Characterization of oxide scales formed on Alloy 82 in nominal PWR primary water at 340 degrees C and in hydrogenated steam at 400 degrees C

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SCC of Alloy 82

Initiation tests performed in hydrogenated steam at 400°C

- SCC initiation is difficult in Alloy 82 → test acceleration
- Previous results on Alloy 600 show that :
  - Stress corrosion cracks exhibit similar features
  - Trend between heats is respected
  - Same activation energy for initiation

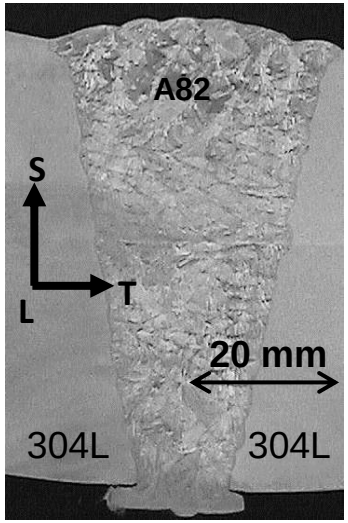
Hydrogenated steam 400°C
vs
Primary water 360°C

1. Representativeness of SCC tests in hydrogenated steam

2. Description of the oxide scale formed on Alloy 82
   - Effect of weld (composition and/or welding process)
   - Effect of thermal treatment

Materials and oxidation conditions

	C	Si	Mn	P	S	Cu	Mo	Ni	Cr	Co	Nb	Ti	Fe
RCC-M	<0.1	<0.5	2.5/3.5	<0.03	<0.015	<0.5	-	>67	18/22	<0.1	2/3	<0.75	<3
Weld A	0.025	0.07	2.57	0.004	<0.001	<0.01	-	71.7	19.12	0.04	2.41	0.1	3.07
Weld B	0.014	0.17	2.88	0.002	0.017	<0.01	0.05	72.9	18.15	0.01	2.83	<0.01	2.3



Weld	A		B
Welding process	Gas tungsten arc welding (GTAW)		Flux core arc welding (FCAW)
Metallurgical state	As-welded	Thermally-treated 7h - 600°C	As-welded

Oxidation tests performed on coupons with 1 µm mirror finish in stainless steel autoclaves.

HYDROGENATED STEAM

- 400°C
- P_{tot} = 200 bar, $P(H_2)$ = 800 mbar
- 1500h / 2500h

PRIMARY WATER

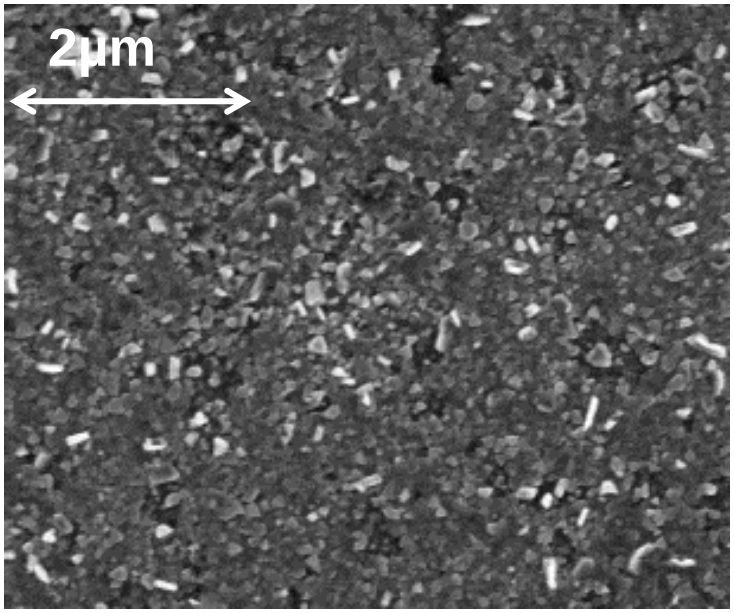
- 340°C
- $[H_2]$ = 37 mL / kg H_2O
- 1500h / 2500h

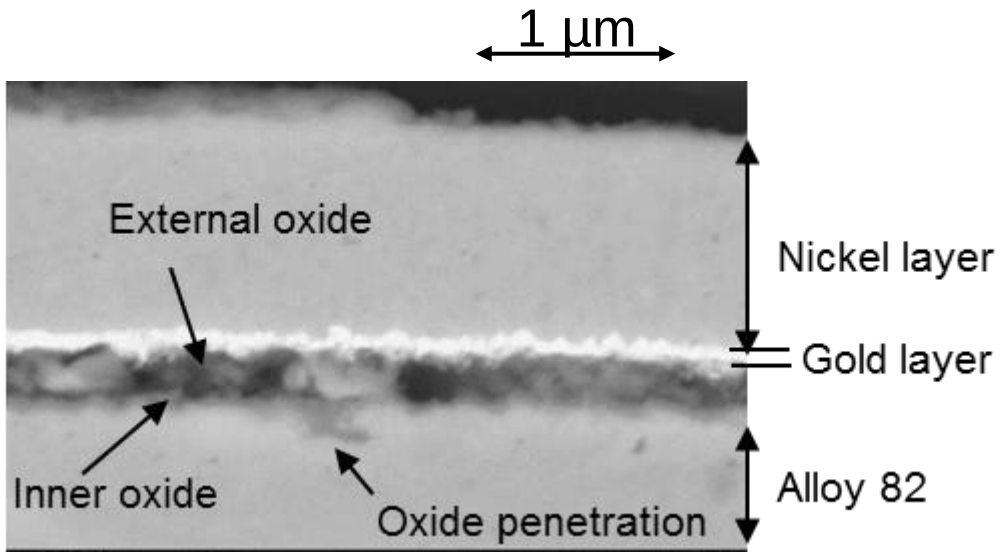
Oxidation in hydrogenated steam at 400°C

Weld	A		B
Welding process	Gas tungsten arc welding (GTAW)		Flux core arc welding (FCAW)
Metallurgical state	As-welded	Thermally-treated 7h - 600°C	As-welded
Oxidation duration (h)	2500	1500/2500	2500

SEM observations

Hydrogenated steam
Weld A – AW – 2500h





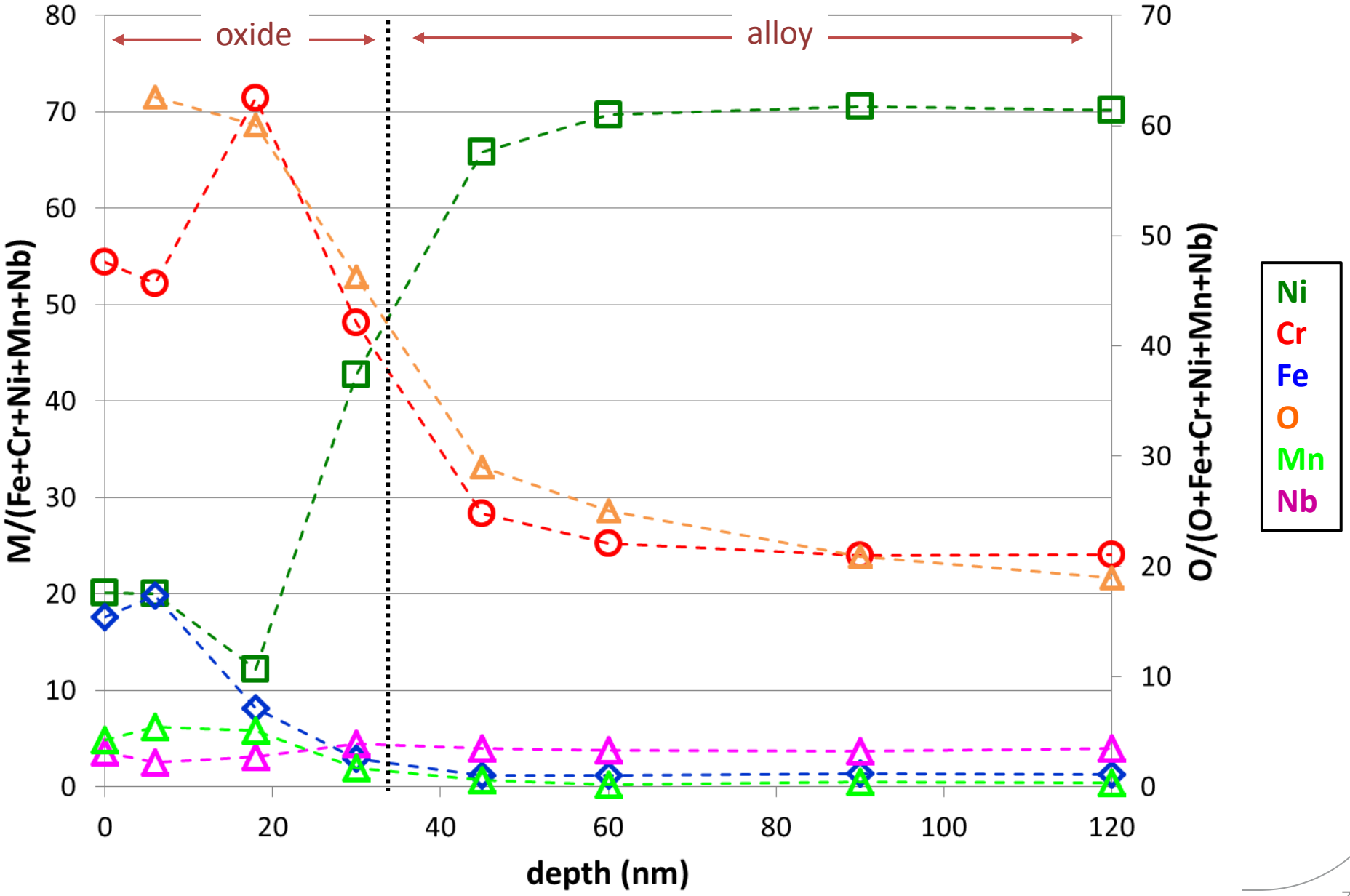
Duplex structure:

- Discontinuous outer layer with pyramidal and platelet-like crystallites
- Continuous inner layer

Oxide penetrations (depth < 500 nm)

