Stainless Steels in Nuclear Industry – Usage and Special Considerations

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OUTLINE

- NUCLEAR INDUSTRY: Constituents
- INDIAN NUCLEAR POWER PROGRAM – STATUS
- MAIN DEGRADATION MODES IN SERVICE
- STAINLESS STEELS IN NUCLEAR INDUSTRY
- “L” AND “LN” VARITIES: MAIN REQUIREMENTS
- “NAG” STAINLESS STEELS FOR RECYCLE PLANTS

25 Years of Indian Stainless Steel Development Association
New Delhi, November 7, 2014
Nuclear Industry

- Nuclear Reactors
- Heavy Water Plants
- Nuclear Spent Fuel Reprocessing & Waste Management Plants
- ITER
Nuclear Reactors

Pressure tube type reactors (PHWR, AHWR)

Pool type reactors (Fast Reactors)

Pressure vessel type reactors (PWR, BWR)

INDIAN NUCLEAR POWER PLANTS: STATUS

2 BWRs at Tarapur
20 PHWRs
Total installed capacity: 4780 MWe in 2014
Under construction: 4 x 700 MWe PHWRs
2 x 1000 MWe VVER
8180 MWe by 2016

Six sites, each for ~ 10 000 MWe identified by India
Mix of reactor types in coming years: PHWR, VVER, PWR, BWR, FBR
Corresponding expansion of closed fuel cycle

Stress corrosion cracking: 39%
Flow accelerated corrosion: 33.6%
Corrosion: 18.7%
Pitting: 1.4%
Under deposit corrosion/MIC: 5.3%
Galvanic corrosion: 1.1%
H induced cracking: 1.1%

Core shroud SCC: non sensitized SS

Dominant degradation mechanisms in carbon steel/stainless steel in Swedish nuclear power plants (2002)

Cracking data base as a basis for risk informed inspection by Karen Gott, 10th International conference on environmental degradation of materials in nuclear power systems – Water reactors
STAINLESS STEELS IN NUCLEAR INDUSTRY

Nuclear Power Plants:
SS 316NG (Nuclear Grade)
SS 304L
SS 304LN
SS 403M
17 – 4 PH / 13 – 8 Mo
SS 440C
SS 420 mod
SS 410
SS 321

Nuclear Fuel Reprocessing & Waste management Plants:
SS 304L
SS 304L (Nitric Acid Grade - NAG)
SS 310L (NAG)
SFSP: SS304L/316L

220 MWe PHWR:
~ 1000 T SS
15,000 m weld length

Weld consumables
Surface area exposed to process fluid in a 540 MWe nuclear reactor:

<table>
<thead>
<tr>
<th>System</th>
<th>Material</th>
<th>Area (m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid Zone Control system</td>
<td>SS 304L</td>
<td>140</td>
</tr>
<tr>
<td>Liquid Poison Injection System</td>
<td>SS 304L</td>
<td>35</td>
</tr>
<tr>
<td>End Shield Cooling System</td>
<td>SS 304L</td>
<td>1000</td>
</tr>
<tr>
<td>Calandria Vault Cooling System</td>
<td>SS 304L</td>
<td>2000</td>
</tr>
<tr>
<td>SFSB Cooling System</td>
<td>SS 304L</td>
<td>3000</td>
</tr>
<tr>
<td>Moderator System</td>
<td>SS 304L</td>
<td>3500</td>
</tr>
<tr>
<td>Active Process Water System</td>
<td>SS 304L</td>
<td>3500</td>
</tr>
<tr>
<td>Service Water System</td>
<td>SS 304L</td>
<td>2500</td>
</tr>
<tr>
<td>Condensate System</td>
<td>SS 304L</td>
<td>6250</td>
</tr>
<tr>
<td>Feed Water System</td>
<td>SS 304L</td>
<td>1400</td>
</tr>
<tr>
<td>Make up Water System</td>
<td>SS 304L</td>
<td>20</td>
</tr>
<tr>
<td>Auxiliary Cooling Water System</td>
<td>SSs</td>
<td>2000</td>
</tr>
<tr>
<td>Non active Process water System</td>
<td>SS 304L</td>
<td>1000</td>
</tr>
<tr>
<td>Condenser Circulating Water System</td>
<td>SSs</td>
<td>100</td>
</tr>
<tr>
<td>Auxiliary Service Water System</td>
<td>SSs</td>
<td>50</td>
</tr>
<tr>
<td>Reactivity Control Mechanism: Various SSs</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Total SS surface area: 20,000 m²
Long term service in nuclear reactors: austenitic SS in AHWR

