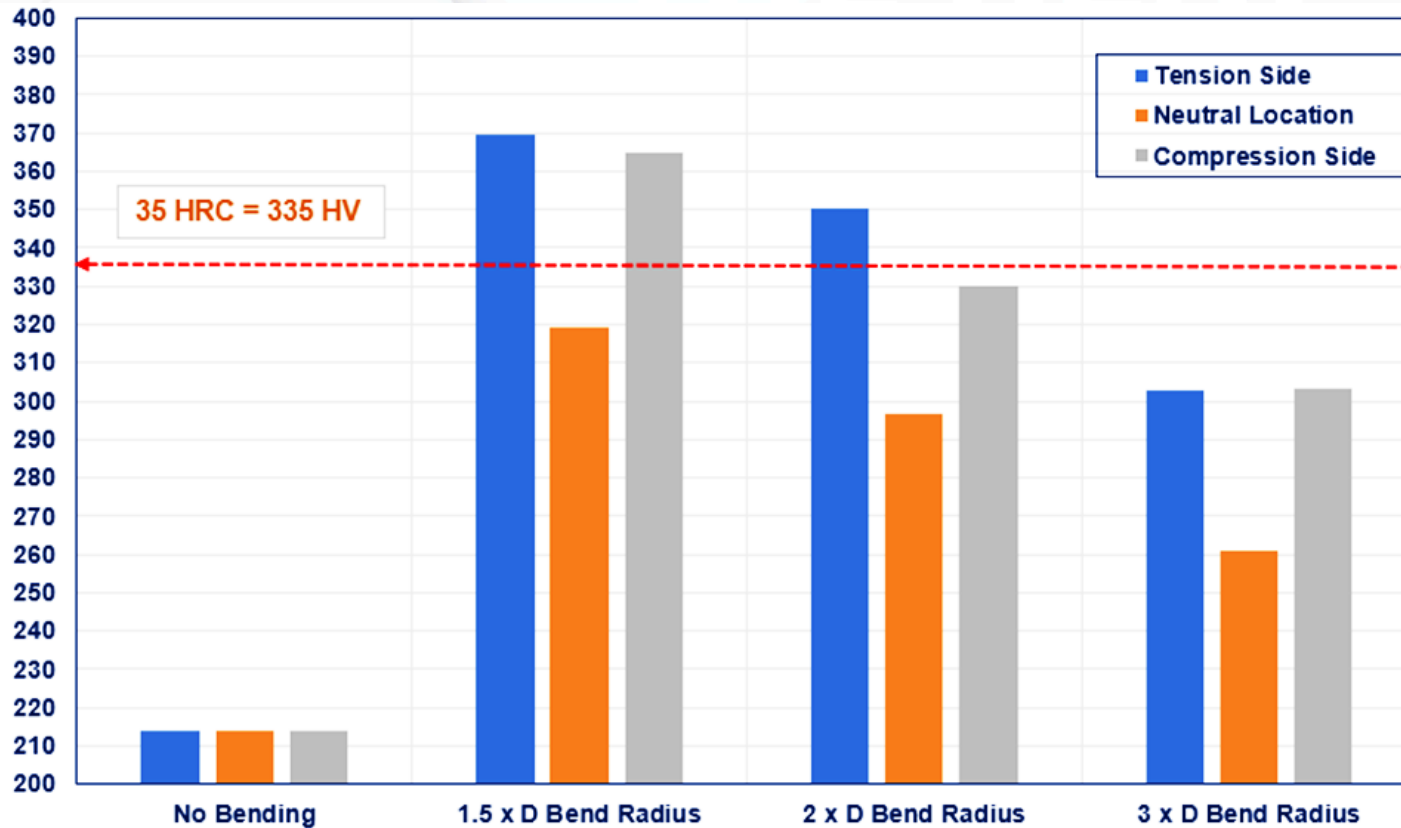
Microhardness results - Finned



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MICRO-HARDNESS OF N308935, 1.000" X 0.083" AW BY BEND RADII.