XPS depth profiles

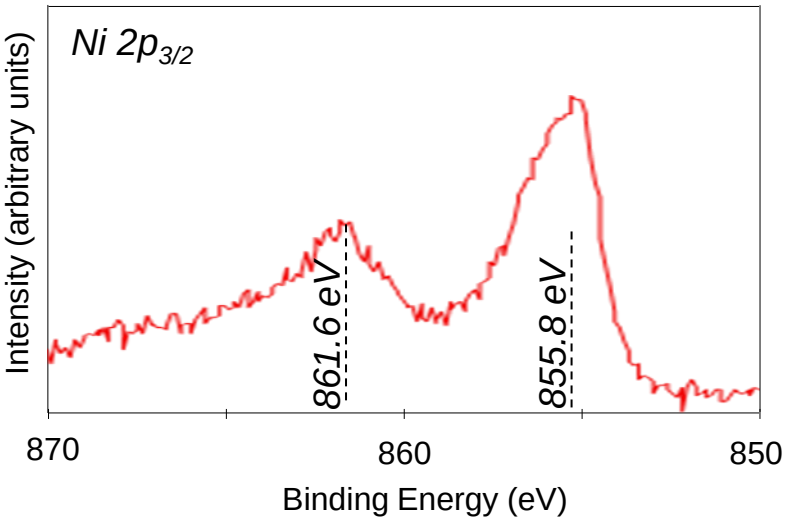
Hydrogenated steam
Weld A – AW – 2500h



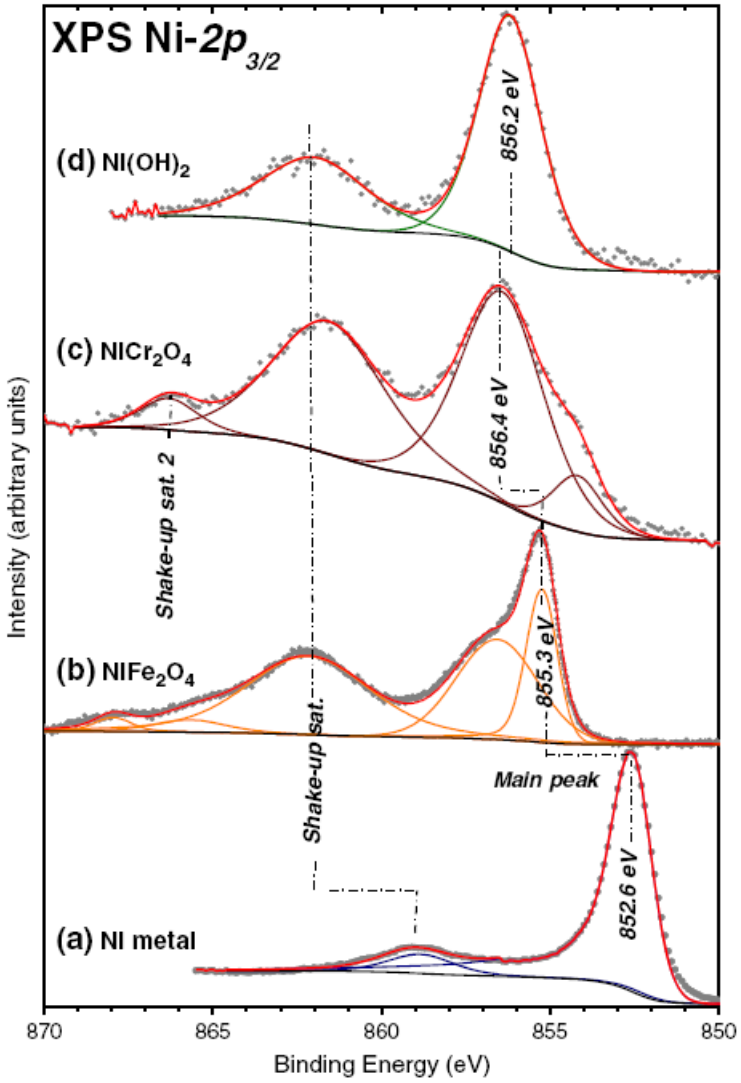
XPS spectra: Ni $2p_{3/2}$

Hydrogenated steam
Weld A – AW – 2500h

Before sputtering



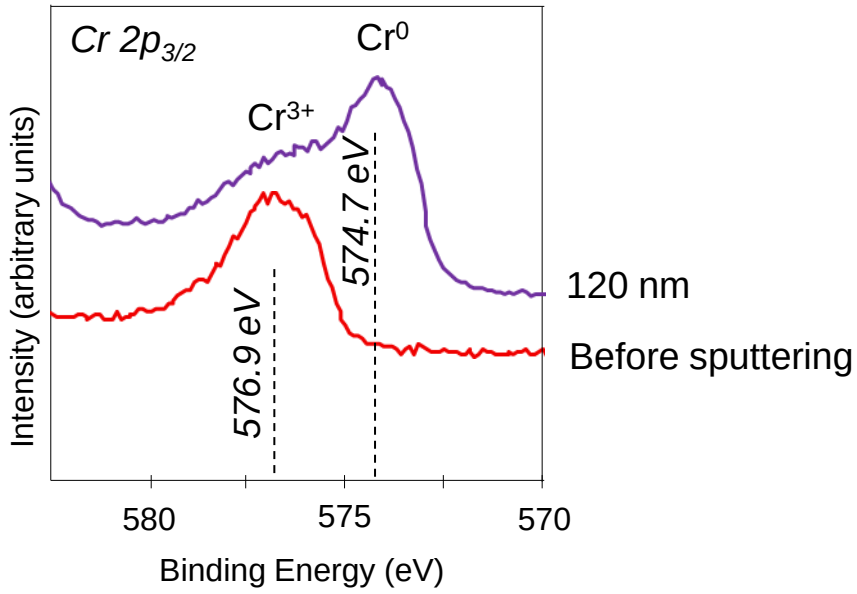
- Shape and binding energies consistent with $NiFe_2O_4$
- $Ni(OH)_2$ cannot be excluded



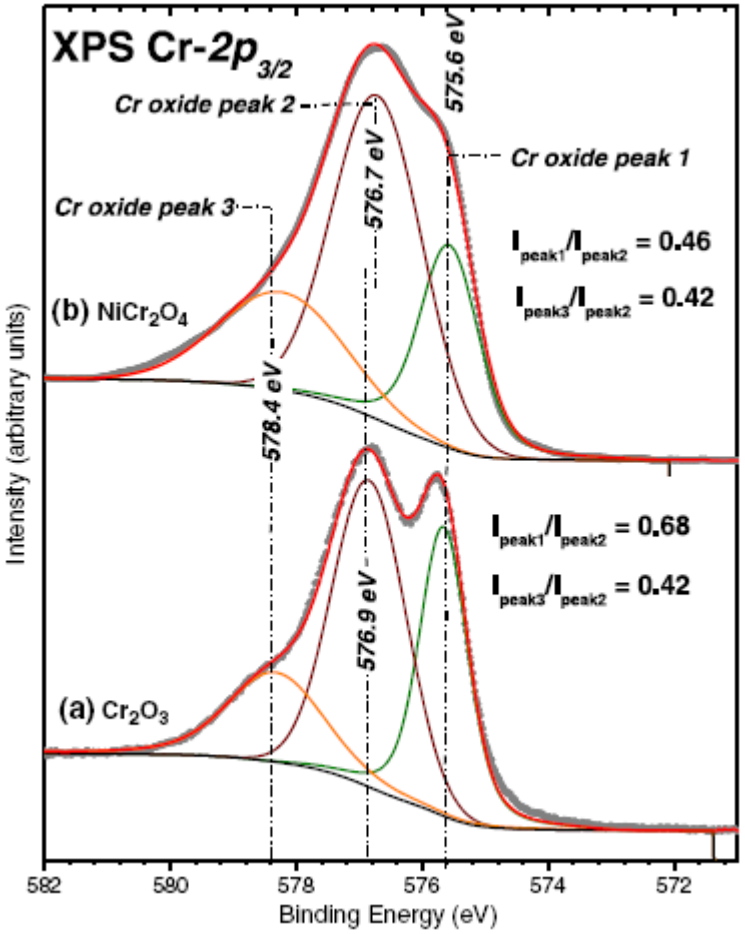
Marchetti et al. (2015)

XPS spectra: Cr $2p_{3/2}$

Hydrogenated steam
Weld A – AW – 2500h



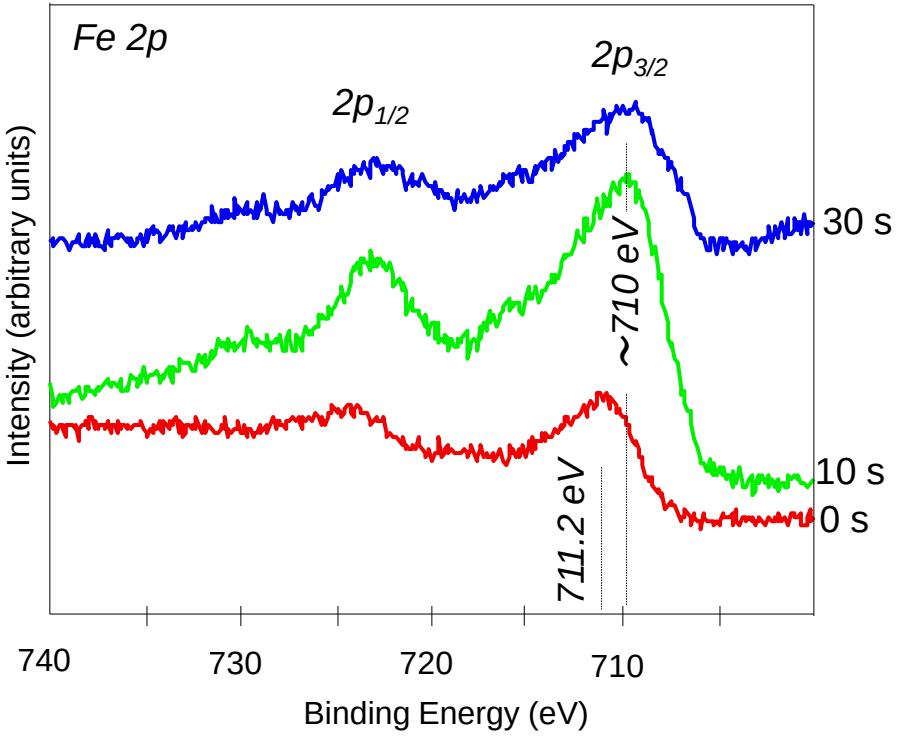
- Before sputtering: hard to distinguish $NiCr_2O_4$ from Cr_2O_3
- Cr with the oxidation state +III is detected for the longest sputtering time

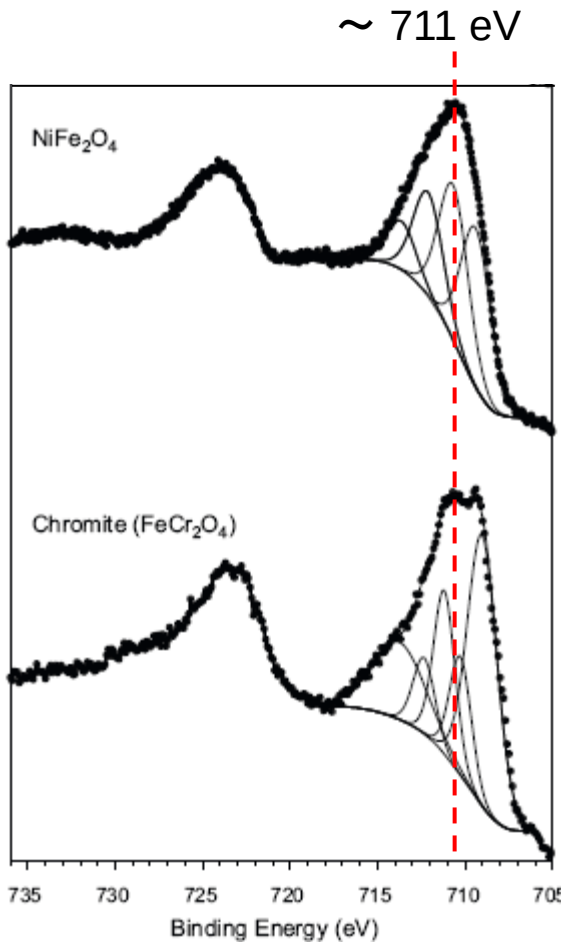


Marchetti et al. (2015)

