

EFFECT OF SURFACE MODIFICATION ON THE CORROSION RESISTANCE OF 316L IN SUPERCRITICAL WATER CONDITIONS

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Introduction

- This presentation summarizes the results of oxidation rate tests, i.e. weight gain tests, of austenitic stainless steel 316L with different surface conditions
- One of the critical technological issues in SCWR is the materials for fuel cladding and core components that must be used in high pressure (25 MPa) and high temperature (up to $\sim 630^{\circ}\text{C}$) SCW conditions
- According to the requirements of the thermal hydraulic design and structural stability, the assembly has to retain its original configuration with high accuracy \rightarrow fuel cladding etc.
- There are lots of open questions such as water chemistry, i.e. radiolysis, and supercritical water interaction with reactor materials
- At this stage, no single alloy has received enough study to ensure its long-term performance under SCW conditions up to 650°C

Test conditions and material

	C	Si	Mn	S	P	Cr	Ni	Mo	Fe
316L	0.017	0.36	1.72	0.010	0.028	17.29	13.13	2.52	Balance

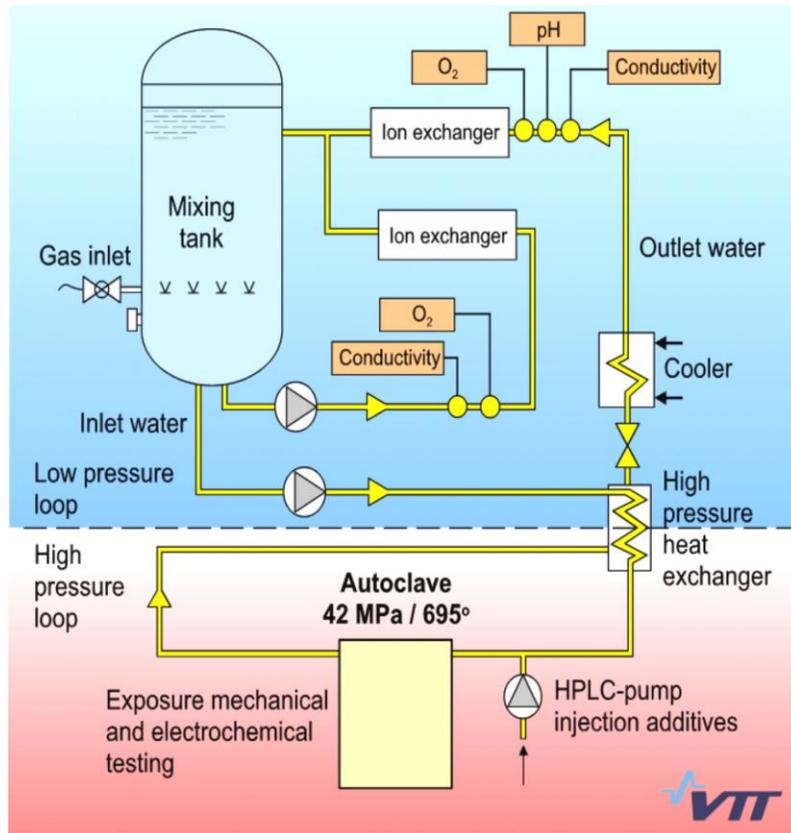
Chemical composition of studied alloy (wt-%)

- Tested material was 316L
- Exposure test (i.e. weight gain) was performed in SCW at 650°C under the pressure of 25 MPa
- Exposure times were 1000h and 3000h
- After exposure test, samples were studied with Scanning Electron Microscopy (SEM) in conjunction with Energy Dispersive X-ray Spectroscopy (EDS)
- Microscopic investigations using FIB and TEM were performed on the selected samples by CANMET, Canada (J. Li and W. Zheng)