- Vickers hardness (HV 0.5V)

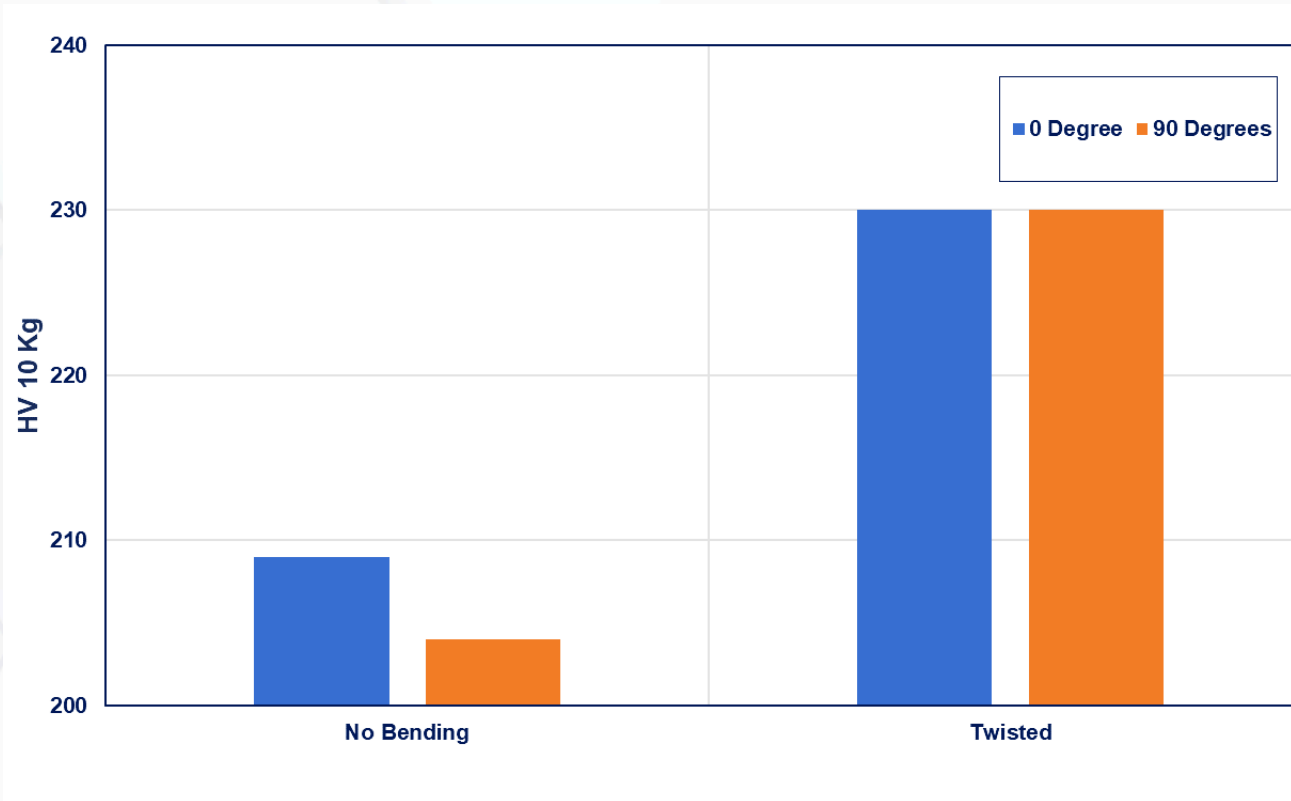
Hardness increase with cold bending

$1.5 \times OD > 2.0 \times OD > 3.0 \times OD$

Dashed red line indicates 35 HRC reference line for sour services per NACE MR103

Microhardness results

UNS N08935, 1.000" X 0.083" AW TWISTED TUBES



- Vickers hardness (HV 10 kg)
- Average hardness value was lower than U-bends hardness
- Slightly increase compared to straight tubes of Alloy 35Mo
- Hardness values were lower than the limit required per NACE MR0103 for sour services (335 HV)

Pitting Corrosion results

S32205 and S32750 u-bend specimens

| Grade | ASTM G48 Method (FeCl ₃ + HCl) | Bend 1 1.5 x OD (1.125 in) | Bend 2 2.0 x OD (1.500 in) | Bend 3 3.0 x OD (2.250 in) |
|---------------|---|----------------------------------|----------------------------------|----------------------------------|
| S32205 | 25°C (77°F), for 24 h | No Pitting | No Pitting | No Pitting |
| S32750 | 50°C (104°F), for 24 h | No Pitting | No Pitting | No Pitting |