XPS spectra: Fe 2p

Hydrogenated steam
Weld A – AW – 2500h





Biesinger et al. (2011)

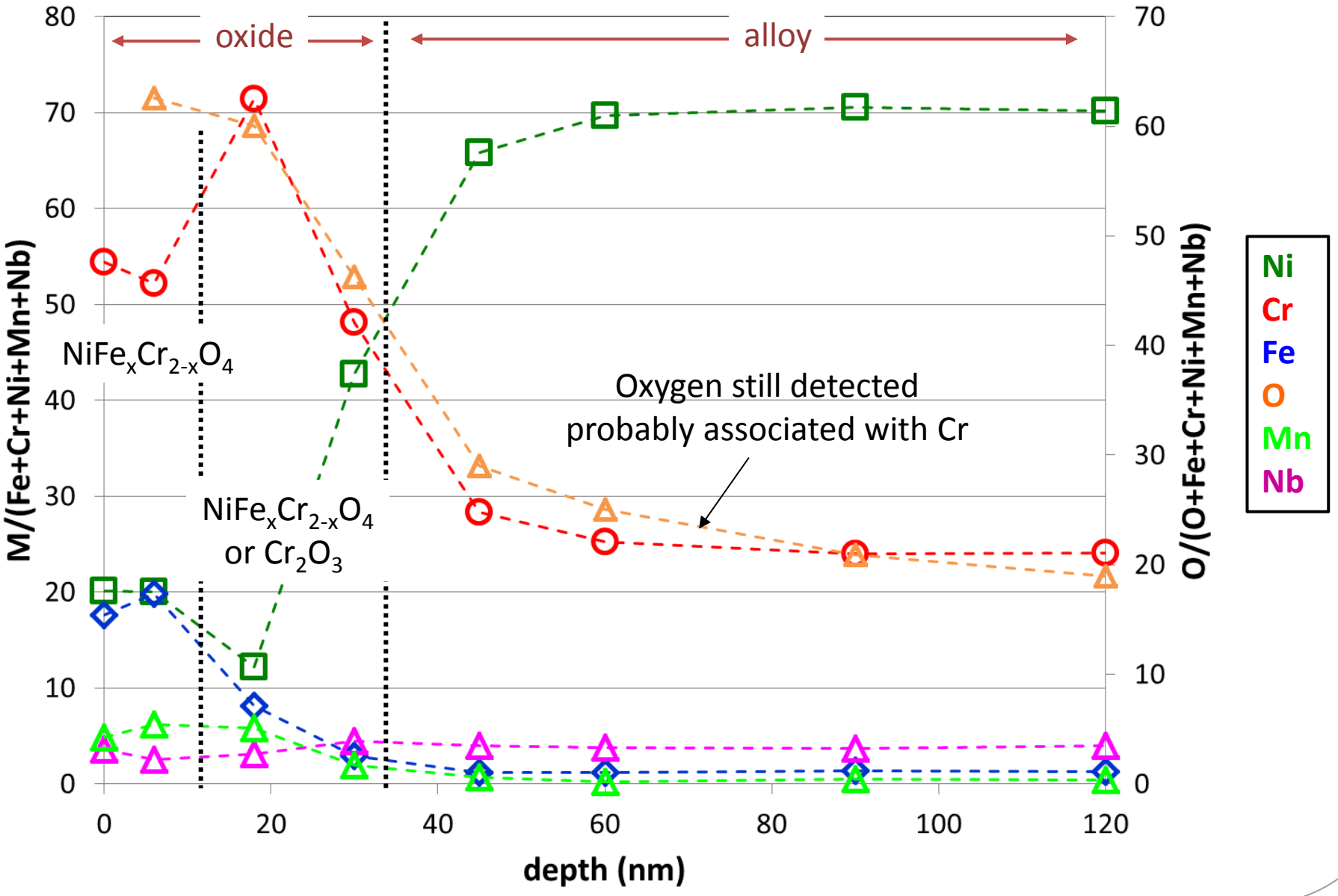
- Before sputtering:

  consistent with $NiFe_xCr_{2-x}O_4$ or $Fe_xCr_{3-x}O_4$

- Slight shift towards lower energies:
  - Fe/Cr ↘ in $NiFe_xCr_{2-x}O_4$? *Allen et al (1989)*
  - Fe (III) → Fe (II)? *McIntyre at al. (1977)*

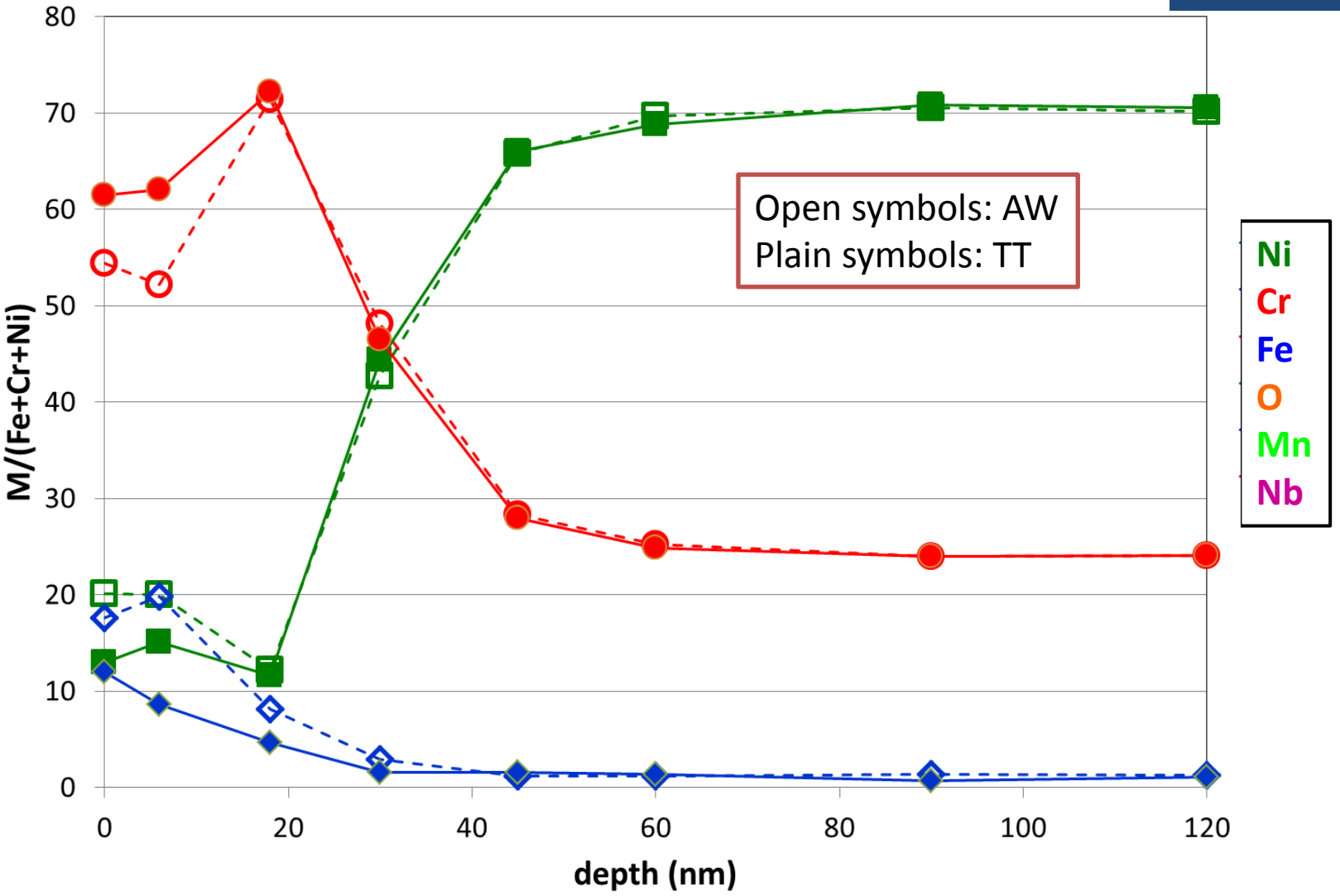
XPS depth profiles

Hydrogenated steam
Weld A – AW – 2500h



XPS depth profiles

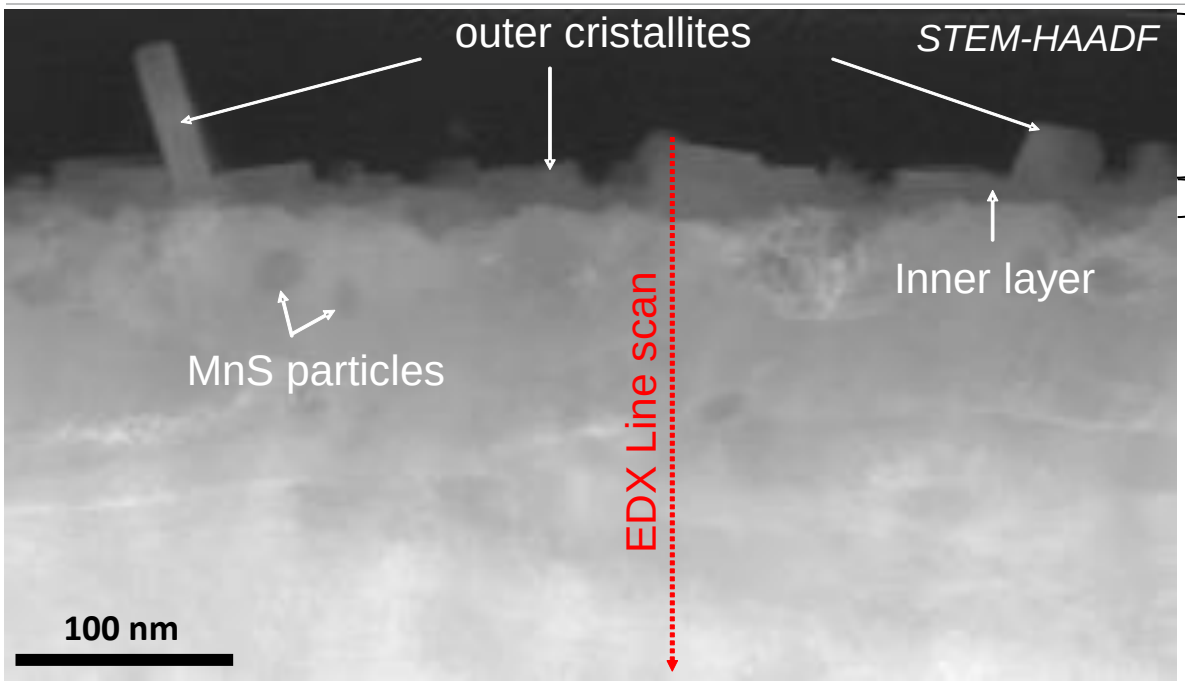
Hydrogenated steam
Weld A – AW – 2500h
Weld A – TT – 2500h



