Business from technology

SKY

Material exposures in Joutseno Recovery Boiler

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VTT

Objective and studies performed

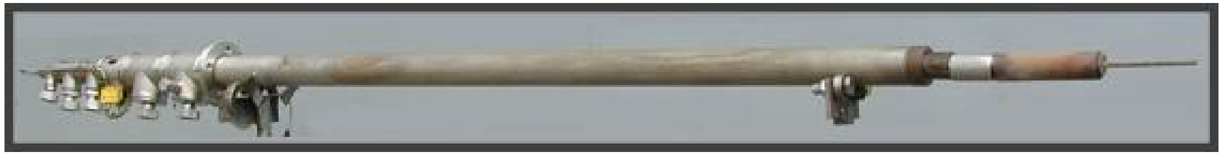
Objective of the work was to study the corrosion performance of various superheater tube materials in recovery boilers at high material temperatures.

Materials selected for the study were 347H, AISI310, HR11N, SAN28, Super 625 and SAN69. Two material samples in the form of rings having a wall thickness of about from 2.7 mm to 2.9 mm were prepared from each material.

Full scale material exposures were carried out in Joutseno RB. Two identical cooled probes 6 material samples in each were exposed in the boiler for a time of one month (600h). Nominal material temperatures on the exposed side of each probe were 530°C and 570°C (concurrent SH material temperature reported to be less than ~ 495°C).

Post exposure the rings were mounted in resin on the site and prepared in laboratory to metallographic cross sections using ethanol as grinding medium. Cross sections were characterised in detail using environmental scanning microscope FEI XL 30 ESEM. Elemental analyses performed were used for predictive calculations using FactSage 6.1.

Probe tests



Air- and water-cooled probes used imitate the behaviour of superheater tubes. The surface temperatures of the probes vary depending on the direction of the flue gas flow.

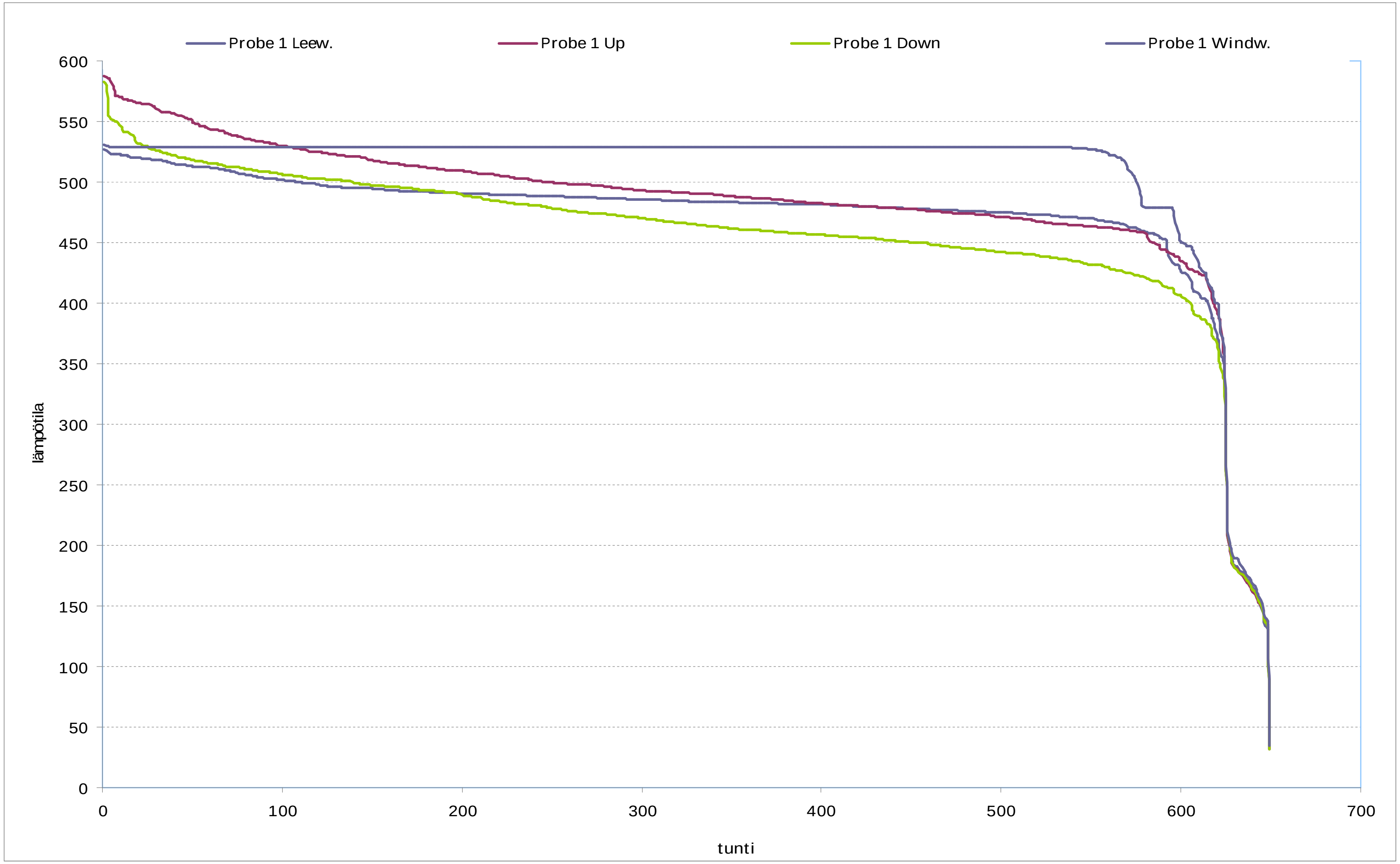
The windward temperature is maintained constant by adjusting the cooling rate and the temperatures on other sides change when deposits are formed.