A typical specimen holder

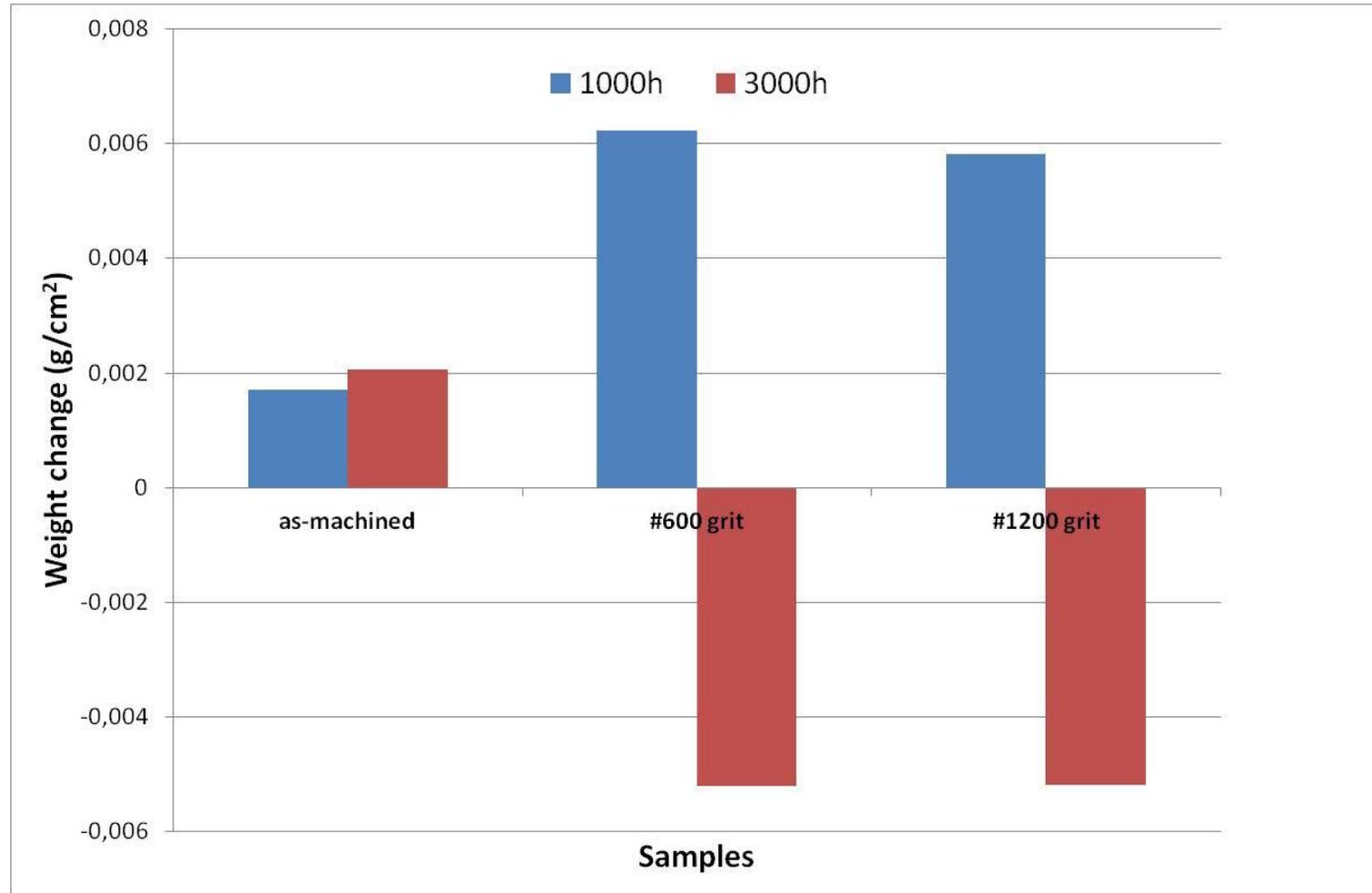
Water recirculation loop with the SC-autoclave at VTT



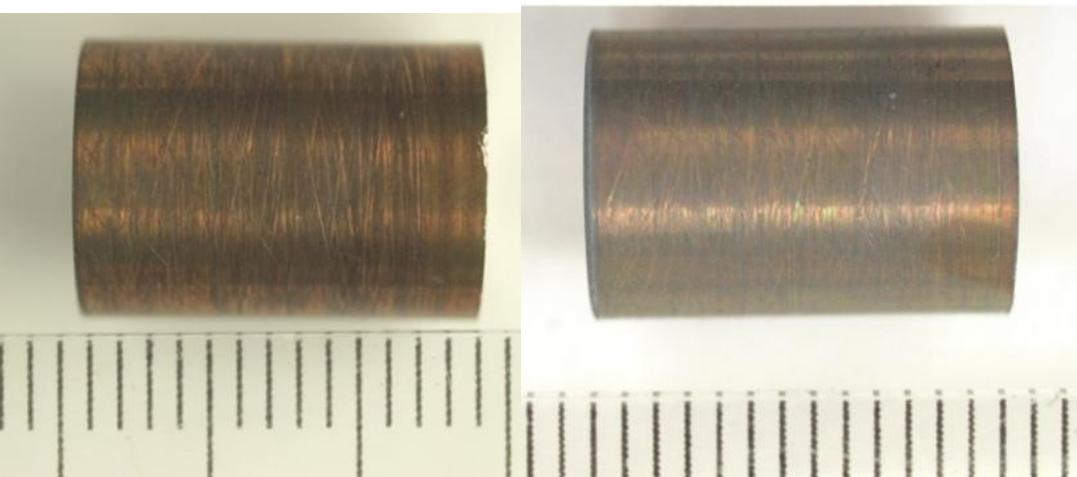
Test matrix for the exposure test at 650°C / 25 MPa