Similar results for all the samples

TEM analyses

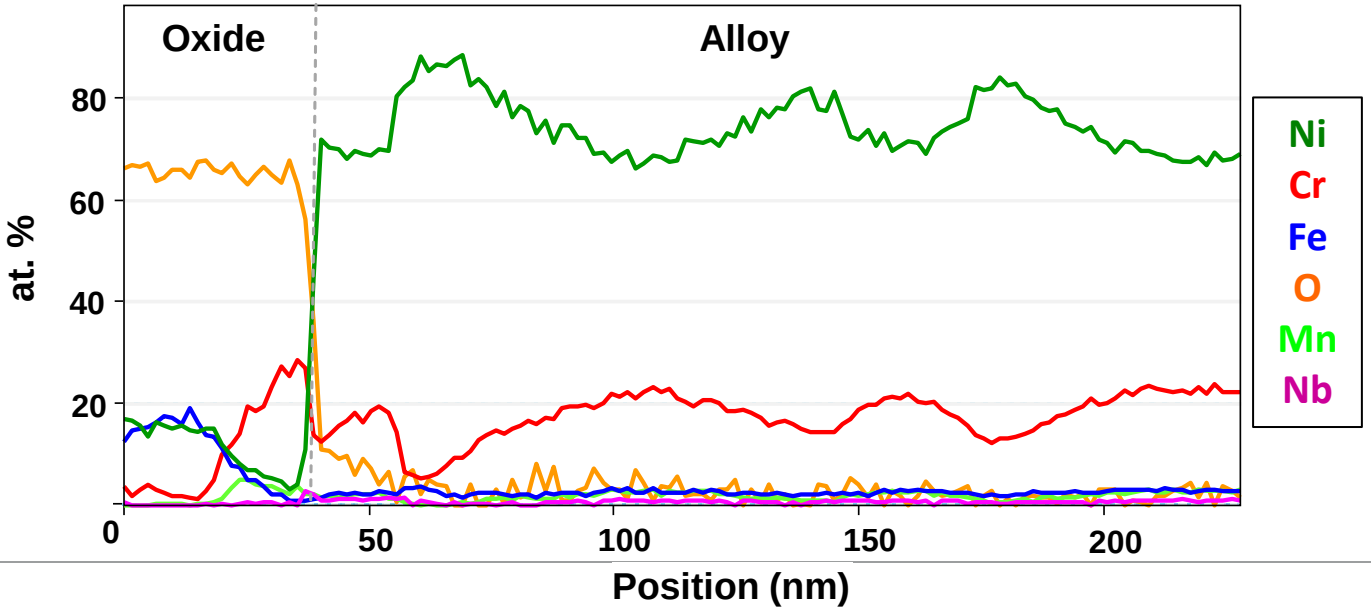
Hydrogenated steam
Weld A – AW – 2500h



Outer layer:
Ni- and Fe-rich cristallite

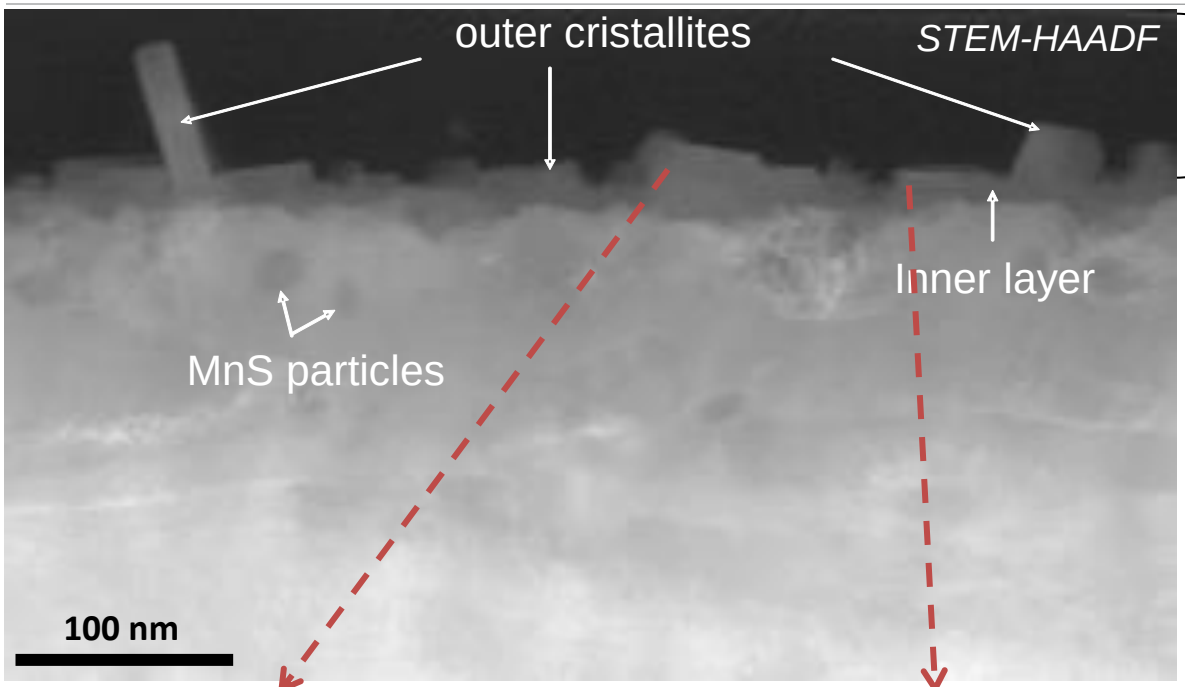
Inner layer:
Cr-rich
Small amounts of Mn

Alloy:
Fluctuation of composition
Strong localized Cr depletion

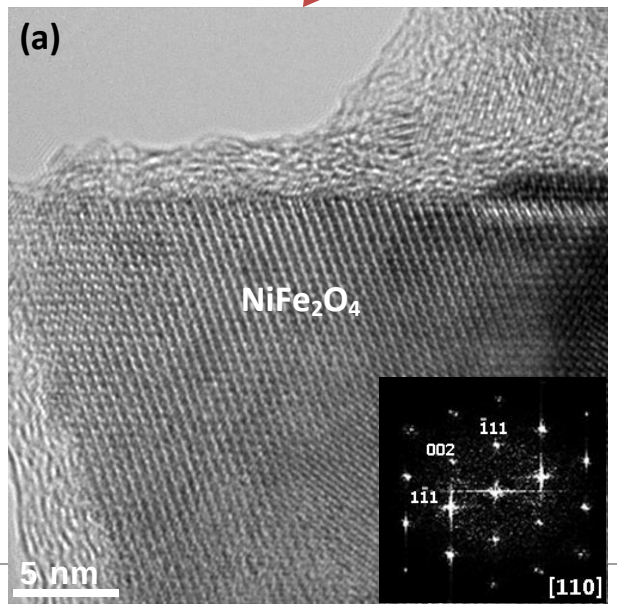


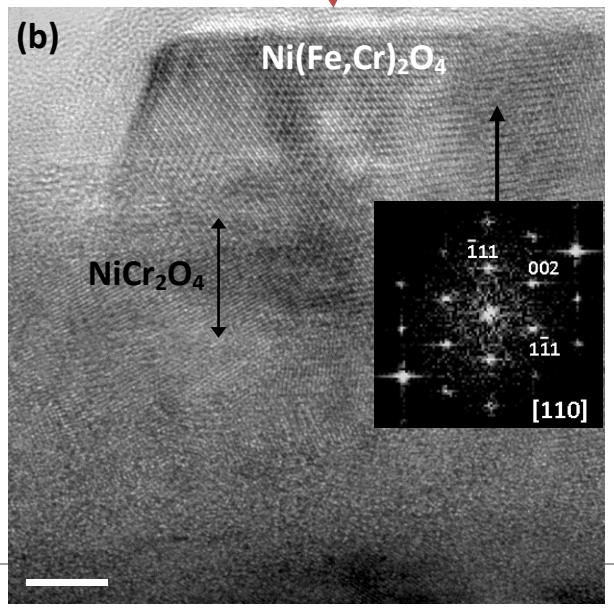
TEM analyses

Hydrogenated steam
Weld A – AW – 2500h



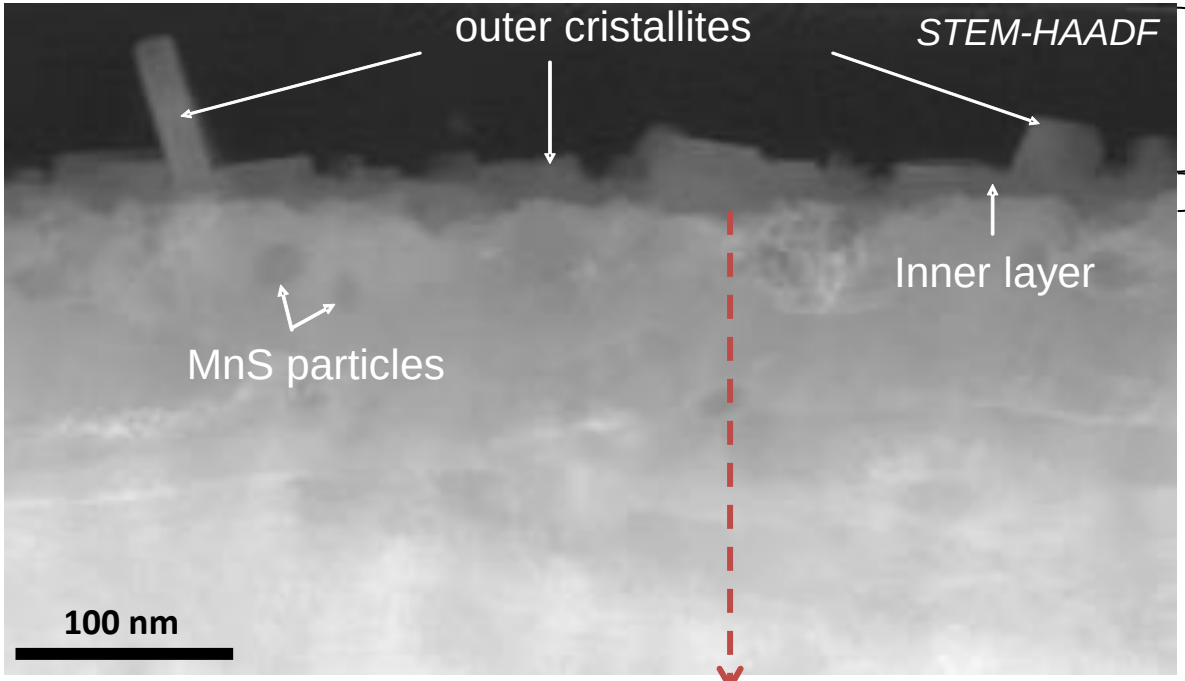
Outer layer:
$NiFe_2O_4$ / $NiFe_xCr_{2-x}O_4$