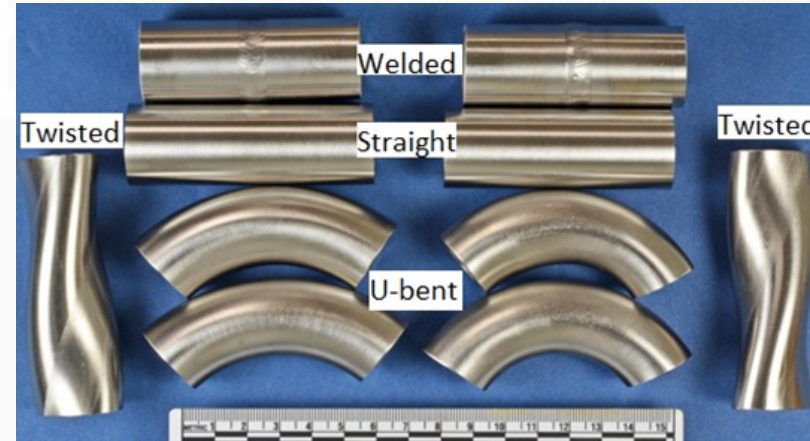
Pitting corrosion testing for S32205 and S32750 as finned tubes

| Grade | ASTM G48 Method (FeCl ₃ + HCl) | As Finned sample 1 | As Finned sample 2 |
|---------------|---|-----------------------|-----------------------|
| S32205 | 25°C (77°F), for 24 h | No Pitting | No Pitting |
| S32750 | 50°C (104°F), for 24 h | No Pitting | No Pitting |

Pitting Corrosion Results

ASTM G48 Method C

- Acidified 6% FeCl₃
- High pitting corrosion resistance



| Grade | ASTM G48 Method C | Results |
|----------------------|-------------------------|------------|
| Twisted N08935 | >85°C (185°F), for 24 h | No Pitting |
| U-bend N08935 1.5xOD | >85°C (185°F), for 24 h | No Pitting |
| U-bend N08935 2.0xOD | >85°C (185°F), for 24 h | No Pitting |
| U-bend N08935 3.0xOD | >85°C (185°F), for 24 h | No Pitting |

Chloride Stress Corrosion Cracking (CSCC)

TWISTED UNS N08935 SHOWED GOOD RESISTANCE TO CSCC

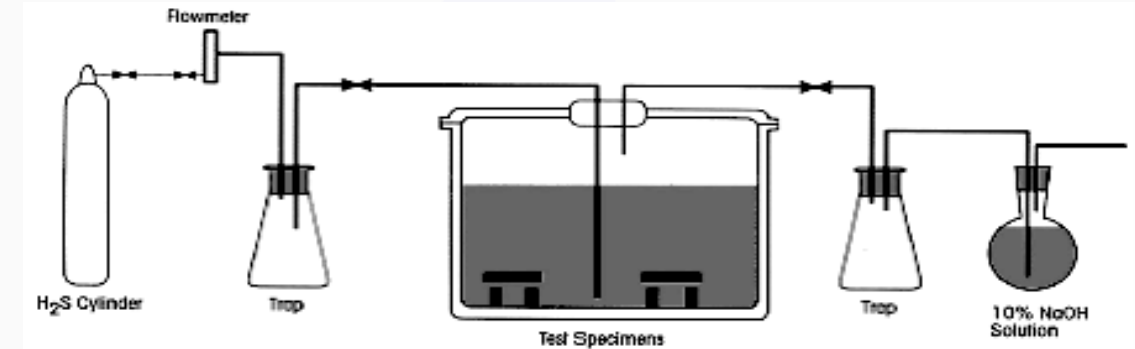
| CSCC Method | Time to failure (h) | Results |
|---|---------------------|-------------|
| ASTM G123 (25%NaCl, pH 1.5 at 106-110°C Boiling) | 1000 h | No cracking |
| 40% CaCl ₂ , pH 6.5 at 100 °C | 1000 h | No cracking |



