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WP4 : NUCLEAR CORROSION
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ALTERNATIVE DISSOLUTION AND
OXIDATION BEHAVIOR OF 316L(N)
STEEL AT 550°C IN LIQUID SODIUM
CONTAINING LOW CONCENTRATION OF OXYGEN

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1) CONTEXT AND STATE OF THE ART

- **CONTEXT**: Generation IV - SFR - ASTRID
  - Corrosion data and prediction of service life-time of reference materials as 316L(N) - 60 y – through corrosion modeling

- **STATE OF THE ART**: large literature in relation to fast reactors applications
  - Excellent corrosion resistance of steels at high T & high flow in pure liquid Na but the semi-empirical models (316L - 1y - T > 600°C) are not conservative
  - As stainless steels and refractory metals present low solubility's even at high temperature in pure liquid sodium
  - But impurities such as oxygen drastically increase the dissolution rates of stainless steels because of the formation of ternary oxides (NaCrO$_2$, Na$_4$FeO$_3$) that are relatively (?) soluble in liquid sodium
  - Oxygen role unclear (catalytic effect, complex formation)

- **Reactor**: Oxygen as low as possible to maintain corrosion low

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**Dissolution and mass transfer**

[Graphs showing dissolution rate as a function of temperature and oxygen level, with data from Thorley et al., 1967, and Kolster et al., 1984]
1) OBJECTIVE AND PLAN

- **OBJECTIVE**: validate the hypothesis that oxidation may occur during transient or alternate chemical conditions in heat transfer systems because of alternate conditions varying with coolant chemistry and materials surface layer evolutions with operating time in agreement with thermodynamic conditions, which is necessary for long term modeling.

- **Plan**: the hypothesis will be supported by experimental results performed with laboratory scale setup to separate effects, and characterizations at the finest scale possible, and discussed as regards some literature results:
  1. Alternate dissolution/oxidation thermodynamic zones
  2. Test at 550°C and low oxygen
  3. Discussions + some insights for corrosion modelling and reactor operation
Ellingham diagram for various oxide in liquid sodium at different oxygen content

The only potential oxide is \( \text{NaCrO}_2 \)

\[
4\text{Na} + \text{O}_2 \leftrightarrow 2\text{Na}_2\text{O}
\]

\[
-RT \ln \frac{a_o^2}{P_{O_2}} = 2\Delta G^0_{f,\text{Na}_2\text{O}}
\]

\[
a_o = a_{\text{Na}_2\text{O}} = \frac{C_o}{S_o}
\]

\[
\log S_o = a - \frac{b}{T}
\]

\[
2\text{Na}_2\text{O} + \text{Cr} = \text{NaCrO}_2 + 3\text{Na}
\]

\[
a_o^2 \cdot a_{\text{Cr}} = \exp \left( \frac{\Delta G^0_{f,\text{NaCrO}_2} - 2 \cdot \Delta G^0_{f,\text{Na}_2\text{O}}}{RT} \right)
\]

K. Natesan, 1975, MET. TRANS. Vol 6A pp1143-1153
Oxygen threshold for the NaCrO$_2$ formation vs. T and Cr activity of surface layer:

$$2\text{Na}_2\text{O} + \text{Cr} = \text{NaCrO}_2 + 3\text{Na}$$

$$\Delta G^0_{f,\text{NaCrO}_2} = -842258 + 189.06T$$

$$\Delta G^0_{f,\text{Na}_2\text{O}} = -421530 + 141.41T$$

$$a_o^2 \cdot a_{Cr} = \exp \left( \frac{\Delta G^0_{f,\text{NaCrO}_2} - 2 \cdot \Delta G^0_{f,\text{Na}_2\text{O}}}{RT} \right)$$

$$\log a_{Cr} = -0.577 + \frac{69.1}{T}$$

$$a_o = \frac{C_{O_{lim}}}{C_{sat}} \text{ (Noden)}$$

**Diagram:**
- Oxidation zone
- Dissolution zone
- Alternate conditions possible by surface modification or coolant chemistry change