- **SS 316NG**: Resists sensitization, LTS and sensitization induced IGSCC
- However, more prone to embrittlement of the weldment (ferrite phase) due to aging at operating temperature for long term
- **SS 304LN**: Assessment of LTS, IGSCC and LTE being established
- Requires higher N levels for resistance against LTS and IGSCC

![Diagram showing sensitization levels](image)

**LOW TEMPERATURE SENSITIZATION (LTS)**

\[ \text{Cr}_{\text{eff(N)}} = \% \text{Cr} - 0.2 (\%\text{Ni}) - 100 (\%\text{C}) + 9.2N \]

\( \text{Cr}_{\text{eff(N)}} > 16 \) would ensure that LTS in the weld HAZ would not develop to a level that makes it prone to SCC, due to sensitization, in 100 years of design life

\( \text{Cr}_{\text{eff(N)}} < ?? \) NEED LARGER DATABASE
Making SS Resistant to RIS
(Resistant against Irradiation assisted SCC in reactors)

APPROACHES:

1. Addition of oversized solute alloying elements like Ce, Hf, Zr, Gd, and Pt

2. Grain Boundary Engineering:
   • Twin/special grain boundaries
   • Random grain boundaries

3. Heat Treatment to create initial segregation of Cr
   – This would retard the onset of RIS

SS 316 (0.06% C): Beneficial effect of Ce on thermal sensitization

No Ce
0.01wt% Ce

Carbides after 650°C, 100h

No Ce
0.01wt% Ce

Attacked Cr depletion after 650°C, 100h

Bruemmer et al, JNM 1999
Kain et al, BARC
Methods to control sensitization & Inter Granular Corrosion

1. Low carbon (<0.03%) grades

2. Stabilized (with Ti, Nb) grades

3. Use Solution annealed components

Controlling grain boundary nature to control sensitization, IGC and IGSCC

1. Increase the fraction of special ($\Sigma = 3 - 29$) grain boundaries
   ( ~ 5% cold working + controlled solution annealing increases the fraction of twin boundaries)
   Makes precipitation of carbides difficult and improves resistance to sensitization.

2. Increase fraction of random ($\Sigma > 29$) grain boundaries
   ( ~ 80% cold working + controlled solution annealing increases the fraction of random boundaries)
   Improves resistance to sensitization, IGC and IGSCC
TWIN ENGINEERED STAINLESS STEELS

Kokawa et al. 2002

5% CW + 927°C, 72 h
Thermo-mechanical treatment to control sensitization

Solution Annealed SS 304 (1100°C for 1 hour and water quenched)

Sensitized at 575°C for 1 h

80% cold rolled + Annealed + Sensitized(575°C for 1 h)
Testing for susceptibility to Intergranular Corrosion (IGC): Pr B, A262
(Exposure in boiling solution of $\text{H}_2\text{SO}_4 + \text{Fe}_2(\text{SO}_4)_3$ for 120 hours)

Control of Grain Boundary Character Distribution (GBCD)
to control IGC: Pr B, A262 Results for 304 SS
After DL-EPR test
- Severe IGC attack
- No attack
- Deep attack at grain boundaries

After IGC Test - Practice B ASTM test
- No IGC attack

Kain et al, BARC
Testing for susceptibility to IGSCC: U bent (strained) samples of cold rolled, annealed and sensitized SS 304

After 200 hours testing in boiling 25% NaCl solution (pH=1.5): G 123, ASTM

Intergranular cracking

Mixed mode of cracking

40% CW + Sol. Annealed + Sensitized

20% CW + Sol. Annealed + Sensitized

No cracks at high percentage of reduction

80% CW + Sol. Annealed + Sensitized
Main results of the Orientation Imaging Microscopy analysis

Fraction of random boundaries increased from 32% in as received material to 77% in the sample with 80% CW + Annealing.

Connectivity of random – random boundary is required.

This required >75% random boundaries.