Sulfide Stress corrosion cracking testing

NACE TM0177 Method C

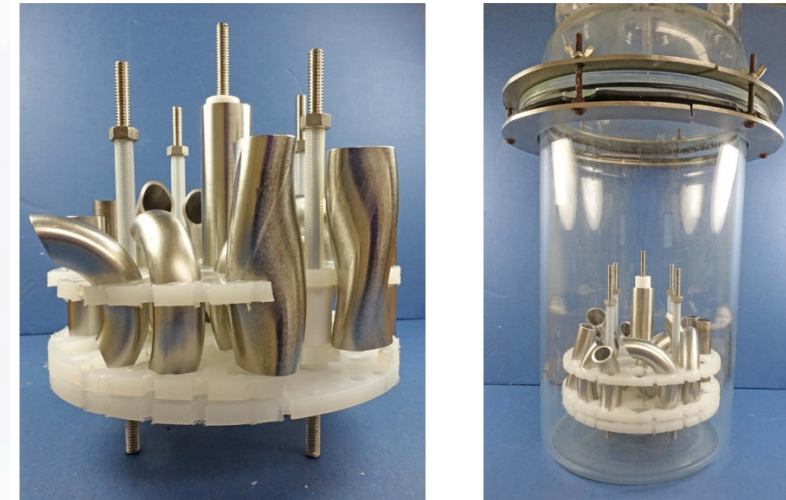
- NACE TM0177 Solution A, acidified NaCl
- 60,000 ppm H₂S in Nitrogen at 90°C (194 °F)
- Pressure: Ambient pressure
- Final pH = 3.1



Test apparatus for NACE TM 0177

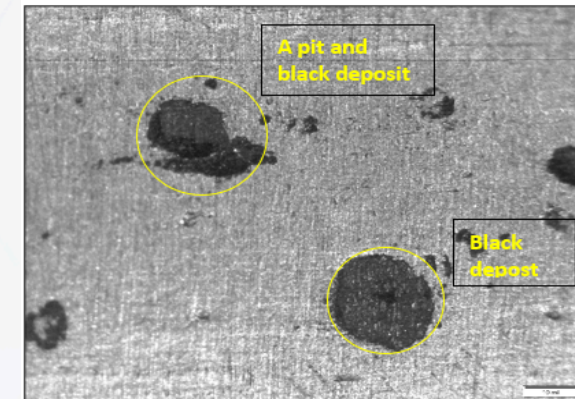
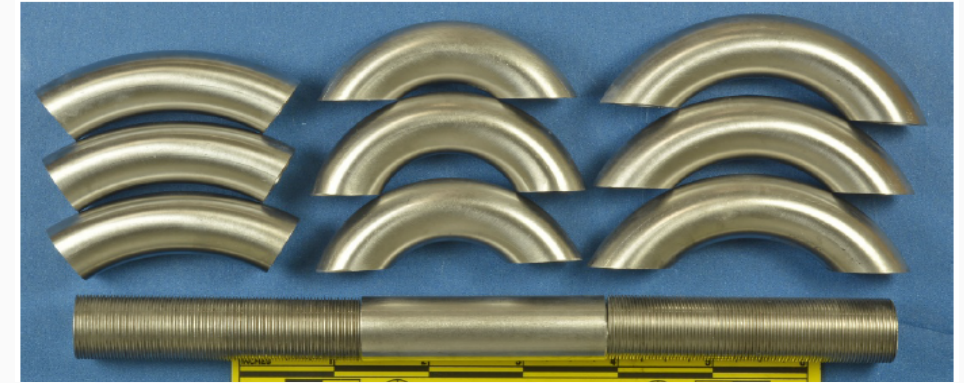
Alloy UNS N08935

No cracks were detected in any straight, u-bend, twisted and welded specimens



Specimens in test vessel

- No cracks were observed by dye penetrant
- No cracks on the mid-wall and inside surface of 1.5D samples by microscopic analysis
- One SDSS S32750 sample from vessel A and three duplex S32205 samples from the vessel B show signs of OD pitting with shallow depth
 - OD pitting appear to be from under deposit corrosion and not related to stress corrosion cracking.
- No tube ID surface pitting was identified.



Conclusions

1. Hardness values increased with cold forming of u-bends, twisting, and integral finned tubes.
2. DSS and SDSS: Bend radius below 3D tube diameter and integral finning of tubes results in hardness values above the acceptable level recommended by industry standard NACE MR0-103, making the materials, in theory, not suitable for wet H₂S applications.
3. Super austenitic stainless steel: Bend radius 2D tube and below diameter brings hardness values above the acceptable level recommended by industry standard NACE MR0103 which in theory would not be suitable for wet H₂S applications.
4. Solution annealing is not necessary as the as cold work twisting finning and bending do not have any negative impact on the corrosion resistance of the alloy.

Thank you!

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