**Chemical Reaction:**
$$2\text{Na}_2\text{O} + \text{Cr} = \text{NaCrO}_2 + 3\text{Na}$$
2) DISSOLUTION/OXIDATION TEST GRID
PRIOR RESULTS

Test achieved up to now at 550°C and 650°C - <1ppm, 40 ppm and 200 ppm in both oxidation and dissolution zones according to sodium chromite

Weight gain for slight oxidation, kinetics assessment by GD-OES for 316L(N) and T91:

Oxide :
Cr depleted zone : 

\[ e_1(t) \pm 0.14 = -5.55 \times 10^{-2} + 3.63 \times 10^{-4} \cdot t \]

\[ e_2(t) \pm 0.14 = 0.966 + 2.41 \times 10^{-4} \cdot t \]

This test to reassess the dissolution

316L(N) 5000h, 550°C, 40 ppm TEM
Fast Reactors, 2013

J-L. Courouau - EUROCORR 2015
316L(N) : grade X2CrNiMo17-12-2

- Nitrogen controlled, elaborated in accordance with the RCC-MR codification (RM 3331 level 2). After rolling, the steel was annealed at 1120°C and quenched in water.
- Mean grain size is between 30 to 40 µm
- Electrical discharge machine (EDM)

**TABLE I**
Composition of the 316LN stainless steel tested.

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>Balanced</td>
</tr>
<tr>
<td>Cr</td>
<td>17.27</td>
</tr>
<tr>
<td>Ni</td>
<td>12.13</td>
</tr>
<tr>
<td>Mo</td>
<td>2.54</td>
</tr>
<tr>
<td>Mn</td>
<td>1.74</td>
</tr>
<tr>
<td>C</td>
<td>0.026</td>
</tr>
<tr>
<td>Si</td>
<td>0.31</td>
</tr>
<tr>
<td>P</td>
<td>0.025</td>
</tr>
<tr>
<td>S</td>
<td>0.001</td>
</tr>
<tr>
<td>N</td>
<td>0.069</td>
</tr>
<tr>
<td>B</td>
<td>0.0004</td>
</tr>
<tr>
<td>Cu</td>
<td>0.0029</td>
</tr>
<tr>
<td>Co</td>
<td>0.09</td>
</tr>
</tbody>
</table>

SEM / SE – 15 kV
3) MATERIAL AND CORROSION CONDITIONS

- Liquid metal setups: CORRONa (as Corrosion sodium) α + β

- Closed and tight system
- Ar purified glove-box
- Mo-crucible
- 2.3 kg Na
- Safety (double barriers)

1- Liquid sodium, 2- Molybdenum crucible, 3- Thermal well, 4- Oven, 5- Cooling channels, 6- Gloves box floor, 7- Gas inlet and pressure monitoring, 8- Well cover, 9- Temperature well, 10- Upper cover cooling section, 11- Gas outlet, 12- Sodium vapor reflux condenser, 13- Aerosols filter, 14- Bursting disks, 16-Molybdenum wires, 17- Corrosion specimen

Icapp-2011
3) MATERIAL AND CORROSION CONDITIONS

- **Corrosion Tests**: 550°C in static sodium for 4577 h for low oxygen condition (<~1 wppm)
  
  a) Preconditioning (melting, settling for 300h at 108°C, skimming out residual oxide at free level)
  b) Zirconium foil purification (75 h at 628°C, 9 dm²)
  c) Exposition in Na for step 1 to 5 **one sample in and one out**
  d) Ethyl alcohol, then pure water quick cleaning + desiccator storage
  e) Weight variation - SEM /EDS – GD/OES – FIB/TEM (HRTEM, EDX, EELS)

- Others samples tested at the same time: Fe-9Cr-1Mo, A800, Fe, Ni, Hf, Al₂O₃, HfO₂
Weight variation + Macroscopic examination

- Cleaning: weight gain after ethanol cleaning higher than after water cleaning, meaning sodium remains in the porosities present in the corrosion surface layer.
- Sample immersed from the beginning, weight gain small but not null: + 0.006 mg/dm²/d (if supposed linear).
- Up to 100 times larger weight gain for 650h for the same duration.