U – Unidirectional Rolling
CR – Cross Rolling
### SS 403 Modified: End Fitting

#### Absorbed energy vs test temperature for AISI 403 SS

<table>
<thead>
<tr>
<th>Element</th>
<th>SS 403</th>
<th>Modified SS 403 (Indian)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>0.15</td>
<td>0.06-0.15</td>
</tr>
<tr>
<td>Manganese</td>
<td>1.0</td>
<td>0.25-0.80</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>0.04</td>
<td>0.03 max</td>
</tr>
<tr>
<td>Sulphur</td>
<td>0.03</td>
<td>0.03 max</td>
</tr>
<tr>
<td>Chromium</td>
<td>11.5-13.0</td>
<td>11.5-13.0</td>
</tr>
<tr>
<td>Nickel</td>
<td>-</td>
<td>0.5 max</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.5</td>
<td>0.5 max</td>
</tr>
<tr>
<td>Cobalt</td>
<td>-</td>
<td>0.025 max</td>
</tr>
<tr>
<td>Boron</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Copper</td>
<td>-</td>
<td>600 ppm max</td>
</tr>
<tr>
<td>Oxygen</td>
<td>-</td>
<td>100 ppm max</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>-</td>
<td>250 ppm max</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>-</td>
<td>2 ppm max</td>
</tr>
<tr>
<td>Impurities Cu+V+Sb+Al+As</td>
<td>-</td>
<td>1500 ppm</td>
</tr>
</tbody>
</table>

- **Before irradiation**
- **After irradiation**

Absorbed energy vs test temperature for AISI 403 SS

75°C
Wide range of austenitization temperature range. The range of alloying elements (especially C and Cr) is narrowed down to reduce the scatter in the mech props and HT range. Aim C at 0.13% and Cr less than 12.3% to reduce the tendency for formation of δ-ferrite stringers in the microstructure & higher strength levels.

DBTT shift by neutron irradiation: Control by Cu < 100 ppm and Ni < 500 ppm.

Further improve the toughness: (Cu, V, Sb, Al & As) < 1500 ppm.

Inclusion content: No heavy series is allowed.
- Sulphide A : 1.5 thin
- Alumina B : 2.0 thin
- Silicate (C) : 1.5 thin
- Globular oxide (D) : 1.5 thin

Other elements: Co < 250 ppm and B < 20 ppm

Mg, Ca, S and O present in inclusions have high (n, α) cross-section: lead to He conc at grain boundaries and cause embrittlement. Avoid by remelting processes like VAR and ESR.

Forging, the H content is < 2 ppm to avoid flake formation
No flute cracks, gassy appearance, butt tears, splash, flakes etc.
Irradiation to a neutron fluence of $1.0 \times 10^{19} \text{ n cm}^{-2} (E>1.0 \text{ Mev})$ at $290^\circ \text{C}$ has caused an increase in DBTT of $75^\circ \text{C}$ and a decrease in the upper shelf energy of $44 \text{ J}$.

At the end of life fluence of approximately $6.0 \times 10^{19} \text{ n cm}^{-2} (E>1.0 \text{ Mev})$, an increase of $136^\circ \text{C}$ in DBTT is estimated for the end fitting.

The estimated $RT_{NDT}$ of $170^\circ \text{C}$ is well below the operating temperature of the end fitting both during normal operation and during reactor start up.

This study ensures the safety of the end fitting against brittle failure throughout its expected service life.
Presence of Sigma Phase in 17-4 PH Bobbin Shaft: DELETERIOUS $\sigma$ PHASE

Retained Austenite in SS 403 of End-Fitting

- Retained austenite: 168 – 200 HV
- Martensite: 320 – 335 HV
- Martensite: 350 – 380 HV

Ferrite in Martensitic Stainless Steel SS 410

Kain et al, BARC

Loss of impact toughness
17 – 4 PH STAINLESS STEEL FOR FUELLING MACHINE
Shielding plug, Sealing plug

High resistance to sliding wear, good toughness, shock resistance

Cr: 15.5 – 17
Ni: 3 – 5
Cu: 3 – 5
Si: 1 max
Mn: 1 max
Nb: 0.15 – 0.45
C: 0.07 max
S: 0.03 max
P: 0.04 max

H 1100 condition: Sol Ann at 1035°C, 30 min + 580°C, 4 h, AC

During melting, aim to keep:

Cr < 16.5% to keep δ-ferrite under control
C < 0.04 % to keep Mf ~ 30°C
Nb/C < 6 to keep impact toughness
Contamination during fabrication

Embedded iron in stainless steels
- Iron corrodes in moist atmospheres in coastal areas during storage
- Concentration of chlorides
- Iron oxides are voluminous, causing high stresses
- TGSCC of even annealed stainless steels during storage

Organic contamination
- Grease, Oil, Crayon markings, Paint, Adhesive tape, Sediments, Other sticky deposits
- In aggressive environments it induces crevice corrosion
- Removal essential in order to remove iron contamination

Welding related contaminants
- Slag from coated electrodes
- Heat tint
- Arc strikes
- Welding stop points
- Weld spatter

Cold work/heavy machining leading to surface cold work/strain

Chloride build up during long term storage
16h exposure to Boiling \( \text{MgCl}_2 \)