In this particular case, 10-15 mm hard deposit acing as insulator did rapidly form on the flue gas side causing that material temperature on other locations did rise (up to 590^{o}C for few hours). See the next slides.

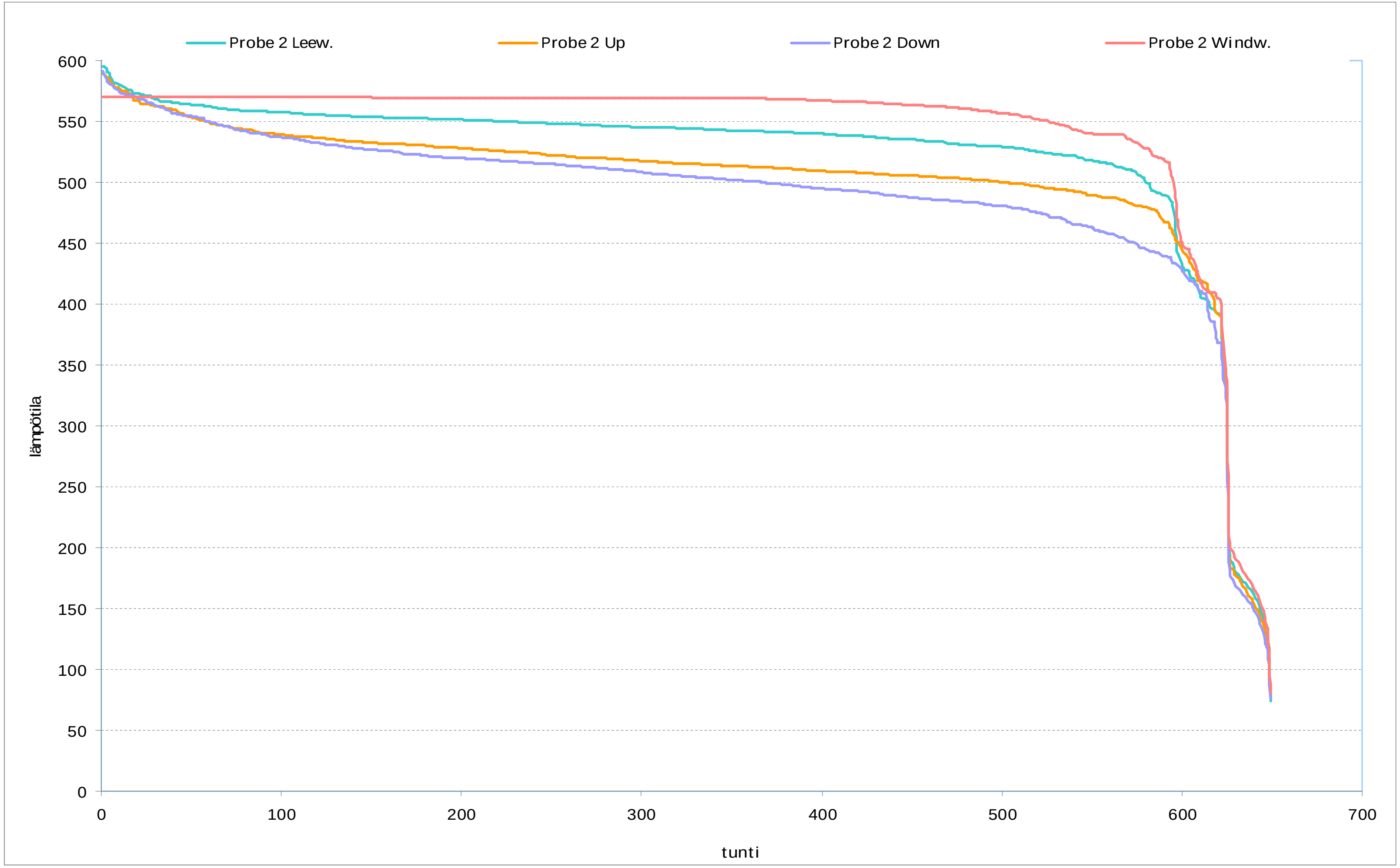
This problem was corrected by changing the regulating thermocouple from windward side to up side (by 90 degrees).