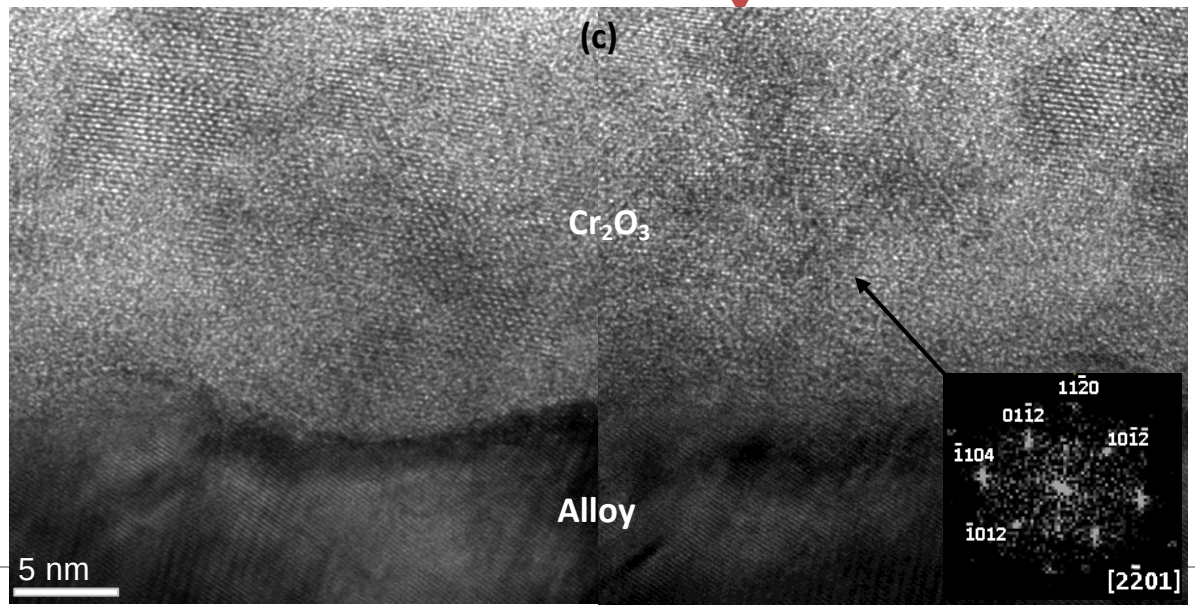
TEM analyses

Hydrogenated steam
Weld A – AW – 2500h



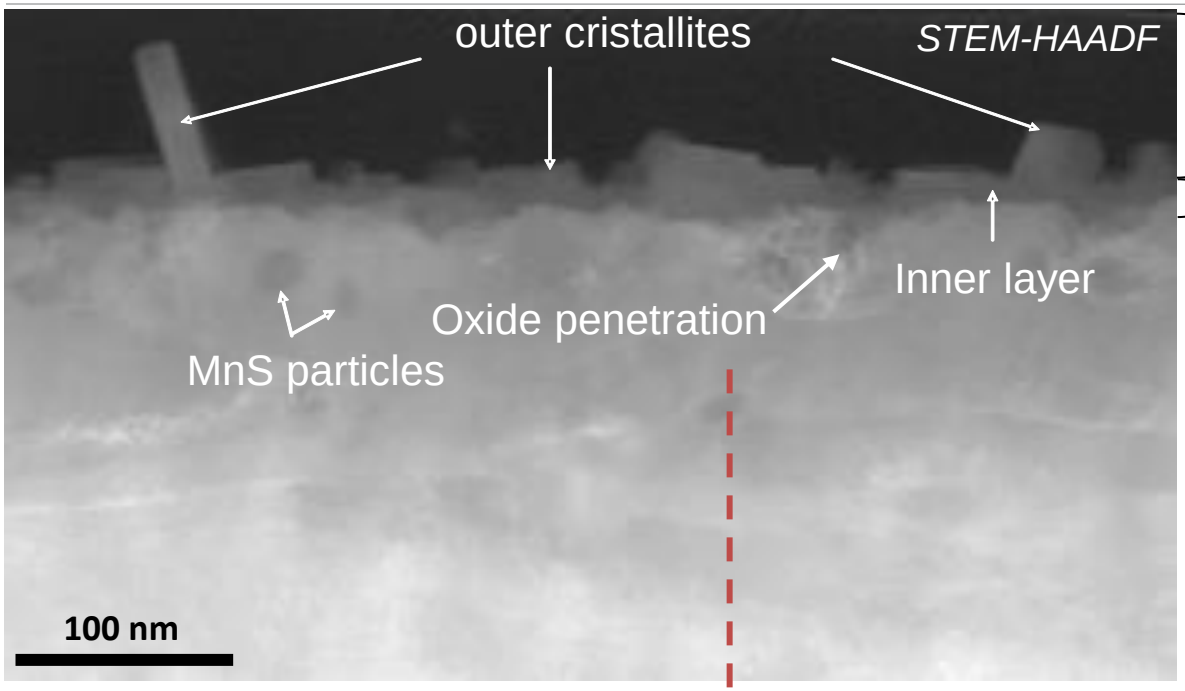
Outer layer:
$NiFe_2O_4$ / $NiFe_xCr_{2-x}O_4$

Inner layer:
- $NiCr_2O_4$
- Cr_2O_3



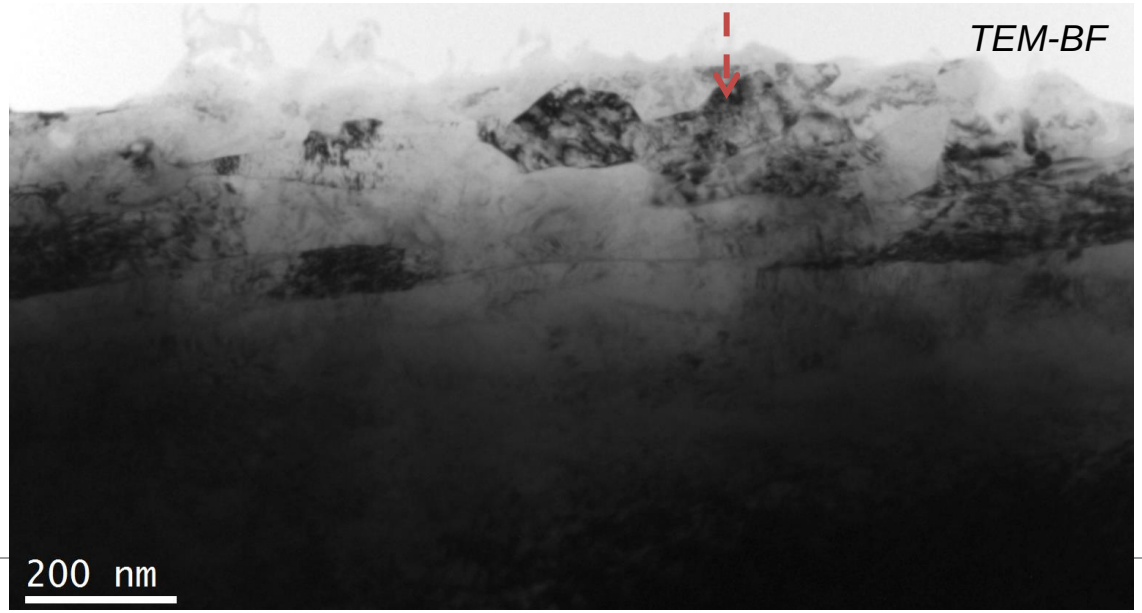
TEM analyses

Hydrogenated steam
Weld A – AW – 2500h



Outer layer:
$NiFe_2O_4$ / $NiFe_xCr_{2-x}O_4$

Inner layer:
- $NiCr_2O_4$
- Cr_2O_3



Alloy:

Recrystallized sub-layer

Thickness: 150 – 300 nm

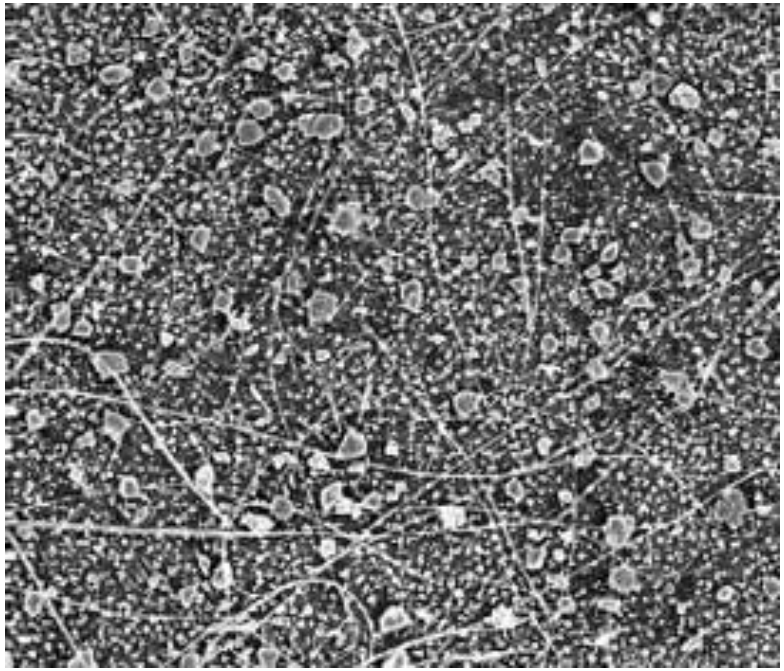
Nanograins: varying composition

Oxidation in primary water at 340°C

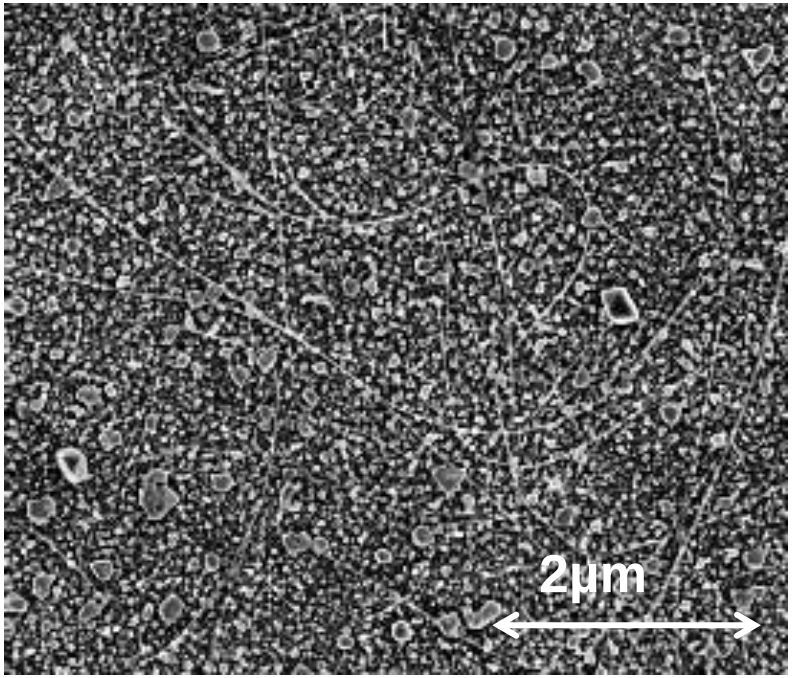
Weld	**A**	
Welding process	Gas tungsten arc welding (GTAW)	
Metallurgical state	As-welded	Thermally-treated 7h - 600°C
Oxidation duration (h)	1500	1500