Specimen	Surface modification	Exposure times
316L tube	as-machined	1000h and 3000h
316L tube	#600 emery paper	1000h and 3000h
316L tube	#1200 emery paper	1000h and 3000h

Weight changes for 316L tube samples with different surface conditions at 650°C after 1000h and 3000h exposures



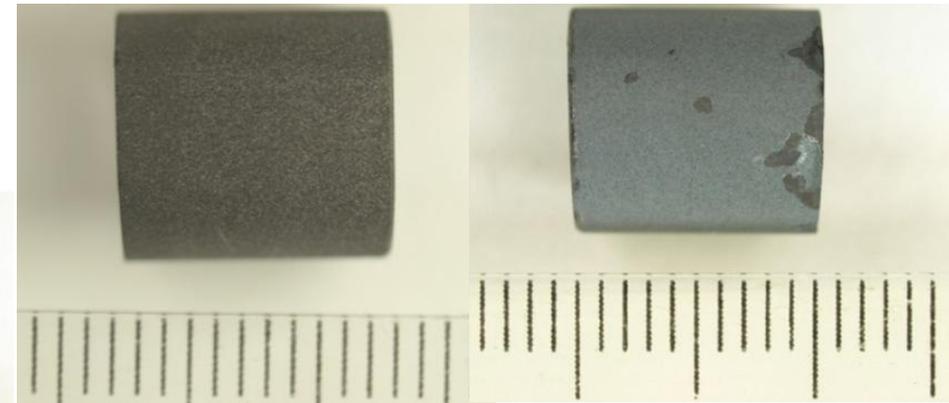
316L tube samples after 1000h (left) / 3000h (right) exposures at 650°C



