RATE OF OXIDATION OF 316L STAINLESS STEEL IN THE PRESSURIZED WATER REACTOR ENVIRONMENT

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- Exposure tests – MAI at Electricité de France (EDF) R&D.
Primary Water Stress Corrosion Cracking (PWSCC) - the predominant ageing mechanism in light water reactors.

Uncertainty: Long term susceptibility of 316L to PWSCC.

PWSCC propagation by intergranular cracking. Therefore intergranular oxidation considered as a precursor for SCC initiation.

This investigation aims to measure the rate of oxide growth on 316L stainless when exposed to simulated PWR primary water, and produce a predictive model for oxide growth.
Methodology

Experimental Matrix for Oxidation Kinetics

<table>
<thead>
<tr>
<th>Sample prep.</th>
<th>EBSD mapping</th>
<th>Autoclave exposure</th>
<th>Oxidation measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>316L Stainless Steel</td>
<td>290°C</td>
<td>320°C</td>
<td>360°C</td>
</tr>
<tr>
<td>Annealed</td>
<td>-</td>
<td>-</td>
<td>1000 h</td>
</tr>
<tr>
<td>Cold Rolled: 20% thickness reduction</td>
<td>-</td>
<td>-</td>
<td>1000 h</td>
</tr>
</tbody>
</table>

• Preparation: Used Focused Ion Beam (FIB-SEM) to section through surface oxide.

• Measurements: Physical oxide thickness with SEM or TEM (shorter durations).
Methodology

Physical measurements of maximum oxide depth (surface and intergranular) from selected regions on the surface.

Sample: 316L Annealed –1000 hour exposure at 320°C
TEM image with EELS elemental maps

Iron
Oxygen
Cr rich layer: spinel \((Fe_xCr_{1-x})_3O_4\)
Fe rich layer: Magnetite \((Fe_3O_4)\)

Chromium
Composite

original surface

144 nm
402 nm

0.2 \(\mu m\)

Iron
Chromium
Oxygen
Composite
METHODOLOGY

Intergranular oxidation measurement

• Grain Boundaries were selected based on SEM back-scatter imaging.
• Selected GBs were sectioned by FIB for intergranular oxidation measurements using SEM or TEM.
• Boundaries <30° with surface rejected.
RESULTS – Oxide growth kinetics

The graph shows the oxidation depth (nm) on the y-axis and the time of exposure (hrs) on the x-axis. Two conditions are compared:

- **Annealed 320°C** (represented by orange circles)
- **20% Cold Rolled 320°C** (represented by blue triangles)

The data points indicate the oxidation depth at different times of exposure for each condition.
RESULTS – Oxide growth kinetics

![Graph showing oxide growth kinetics](image-url)
RESULTS – Oxide growth kinetics

![Graph showing oxide growth kinetics](image-url)
MODELLING – Point Defect Model Calibration
MODELLING – Modified Point Defect Model

![Graph showing oxidation depth vs time of exposure](image)

- **Annealed 290°C**
- **Annealed 320°C**
- **Annealed 360°C**
- **20% Cold Rolled 290°C**
- **20% Cold Rolled 320°C**
- **20% Cold Rolled 360°C**
- **Penttilä - 316L, 600°C**
- **Penttilä - 316L, 500°C**
- **Ziemiak - 304, 260°C**
- **Tapping - 304, 300°C**
- **Castle - 18/8, 200°C**
- **Castle - 18/8, 160°C**
- **Castle - 18/8, 120°C**

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MODELLING – Modified Point Defect Model
MODELLING – Modified Point Defect Model

![Graph showing oxidation depth vs. time of exposure for various conditions. The graph includes data points for different annealing temperatures, cold-rolled conditions, and tapping temperatures, with different symbols and colored markers to distinguish between conditions. The y-axis represents oxidation depth in nanometers (nm), while the x-axis represents time of exposure in hours (hrs). The graph includes a trend line for each condition, showing the expected oxidation depth over time.]
MODELLING – Modified Point Defect Model

Graph showing oxidation depth vs. time of exposure for different conditions and materials.
MODELLING – Modified Point Defect Model
MODELLING – Modified Point Defect Model

[Graph showing oxidation depth vs. time of exposure for various conditions, with different markers and line styles for different treatment temperatures and conditions.]
MODELLING – Modified Point Defect Model
RESULTS – orientation dependence

Oxide growth in annealed samples dependent on orientation
e.g. 1000 hr exposure at 320°C
RESULTS – orientation dependence

Annealed, 1000 hr exposure at 320°C
RESULTS – orientation dependence

Annealed, 1000 hr exposure at 320°C
RESULTS – orientation dependence

Annealed 320°C 1000 h exposure

Time of flight secondary ion mass spectroscopy (ToF SIMS)
Volume of O⁻ ion

EBSD preferred orientation

SEM back-scatter image
RESULTS – orientation dependence

Annealed, 1000 hr exposure at 290°C
RESULTS – orientation dependence

Annealed, 1000 hr exposure at 290°C
RESULTS – orientation dependence

- A coherent interface results in a higher probability that ions will overcome the jump distance to transfer into vacancy positions.
  i.e. higher coherency $\rightarrow$ lower transfer coefficient $\rightarrow$ greater oxide depth.
- In contrast an incoherent interface produces less opportunities for ion transfer.
- The growth inverse with temperature due to degrading of metal/oxide interface coherency.
Discussion

- Oxide growth on 316L SS has been measured with a temperature inversion evident at 290°C-360°C.
- The PDM has been modified to accommodate this inversion by expressing the transfer coefficient at the metal/oxide interface as a function of temperature.
- Oxide growth dependent on grain orientation, this dependence changes as temperature varies.
- The observed influence of temperature on both i) metal/oxide interface transfer coefficient, and ii) orientation dependence, suggests that the coherency of the metal/oxide interface degrades with temperature due to differential rates of thermal expansion.
- More reliable prediction of oxide growth in critical 290°C-360°C temperature range.