Conclusion: from 2 to 28 mg/dm²/y on the corrosion kinetics based on weight variation.
4) RESULTS - 2 DISTINCT BEHAVIORS

3025 h (1500h in Common):
Δm/S : +0.67 // + 9.63 mg/dm²  

8R- 3023 h

8W – 3028h

Conclusion: 2 totally distinct behaviors observed even though sample were exposed for common periods, then to the same liquid metal chemistry,
But
- some were exposed from the beginning
- others immersed during the test

Oxidation + ‘Dissolution’ (carburization) can happen at the time?

ratio 14
Oxidation characterization: SEM

- Zone 2: black patches that expand for the last period
- Crystallites enriched in Na, Cr and O (1µm – triangular shape)

SEM surface observation (SE) of zone 2 last 3900 h (periods 2+3+4+5) of the test

Conclusion: zone 1 = sodium chromite oxide scale (NaCrO$_2$)
4) RESULTS – CORROSION LAYERS IN OXIDATION

Oxidation characterization: GD-OES

- Oxide scale (Na-Cr-O): 500 nm, not function of exposure duration
- Cr depleted zone: 1 µm thickness steady with time (no Ni leaching<-> Fe), porosities, carburization zone which is more intense and larger than the one caused by EDM machining, some indications of internal oxidation (SiO₂)
- In between: a Mo enriched zone, 0.1 to 0.2 µm
- Sodium profile extends to 4 to 6 µm in depth: sodium penetration zone?

Conclusion: steady thickness but surface extends for the last exposure period even though durations are shorter

Oxide scale formation lead to a Cr chemical activity at the surface layer lower than the bulk
‘Dissolution’ characterization: SEM

- No apparent evolution with exposure duration, with quasi-null weight gain
- Porosities ~500nm (Mo enriched) -> coral like structure
- Crystallites (250 nm to 1 µm, Fe, Cr or Cu rich)
- Na penetration

SEM surface observation (SE) 4577 h (periods 1+2+3+4+5)

Conclusion: - No oxide present
- Little and homogenous corrosion (porous zone + crystallites formation)

Cross-section: Cr depleted zone, Mo enriched at the interface, Cr rich particle’s at the surface
Dissolution’ characterization: GD-OES

- No oxygen except surface contamination
- Carburization: precipitation of carbides (Fe, Cr, Mo), C and diffusion profile up to 3 µm for 4577h
- Mo and Cr depletion zone, roughly steady after 3000h to 2-2.5 µm
- Na penetration but limited to porosities present in the surface layer (size seems to increase with exposure duration)
- Cu: dissolution (up to 2.5-3µm at 4577h) and surface precipitation ($s_{Cu}$=55 wppm – precipitation)

Conclusion: Carburization + dissolution evidenced but superposition of the phenomena,
Dissolution of Fe and Ni leading to cavities and to Mo rich nodules formation ($Cu$ = marker)
TEM characterization:
1. 90% Fe-rich grains of 400-800 nm in size in the surface layer, most probably ferrite
2. Mo-rich grains of 200 nm in size at the interface, which may be carbide or Chi intermetallic phase
6. Chromium carbide (EELS)

Conclusion: carbide precipitation at surface and in the Cr depleted zone, leading to a Cr chemical activity at the surface layer lower than alloy bulk activity
- 1st stage of ferrite scale formation as indication of Ni preferential dissolution of Cr depleted zone to be further studied
TEM characterization:

3. Porosities of 500 nm in size, which may be grains ripped off during sodium test or sample preparation
4. 10-50 nm inclusions in the Cr depleted zone, rich in Si and O (ratio $\frac{1}{2}$) = internal oxidation with SiO$_2$ formation
5. Cr-rich spherical inclusions of 100 nm in size, which are intra-granular Chromium rich carbide and are noticeably absent from ferrite grains

4577 h (periods 1+2+3+4+5)

| Conclusion: internal oxidation as marker of oxidation transient = open issue |
4) RESULTS - FE AND NI PURE METALS

**Dissolution**: negligible at 550°C, as observed with pure metals of the same test
Ni: +0,1 mg/dm²/d - weight gain – Fe mass transfer - Na porosities - deposition

Ni – 4577h

- Mass transfer did occur in between sample function of surface layer activities
- Cu: dissolution + precipitation
5) DISCUSSION - LIQUID METAL CHEMISTRY

1- Liquid metal chemistry evolved during test:
   - Carbon: initially high in new Na, decreased by reaction with materials
   - Oxygen: initially low, gradual increase at each opening for sample extraction and immersion at 110-120°C (no continuous Zr getter) (1-5 ppm max,)

2- Oxidation and carburization: lower surface layer a_{Cr} that increases a_{o min} for oxidation

3- Dissolution happened but negligible

Sample immersed from the beginning
1- [O] initially low, high [C], carburization occurred
2- a_{Cr} decreased due to carburization that increased a_{o min} for oxidation
3- [O] increased with testing time but not enough to exceed a_{o min}
4- Dissolution happened as well
5) DISCUSSION - LIQUID METAL CHEMISTRY

Sample immersed during the test

1- [O] slightly higher to exceed $a_o^{\text{min}}$, low because of new unaffected sample, [C] lower
2- $a_{\text{Cr}}$ decreased due to oxidation that increased $a_o^{\text{min}}$
3- The oxidation driving force is larger for the late specimen, where [O] and $a_{\text{Cr}}$ presented probably their highest values
4- Sodium chromite might have been slightly dissolved or reduced for prior oxidized specimen when compared to late specimen

Conclusion:
This test demonstrates that liquid metal chemistry combined to surface layer evolution changed thermodynamic threshold for oxidation that explain alternate oxidation/dissolution behavior observed in this test
This interpretation agrees with experimental results obtained in sodium loops:

- Cavell & Nicholas 1980 – experimental fit for higher than expected $C_0^{\text{lim}}$

- Unexplained initial weight gain followed by weight loss in specimen exposed to HT section of a loop (oxidation – reduction)

- Sodium aged specimen less prone to oxidation as dissolution zone is enlarged (Crouch-1978)
New surface more prone to oxidation for little contamination (5 ppm) when compared to aged surfaces

- all of available oxygen concentrate on smaller surface giving larger than expected oxide scale
- Refuel – component handling – maintenance and repair

For a closed anisothermal system, oxygen will be buffered with time at a very low concentration by the low T equilibrium with NaCrO₂, causing oxide reduction in the medium and high T section of the loop

Long term corrosion prediction could be improved by taking into account alternate phases of oxidation/reduction over service life time
Corrosion is the result of a number of competing mechanisms that affect the surface layer of the material as well as the coolant chemistry. These mechanisms include:

- Oxidation + carburization mass transfer + dissolution

Thermodynamics defines the reaction paths vs. chemical potentials. Models require multicomponent systems with retrofit loops due to traces evolution of the liquid metal chemistry caused by corrosion processes to account for the complexity.

- Coolant chemistry (traces amounts)
- Surface layer modification
- Contamination precipitation
- Mass transfer
- Oxidation/reduction
- Dissolution metals & oxides
- Operations (start, refuel, maintenance and repair, incidental contamination ...)
- Data (solubilities, enthalpies, diffusivities ...)
- Kinetics of separate effects
Thank you for your attention