1000h

3000h

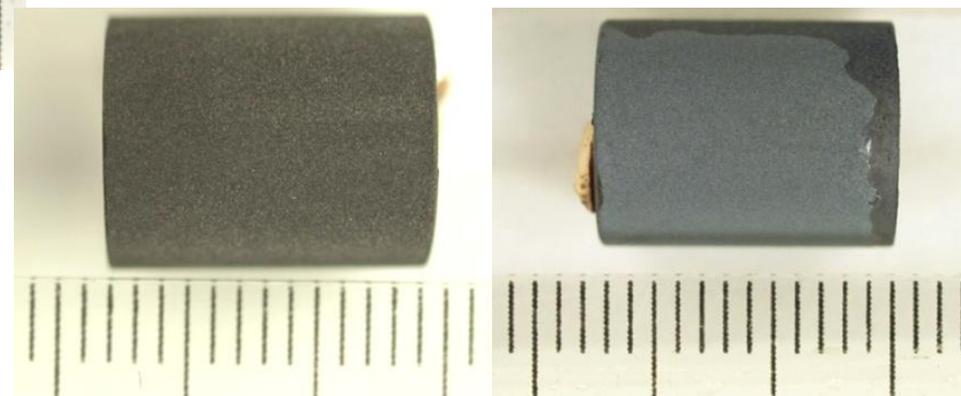
as-machined



1000h

3000h

grit #600



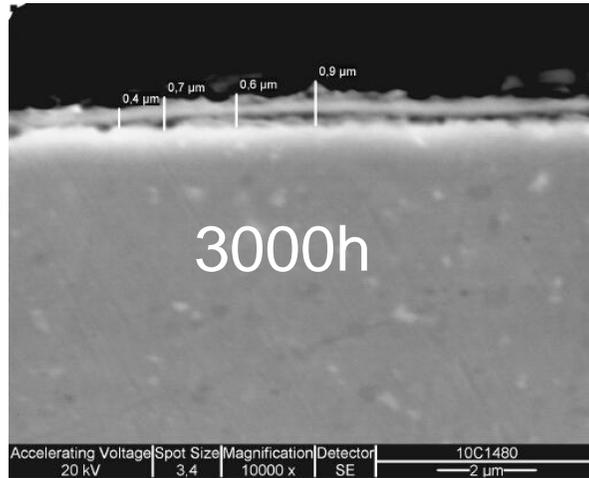
1000h

3000h

grit #1200

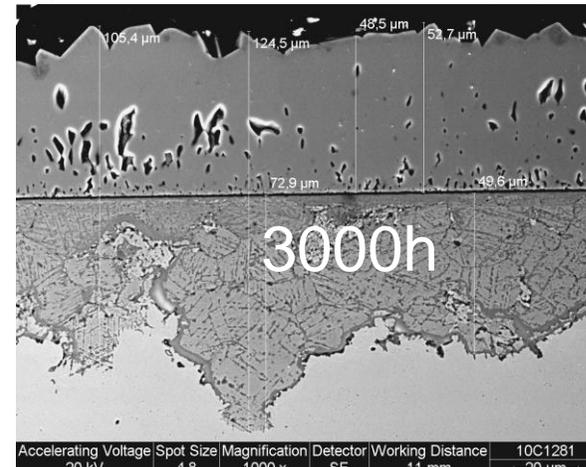
SEM cross-sections and EDS line-scans of 316L tube samples after 3000h exposure at 650°C

as- machined

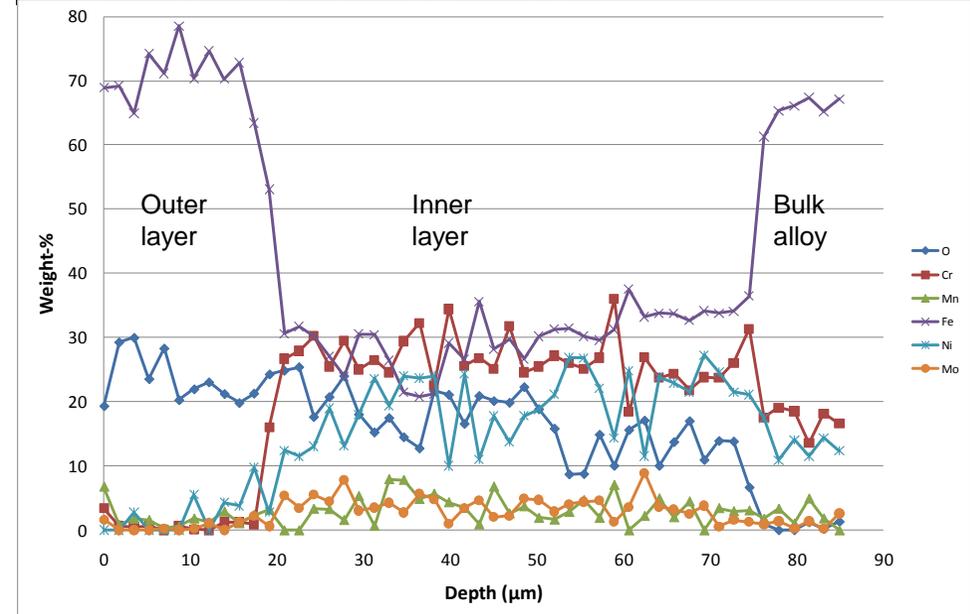
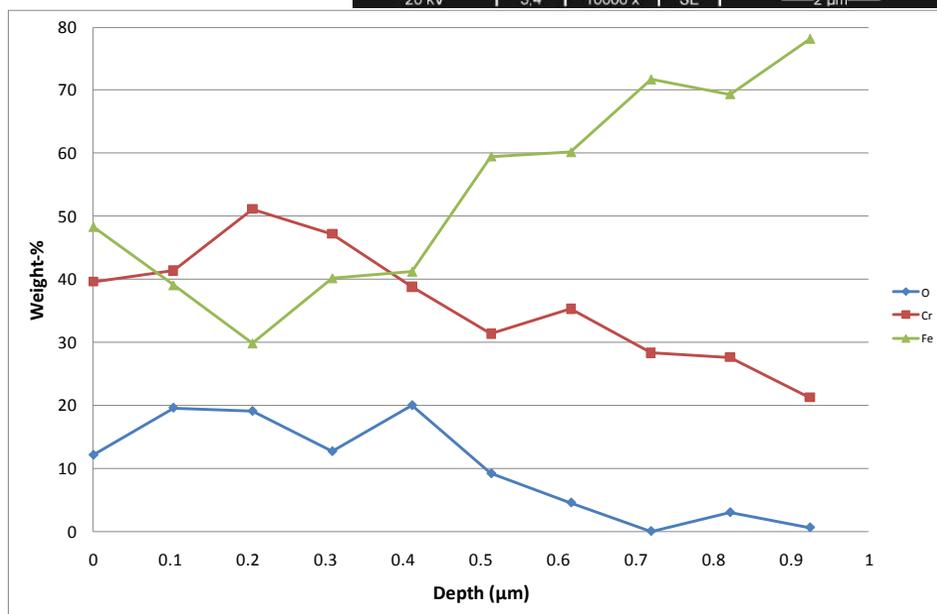


