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WP4 : NUCLEAR CORROSION CONTRIBUTION ID N°: 860

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

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- 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 (NaCrO₂, Na₄FeO₃) that are relatively (?) soluble in liquid sodium
 - Oxygen role unclear (catalytic effect, complex formation)
- <u>Reactor</u>: Oxygen as low as possible to maintain corrosion low





 <u>OBJECTIVE</u>: 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

2) ALTERNATE DISSOLUTION/OXIDATION THERMODYNAMIC ZONES 1/4

Ellingham diagram for various oxide in liquid sodium at different oxygen content



K. Natesan, 1975, MET. TRANS. Vol 6A pp1143-1153

Oxygen threshold for the NaCrO₂ formation vs. T and Cr activity of surface layer :

 $2Na_2O + Cr = NaCrO_2 + 3Na$

 $\Delta G_{f,NaCrO_2}^0$ =-842258+189,06T

 $a_o^2 \cdot a_{Cr} = \exp \frac{\Delta G_{f,NaCrO_2}^0 - 2 \cdot \Delta G_{f,Na_2O}^0}{RT}$ $\Delta G_{f,Na2O}^0$ =-421530+141,41T

39,115-123(1988) 691

Bhat, Borgstetd, Werkstoffe und Korrosion

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$$loga_{Cr} = -0.577 + \frac{0.017}{T}$$

 $a_o = C_o^{\lim} / Csat$ (Noden)





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 :

 $e_1(t) \pm 0.14 = -5.55.10^{-2} + 3.63.10^{-4} \cdot t$

Cr depleted zone : $: e_2(t) \pm 0.14 = 0.966 + 2.41.10^{-4} \cdot t$



reassess the dissolution





J-L. Courouau - EUROCORR 2015

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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)

Element	Concentration (wt. %)			
Fe	Balanced			
Cr	17.27			
Ni	12.13			
Mo	2.54			
Mn	1.74			
С	0.026			
Si	0.31			
Р	0.025			
S	0.001			
Ν	0.069			
В	0.0004			
Cu	0.0029			
Со	0.09			

10 μm SEM / SE – 15 kV

TABLE I Composition of the 316LN stainless steel tested.

• Liquid metal setups : CORRONa (as Corrosion sodium) $\alpha + \beta$





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

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<u>Corrosion Tests</u>: 550°C in static sodium for 4577 h for low oxygen condition (<~1 wppm)







e) Weight variation - SEM /EDS – GD/OES – FIB/TEM (HRTEM, EDX, EELS)

316LN	Exposure duration, h					
steps	<u>1</u>	2	3	4	<u>5</u>	
8 P	657					
8Q	\rightarrow	1549				
8R	\rightarrow	\rightarrow	3023			
8S	\rightarrow	\rightarrow	\rightarrow	3918		
8T	\rightarrow	\rightarrow	\rightarrow	\rightarrow	4577	
8U	\rightarrow	\rightarrow	\rightarrow	\rightarrow	4577	
8V		\rightarrow	\rightarrow	\rightarrow	3920	
8W			\rightarrow	\rightarrow	3028	
8X				\rightarrow	1555	
8Y					659	

• 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



 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?





8R- 3023 h

8W - 3028h

4) RESULTS - OXIDATION INTO NACRO₂



Conclusion : zone 1 = sodium chromite oxide scale (NaCrO₂)

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

4) RESULTS – DISSOLUTION/CARBURIZATION

'Dissolution' characterization: SEM

- No apparent evolution with exposure duration, with guasi-null weight gain
- Porosities ~500nm (Mo enriched) -> coral like structure

Sianal A = SE2

Grand. - 19.66 K XNom de Fichler = 316LN 8T 4577H 02.th

EHT = 15.00 kV

WD = 6.5 mm

ULTRA 55 - SCCME

- 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)



Cross-section: Cr depleted zone, Mo enriched at the interface, Cr rich particle's at the surface



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



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4) **RESULTS** - CORROSION LAYERS IN DISSOLUTION/CARBURIZATION 6/9

Dissolution' characterization: GD-OES

- No oxygen except surface contamination
- Carburization: precipitation of carbides (Fe, Cr, Mo)_xC 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)

4) RESULTS - TEM / DISSOLUTION/CARBURIZATION 7/9

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

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4) RESULTS - TEM / DISSOLUTION/CARBURIZATION

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 SiO₂ 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



Dissolution : negligible at 550°C, as observed with pure metals of the same test Ni : $+0,1 \text{ mg/dm}^2/d$ - 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

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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 occured
- 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^{min}, low because of new unaffected sample, [C] lower
- 2- a_{Cr} decreased due to oxidation that increased a_o^{min}
- 3- The oxidation driving force is larger for the late specimen, where [O] and a_{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

(Crouch-1978)











- 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

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Corrosion is the results of a number of competing mechanisms that affect the surface layer of the material as well as the coolant chemistry Oxidation+ carburization mass transfer dissolution Thermodynamics defines the reaction paths vs. chemical potentials Models => multicomponent systems with retrofit loops due to traces evolution of the liquid metal chemistry caused by the corrosion processes to take into account the complexity **Coolant chemistry** Surface layer (traces amounts) modification Data (solubilities, **Oxidation/reduction** enthalpies, diffusivities... **Dissolution metals &** oxides **Kinetics of separate Operations Contamination** effects (start, refuel, **Dissolution metals &** Precipitation maintenance and Mass transfer oxides repair, incidental contamination ...)

Thank you for your attention

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