SEM observations

As-welded



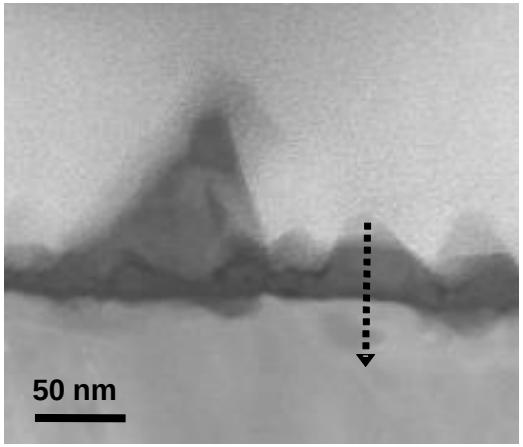
Heat-treated

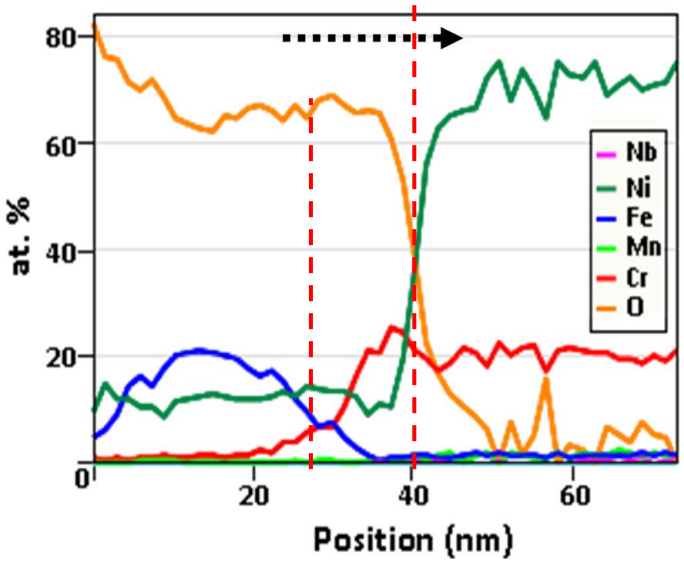


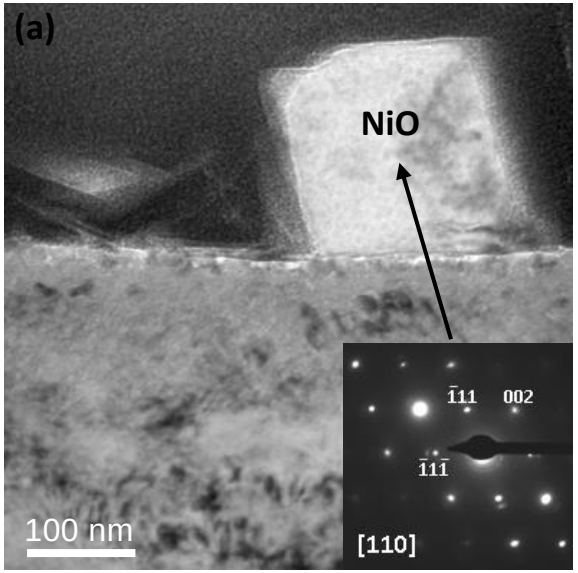
Discontinuous outer layer with pyramidal crystallites and filaments