max. ~1.0 μm

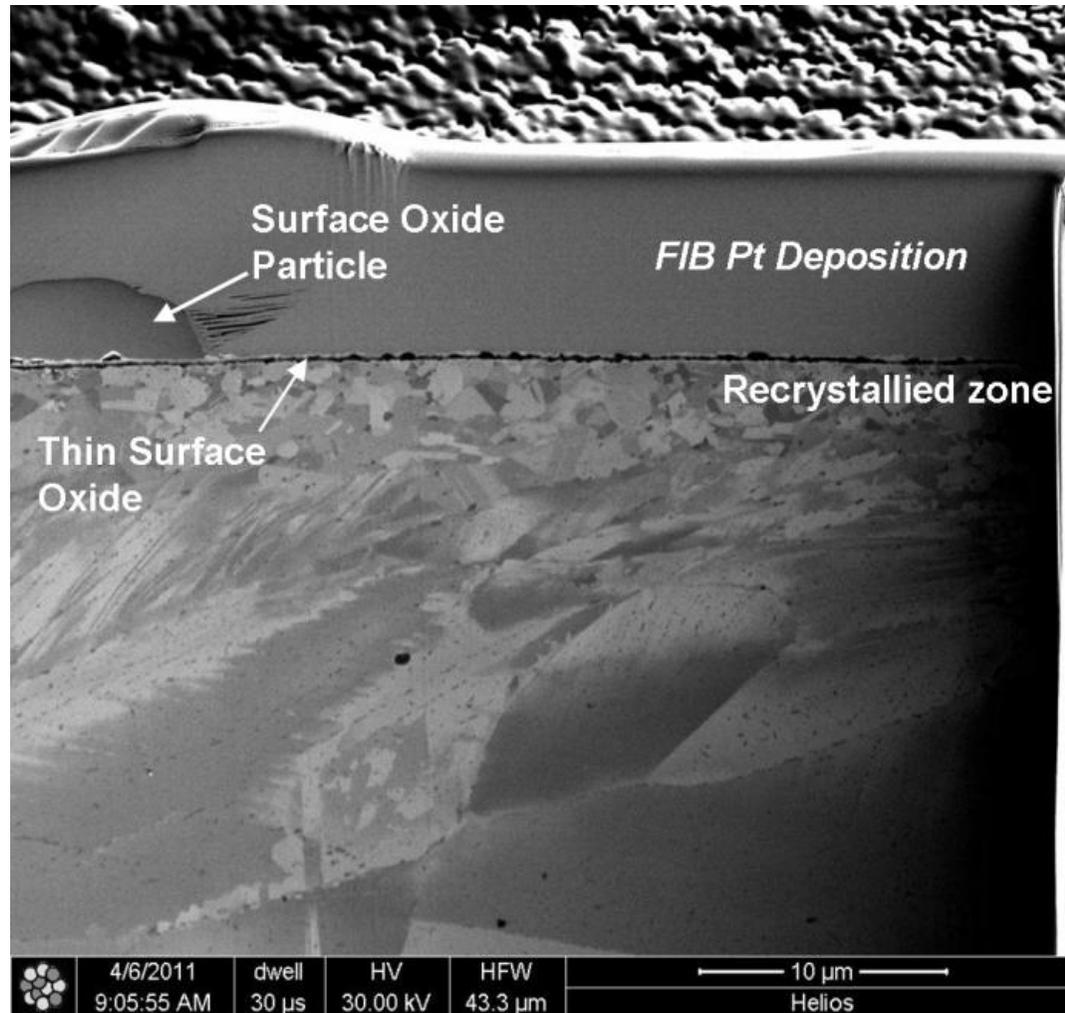
grit #1200 emery paper



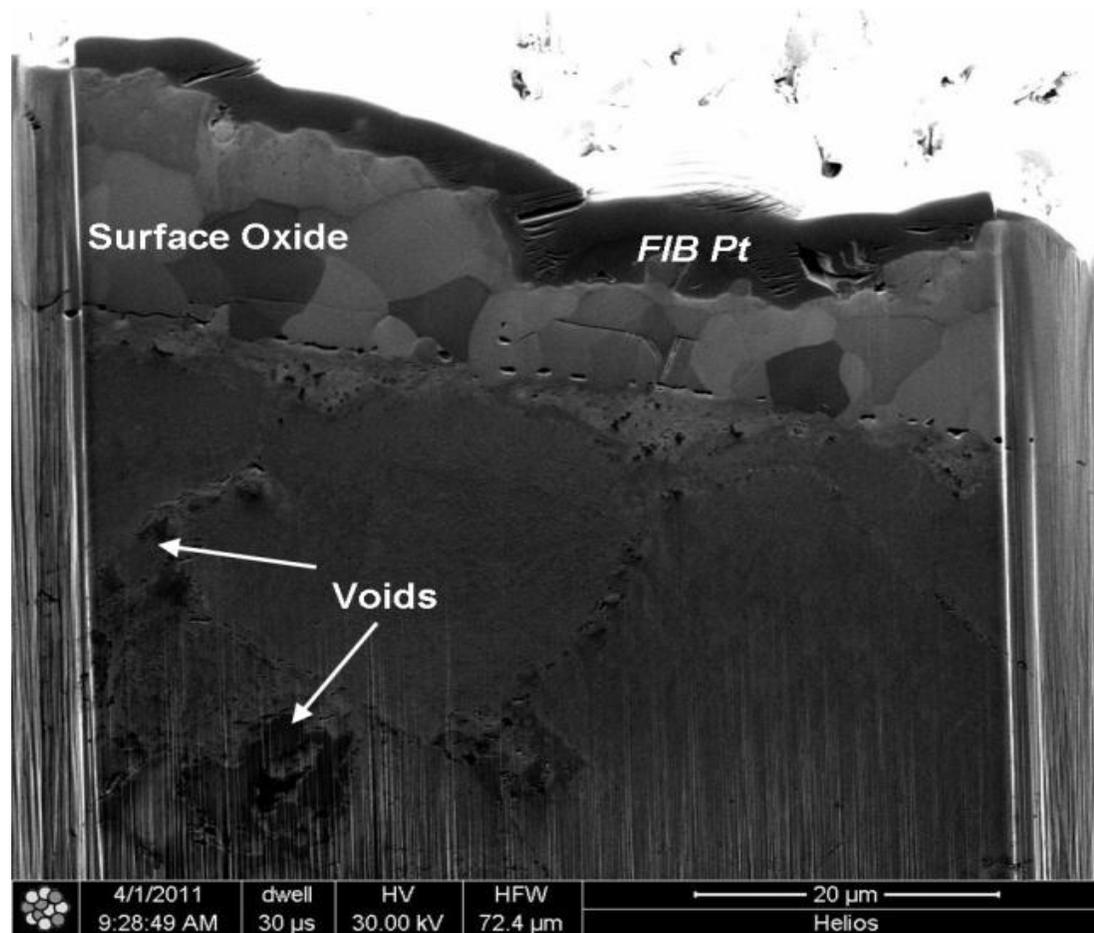
max. ~125 μm



FIB cross-section images of machined sample after 3000h exposure at 650°C



FIB cross-section image of #600 grit sample after 3000h exposure at 650°C

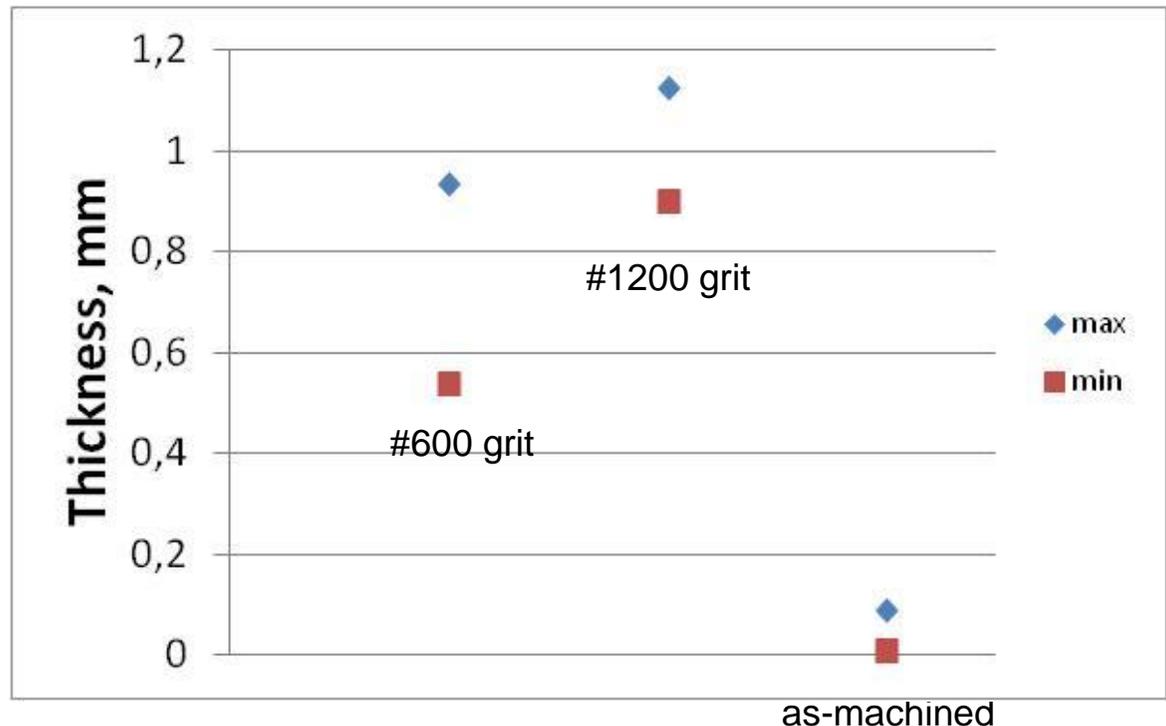
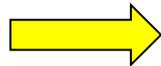


Summary of weight changes and oxide thicknesses (max. value from SEM) for exposed samples at 650°C

Alloy	Surface modification	Oxide thickness and Weight change, 1000h		Oxide thickness and Weight change, 3000h	
		Oxide thickness	Weight change	Oxide thickness	Weight change
316L	machined	2 μm	0.00171 g/cm ²	5 - 10 μm *	0.00207 g/cm ²
316L	# 600 emery paper	60 μm	0.00622 g/cm ²	104 μm	(-) 0.00520 g/cm ²
316L	#1200 emery paper	80 μm	0.00582 g/cm ²	125 μm	(-) 0.00518 g/cm ²