Cracking throughout width along longitudinal direction

10h exposure to Boiling Magnesium Chloride

Condenser tubes of SS 304: High residual stress

Roller straightening: Circumferential stresses
\~ 20 Kg/mm\(^2\)

Stretch straightening – Longitudinal stresses \~ 2 Kg/mm\(^2\)

Kain et al, BARC
Stresses arising from solidification of weld pool

Region of heavy plastic deformation leading to increase in strength and IGSCC susceptibility

Stresses arising from constraintment of the structure preventing weld shrinkage

Welding of thick plate

Residual strain as a function of distance from weld pool

316NG pipe bend

Strain levels about 20% near welded regions

SCC at H3 Weld Line of BWR Core Shroud

Ref. : TEPCO/GE data

SCC on type 316NG Piping System

Ref. : Ulla Ehrnsten et al.;"Tenth International Conference on Environmental Degradation of Materials in Nuclear Power Systems Water Reactors"

Actual IGSCC failures in BWR’s in non sensitised SS

HEAVY PLASTIC STRAIN IN WELDS MAIN CAUSE OF IGSCC IN REACTORS
REDUCE STRAIN: NARROW GAP WELDING; USE INSULATIVE COATINGS?
The Tube side of weldment: Transformation of delta ferrite to sigma phase and cracking during welding

5 – 6 % delta ferrite stringers in the tubes

Same morphology of the cracks and sigma phase

KEEP DELTA FERRITE IN BASE METAL << 0.2%
## Materials for nitric acid environments

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>304L - NAG</td>
<td>For moderate concentrations up to high temperatures. Ideal for recirculating acids for long life of components.</td>
</tr>
<tr>
<td>310L – NAG</td>
<td>Dissolver cell, for higher temperatures and condensates 25 Cr, 21 Ni, &lt; 0.2C, &lt; 0.2Si, &lt; 0.8Mn, &lt; 0.01S, &lt; 0.02P</td>
</tr>
<tr>
<td>1815LCSi</td>
<td>For &gt; 95% HNO(_3), up to boiling temperatures (Especially for piping systems)</td>
</tr>
<tr>
<td>(Type 306)</td>
<td></td>
</tr>
<tr>
<td>SS 329 Duplex</td>
<td>Tube side and shell side coolers. Condensers at low to intermediate temperatures</td>
</tr>
<tr>
<td>Zirconium &amp;</td>
<td>To overcome vapour phase corrosion, up to boiling temperatures, Subject to SCC in &gt; 20 % HNO(_3)</td>
</tr>
<tr>
<td>alloys</td>
<td></td>
</tr>
<tr>
<td>Titanium</td>
<td>For most concentrations of HNO(_3) at room temperature. Corrosion rate increases with temperature, especially in 20 – 60 % HNO(_3), above 90 % HNO(_3) can be subject to SCC</td>
</tr>
<tr>
<td>Aluminum and</td>
<td>Good for “fuming” nitric acids (86 – 100 %) at ambient temperatures. Dilution of acid causes accelerated attack</td>
</tr>
<tr>
<td>alloys</td>
<td></td>
</tr>
</tbody>
</table>
Typical limits for use of SS in nitric acid (boiling) media

NAG varieties:
No IGC in nitric acid
Corrosion rate of 5 – 10 mpy
(as against < 15 mpy for CP)

IGC occurs for SS in boiling HNO$_3$
with few mg/L of Np(VI)
And
with a few g/L of Pu(VI)

La Hague plant, France, JNM 2008
IGC testing in HNO₃ environments: Sensitization induced

Chemical composition based parameter

\[ \text{Cr}^{\text{effective}} = \% \text{Cr} - 0.18 (\% \text{Ni}) - 100 (\% \text{C}) \]

Microstructure

Sensitize at 677°C for 20 minutes: Coverage < 50 %

Sensitize at 677°C for 1 hour: Coverage < 100 %

And \( \text{Cr}^{\text{effective}} > 14.0 \)

SS 304 L would be resistant to IGC in practice C, A262, ASTM

Kain et al, BARC
Mechanism of End Grain Corrosion

Surfaces exposed to oxidizing acid

Dissolution of inclusions

Resultant IGC

Kain et al, BARC
Susceptibility to End Grain Corrosion

- “Active” inclusions
- Flow lines and segregation of Cr, Si and P along it

End Grain Corrosion Test

- Exposure to boiling solutions of \(9N \text{ HNO}_3 + 1 \text{ g Cr}^+6/\text{liter}\)
- 4 periods of 24h each