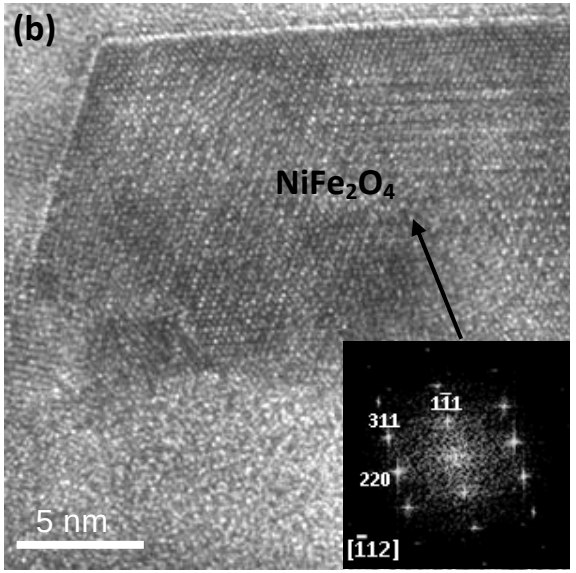
Heat-treated sample

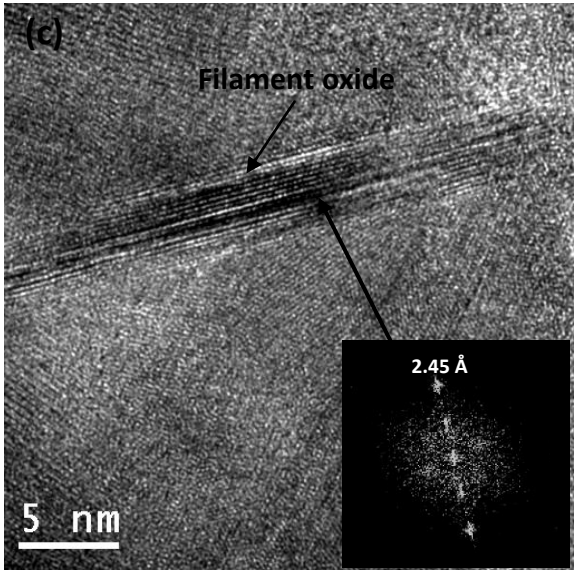
Primary water
Weld A – TT – 1500h







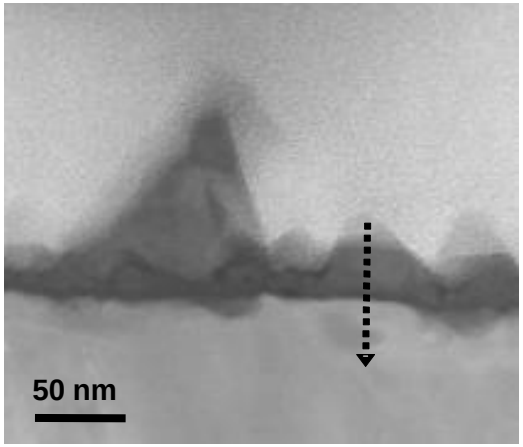


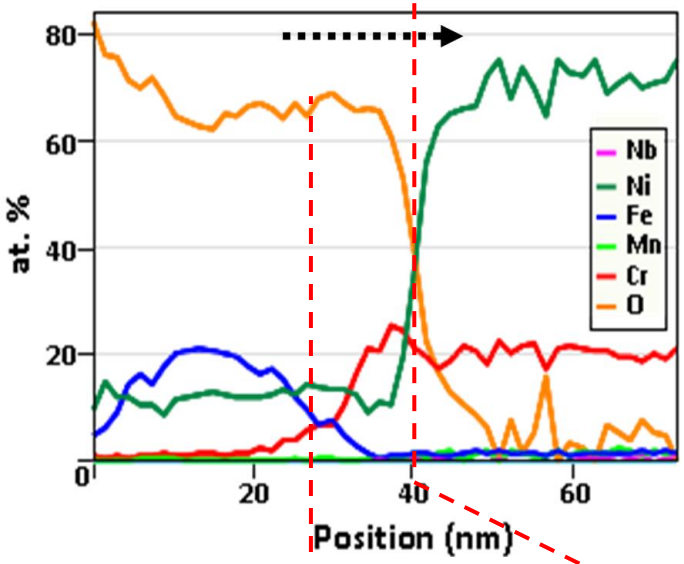


Outer layer
- $NiFe_2O_4$
- NiO
- filament

Heat-treated sample

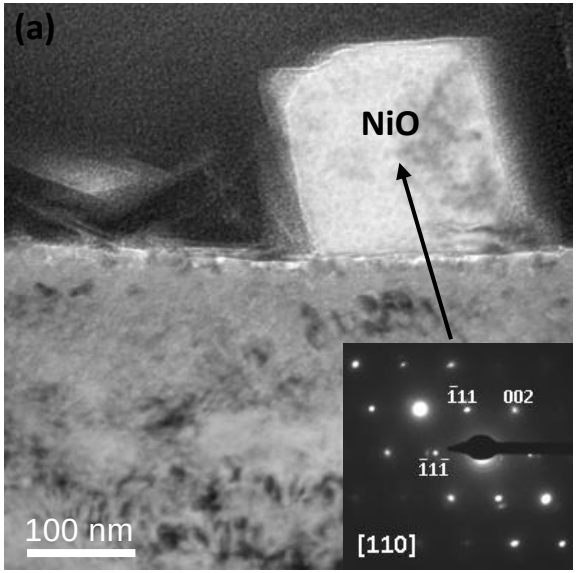
Primary water
Weld A – AW – 1500h

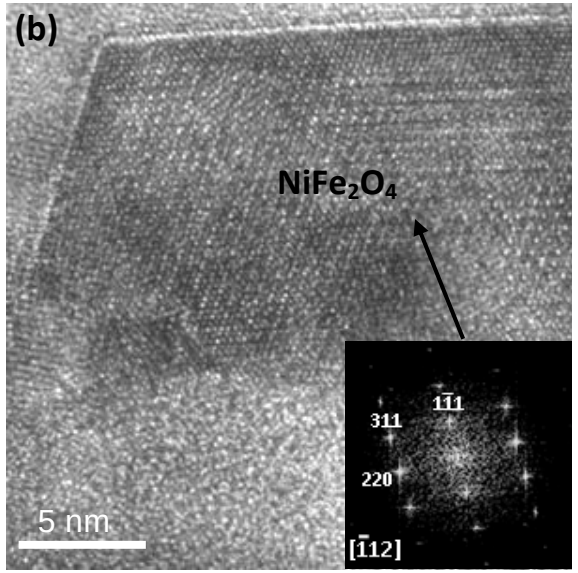


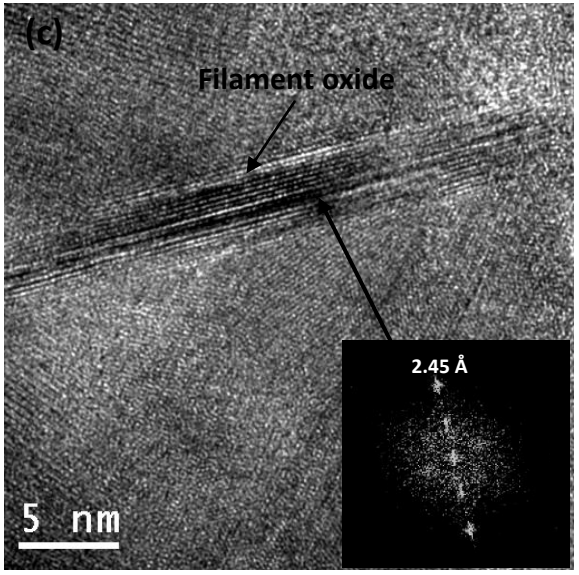


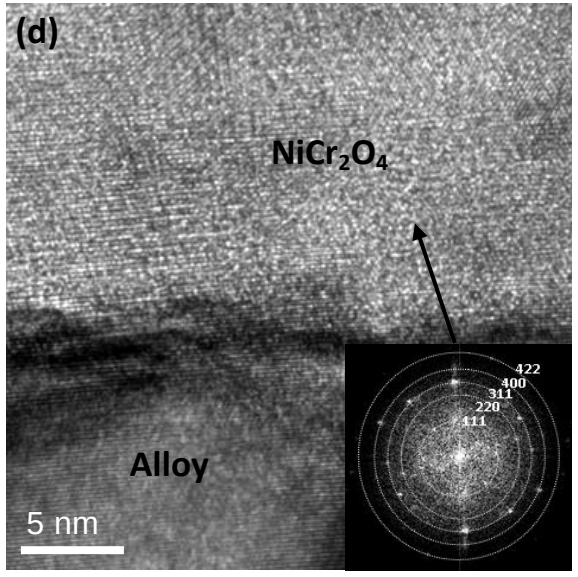
Outer layer
- $NiFe_2O_4$
- NiO
- filament