* measured from patchy oxide island

Linear prediction of the oxide thickness ranges after 3 years exposure at 650°C for the tested samples (calculated from observed min. and max. values after 3000h exposure)



Conclusions (1/2)

- Surface treatment could improve corrosion resistance of stainless steels under certain conditions, as seen in the 316L samples.
- A thin and apparently protective oxide film formed on surface cold worked (machined) 316L sample at 650°C.
- The protectiveness of this thin layer extended at least up to 3000 h.
- The thin oxide film had a maximum chromium concentration of about 50% (or more).
- The machining introduced significant sub-surface plastic deformation, which led to re-crystallization and grain-refining.
- The increased grain boundaries area in the fine grained layer could act as short circuit paths for outward diffusion of Cr.
- This helps to provide sufficient Cr near the surface to maintain a continuous Cr-rich layer during SCW exposure.

Conclusions (2/2)

- In samples with ground surfaces, the oxides were thicker and started peeling locally during the 3000 h exposure.
 - The thicker oxides of the ground specimens showed lower Cr enrichment than the thin oxide of the machined specimen.

- It should be noted that the tests may not be representative of long-term service in all aspects.
 - In particular, the protective nature of chromium diffusion in cold worked layers could diminish in time, at least in alloys with relatively low Cr content such as in 316L.

- However, the apparently strong impact of cold working on the early formation of an even Cr-rich oxide can be seen as a promising result.

Thank you for your attention!