<table>
<thead>
<tr>
<th>Material</th>
<th>Corr. Rate (mpy)</th>
<th>Depth of Attack (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>304L (CP)</td>
<td>1020</td>
<td>500</td>
</tr>
<tr>
<td>304L (NAG)</td>
<td>770</td>
<td>250</td>
</tr>
<tr>
<td>Ti-5Ta-1.8Nb</td>
<td>0.17</td>
<td>Not visible</td>
</tr>
<tr>
<td>Welded Ti-5Ta-1.8Nb</td>
<td>0.28</td>
<td>Not visible</td>
</tr>
</tbody>
</table>
Corrosion in Magnox fuel dissolver: Vapour phase

Local metal loss 2 - 5 mm deeper than in base metal

Corrosion of seam welds

(End Grain Corrosion)

Forgings

(End Grain Corrosion)

Set in branches

R D Shaw, Br Corr J, 1990
## Improved Corrosion Resistance of Type 304 L Stainless Steel – Nitric Acid Grade (NAG)

<table>
<thead>
<tr>
<th>Element</th>
<th>Composition, Wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>304L CP</td>
</tr>
<tr>
<td>C</td>
<td>&lt; 0.03</td>
</tr>
<tr>
<td>Si</td>
<td>&lt; 1.0</td>
</tr>
<tr>
<td>Mn</td>
<td>&lt; 2.0</td>
</tr>
<tr>
<td>P</td>
<td>&lt; 0.045</td>
</tr>
<tr>
<td>S</td>
<td>&lt; 0.03</td>
</tr>
<tr>
<td>Cr</td>
<td>18 – 20</td>
</tr>
<tr>
<td>Ni</td>
<td>8 – 12</td>
</tr>
<tr>
<td>O</td>
<td>~100 ppm</td>
</tr>
<tr>
<td>N</td>
<td>&lt; 500 ppm</td>
</tr>
</tbody>
</table>

**Control of:**

- **Sensitization:** levels of C, Ni and Cr and Si & P
- **End Grain Corrosion:** sulfide inclusions and segregation of Cr, Si and P
- **Uniform Corrosion:** controlled cold work, nature of grain boundaries

**Inclusions:** Total $(A + B + C + D) < 4.0$  
[$C,D$ thin $< 1.5$, $D$ thick $< 1$, others $< 0.5$]
304L CP \( G = 4.0 \)
304L NAG \( G = 6.5 \)

After resolution annealing \((1100^\circ C, 30 \text{ min, WQ})\) and \(677^\circ C, 1h\) sensitization.

Average Corrosion Rate in five periods of practice C, A262

<table>
<thead>
<tr>
<th>Heat Treatment</th>
<th>Corrosion Rate (mpy)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CP</td>
</tr>
<tr>
<td>As Received</td>
<td>12.0</td>
</tr>
<tr>
<td>AR + Sensitized</td>
<td>36.0</td>
</tr>
<tr>
<td>AR + Resolutionized + Sensitized</td>
<td>44.0</td>
</tr>
</tbody>
</table>

Kain et al, BARC
Type 316L Special Grade: Material for future?

Commercial Grade: P – 260 ppm
Special Grade: P – 2 ppm

100 times improvement in corrosion rates in practice, A262, ASTM.
Cr content vs. corrosion rate in boiling nitric acid

Condensate phase corrosion in nitric acid: IGA of annealed SS

IGC OF NON-SENSITIZED STAINLESS STEELS IN BOILING NITRIC ACID CONTAINING OXIDIZING IONS
Performance vs. Making, Shaping and Treating of Stainless Steels – A few examples

Common melting techniques:

Arc/air induction melting followed by refining using Argon Oxygen Decarburization (AOD)/Vacuum Oxygen Decarburization (VOD) techniques

Special melting techniques:

Arc/air induction melting followed by refining using Electro Slag Refining (ESR)

Arc/air induction melting followed by refining using Creusot-Loire-Uddeholm (CLU) or Laddle Injection Control (LIC) techniques
Cleanliness of alloy from different melting techniques

ESR produces clean stainless steels

- AOD/CLU
- LIC
- ESR

Heat Nos.: 1, 2, 3, 4, 5, 6

- Oxides
- Alumina
- Sulfide stringers

Bar chart showing area percentage, length per mm², and number per mm² for different melting techniques and heat numbers.
INDIAN SS INDUSTRY HAS THE CAPABILITY TO MEET ALL THE REQUIREMENTS OF SS NEEDS TO WORK CLOSELY WITH NUCLEAR INDUSTRY AND ESTABLISH THE BEHAVIOUR OF SS IN GIVEN APPLICATION

THANK YOU