Inner layer
- $NiCr_2O_4$



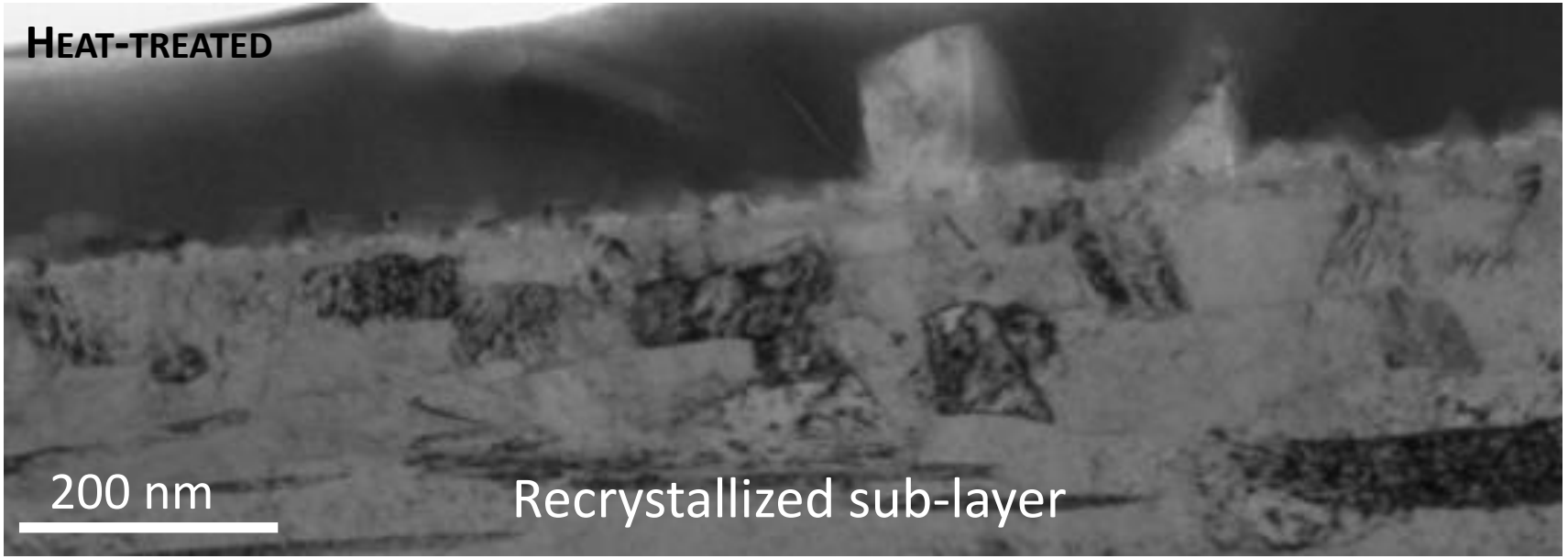


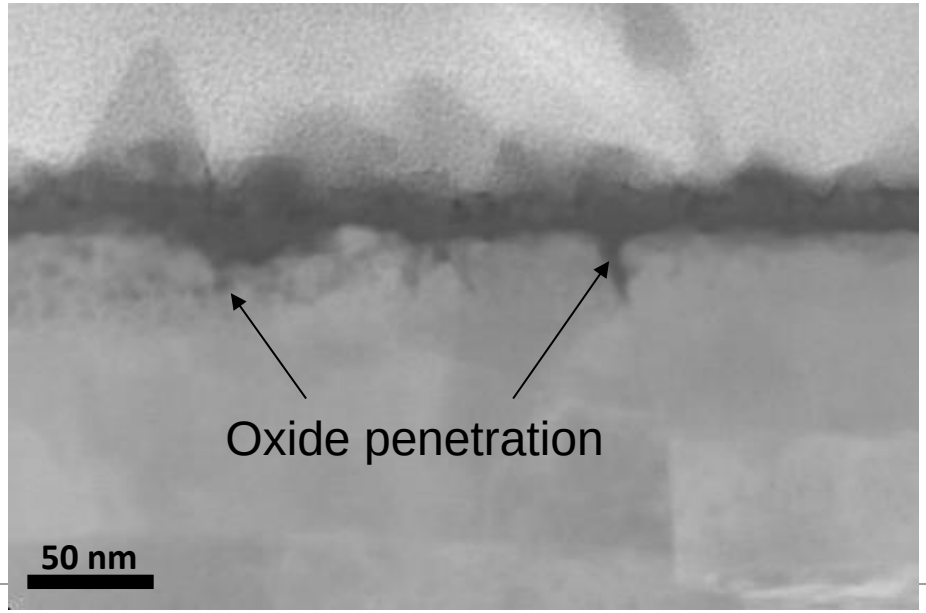




Heat-treated samples

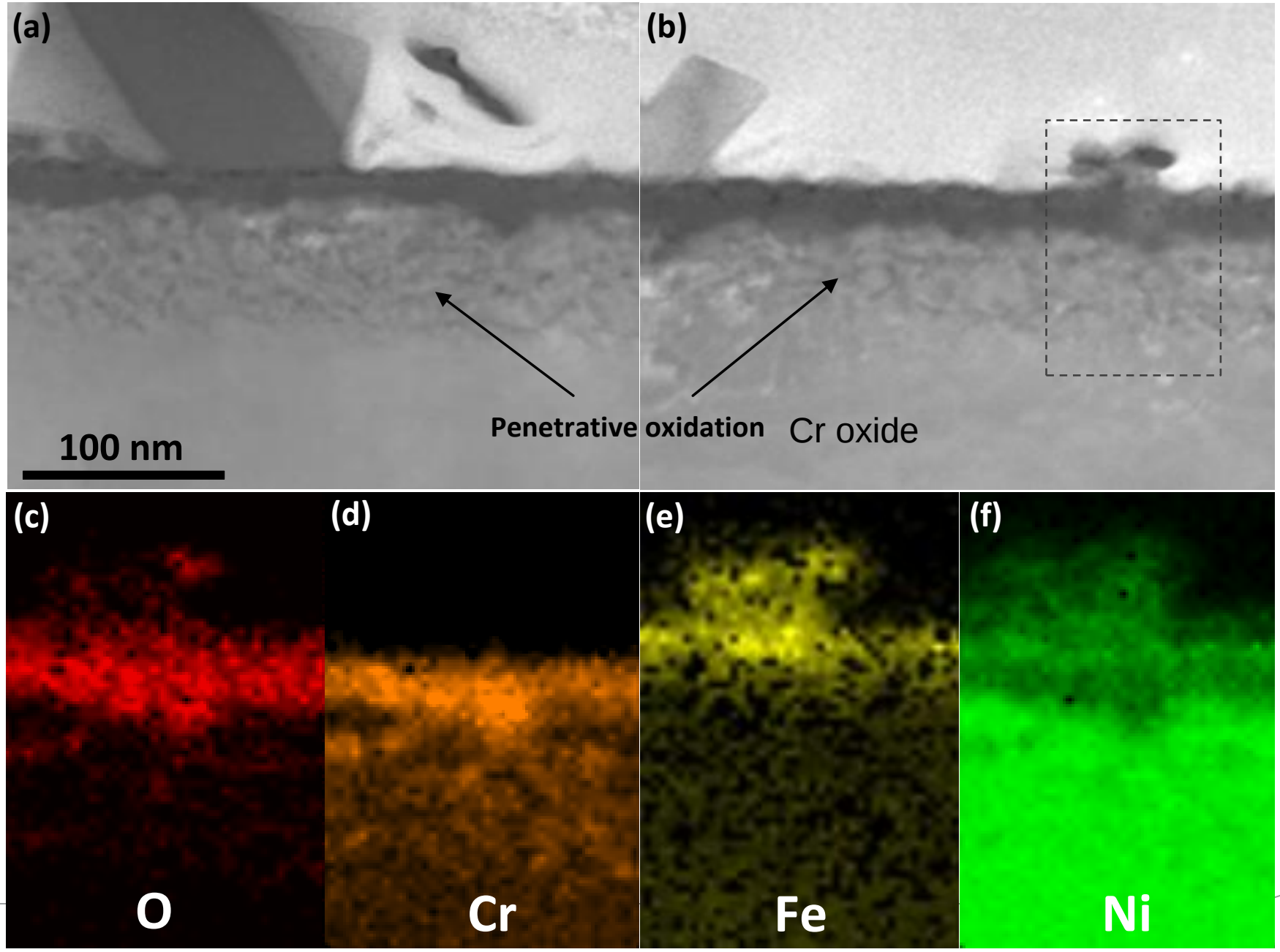
Primary water
Weld A – TT – 1500h





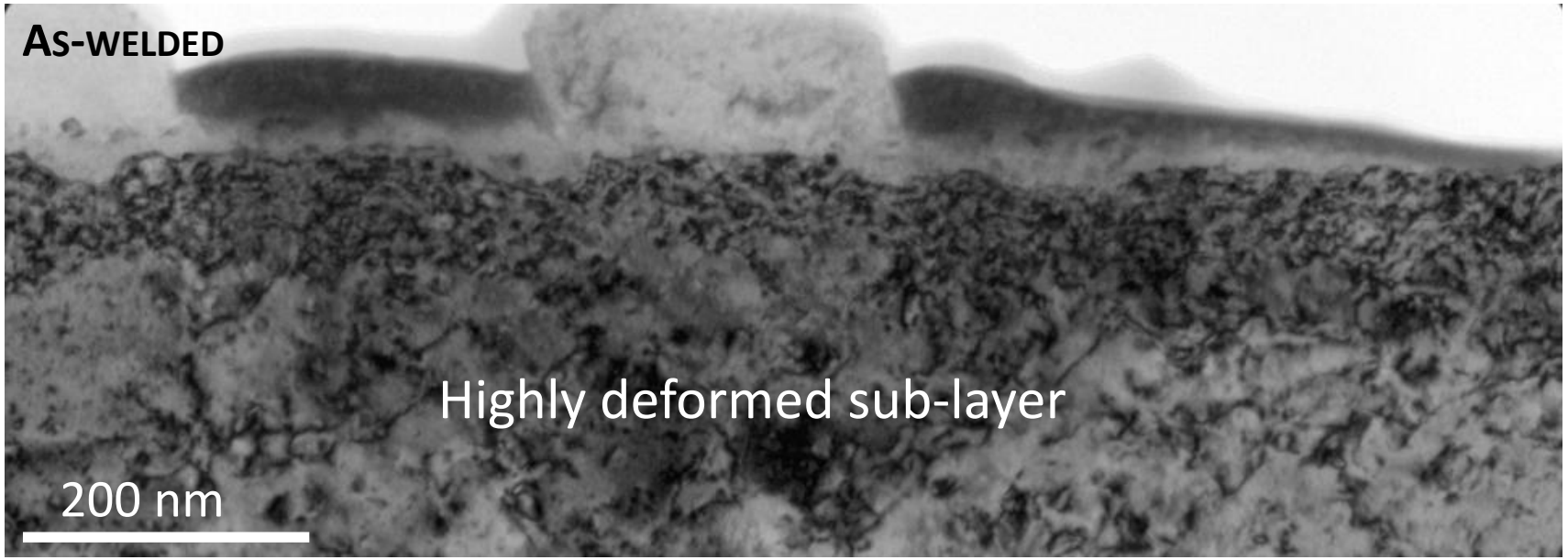
As-welded sample

Primary water – 1500h



As-welded sample

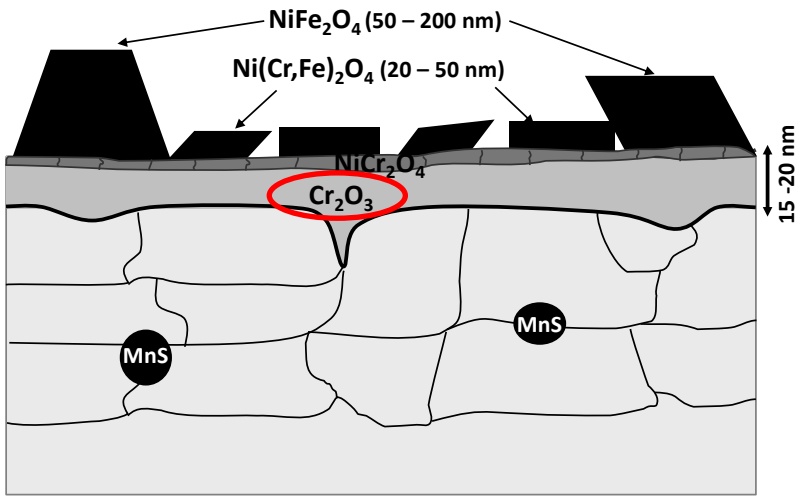
Primary water – 1500h



Summary

HYDROGENATED STEAM – 400°C

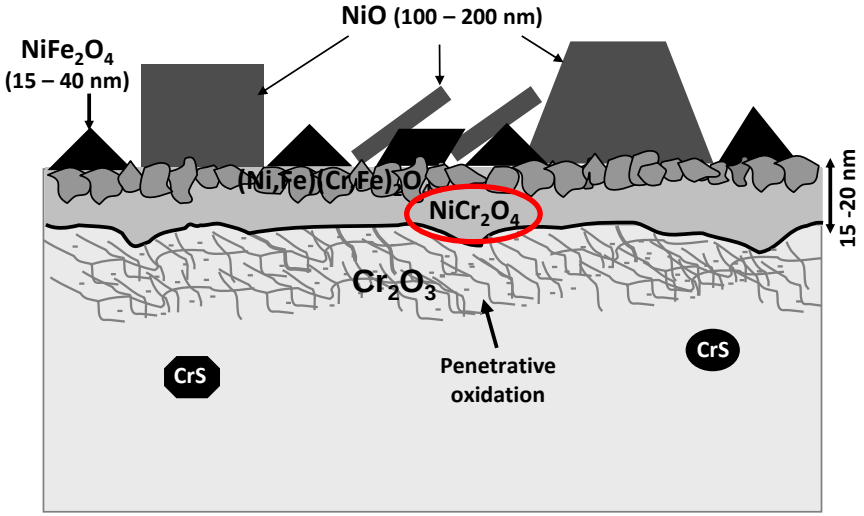
All samples



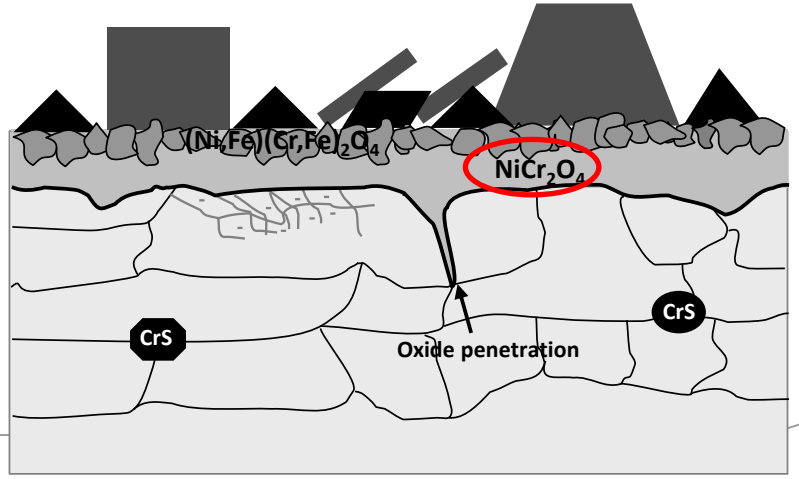
- Similar oxidation kinetics
- Duplex Cr-rich inner layer:
  - $NiCr_2O_4$ in primary water
  - Cr_2O_3 in hydrogenated steam
- Oxide penetrations

PRIMARY WATER – 340°C

As-welded



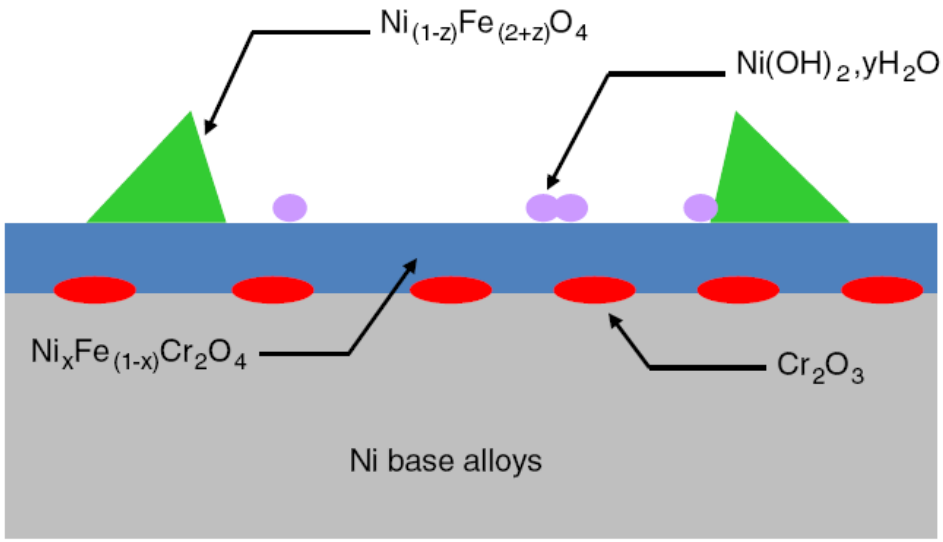
Heat-treated



Conclusions (1/2)

- Environment:

→ Surface oxide layer not strictly identical but consistent with literature data



Marchetti et al. (2015)

→ Similar oxidation tests performed on 304L SS show a difference in the oxidation kinetics but not in the oxide structure

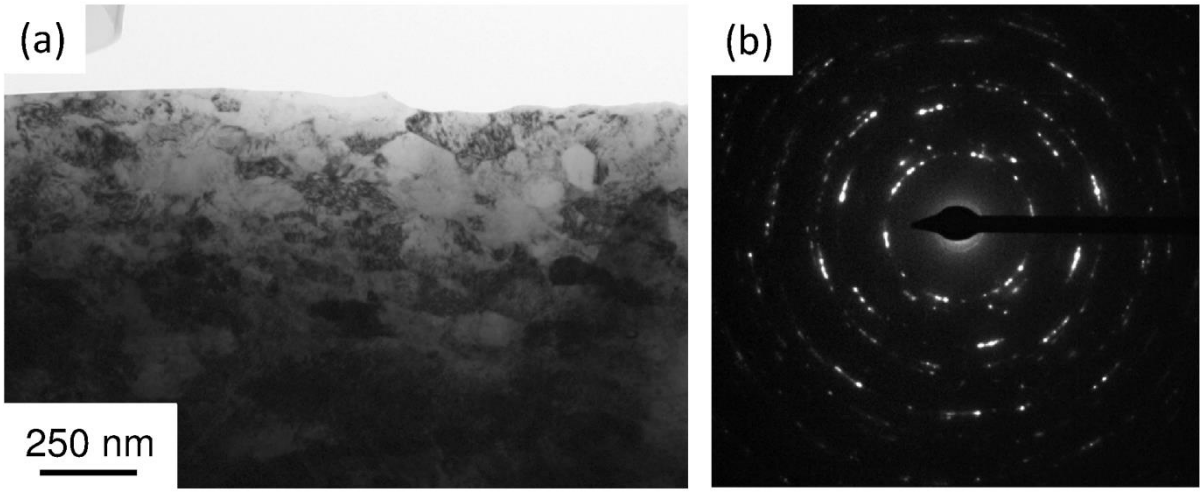
Cissé et al., JNM (2012)

Conclusions (2/2)

- Alloy microstructure:
  - For a given environment, no effect of weld composition, welding process or thermal treatment on the oxidation kinetics and oxide structure
  - Different sub-surface states: recrystallized or high density of dislocations
    - No effect on the continuous inner layer
    - But the morphology of oxide penetration strongly differs

Origin of the recrystallized layer?

As-prepared, non oxidized sample



→ Machining by EDM + grinding + mirror polish

Thank you for your attention