Boiler was shut-down in the middle of the test run. Then, and when the probe was taken out, material falling from the roof etc. did harm few samples (Probe 1: SAN 69, AISI 310, 347H; Probe 2: Super 625, AISI 310; wall thickness measurements of no use).

Temperature stability curve for Probe 1



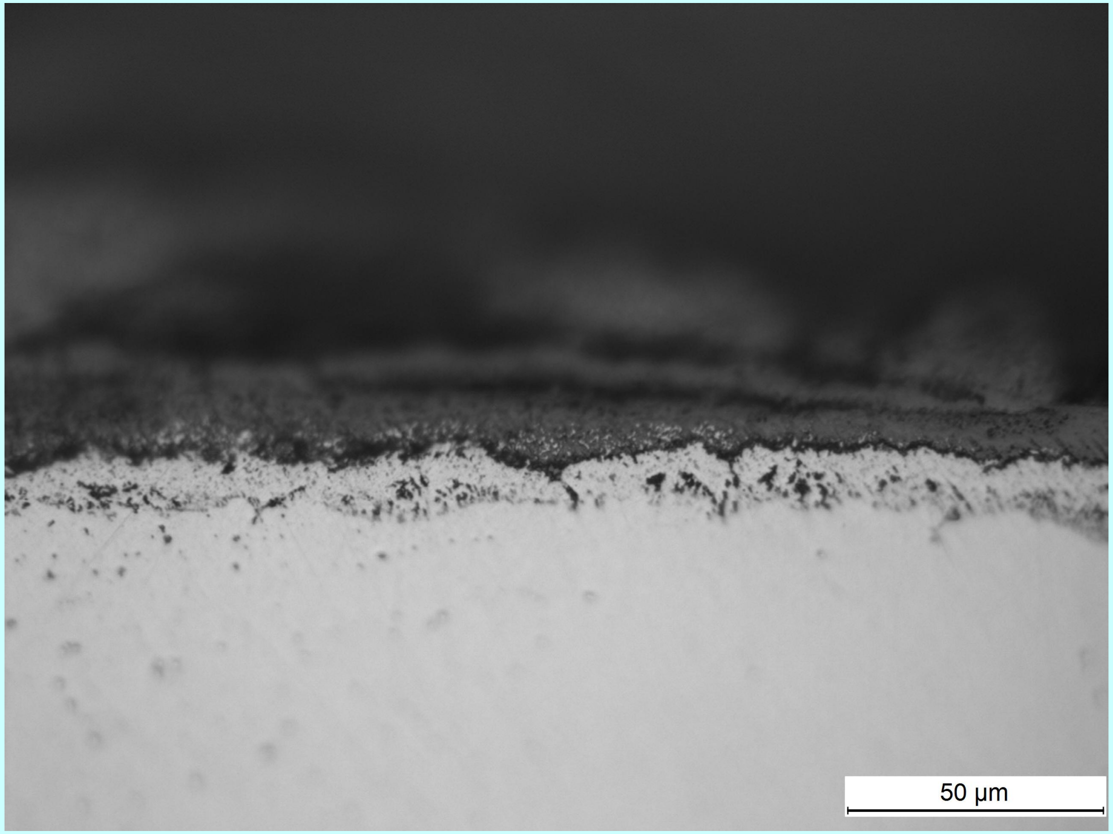
Temperature stability curve for Probe 2



Results of sample characterisations

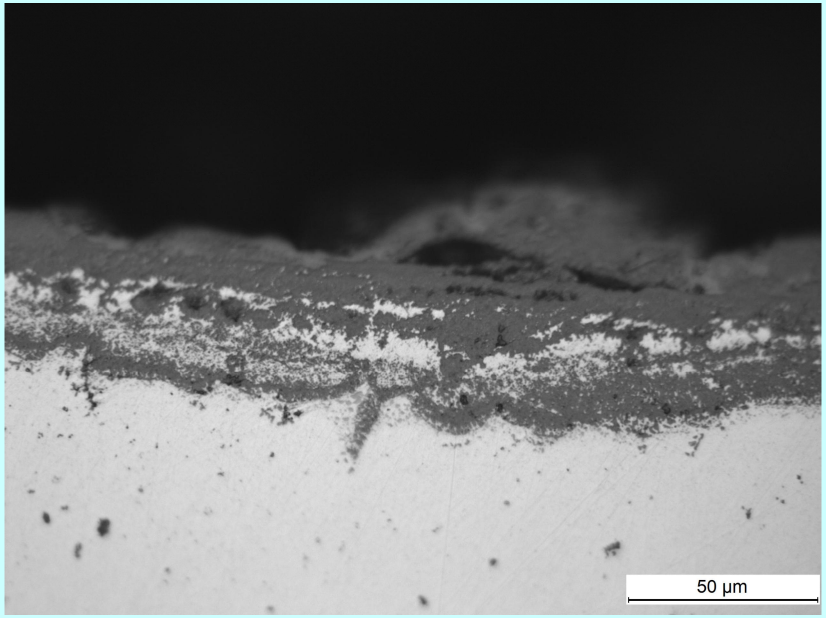
Probe 1, material SAN 28: T_{mat} ~ 527°C

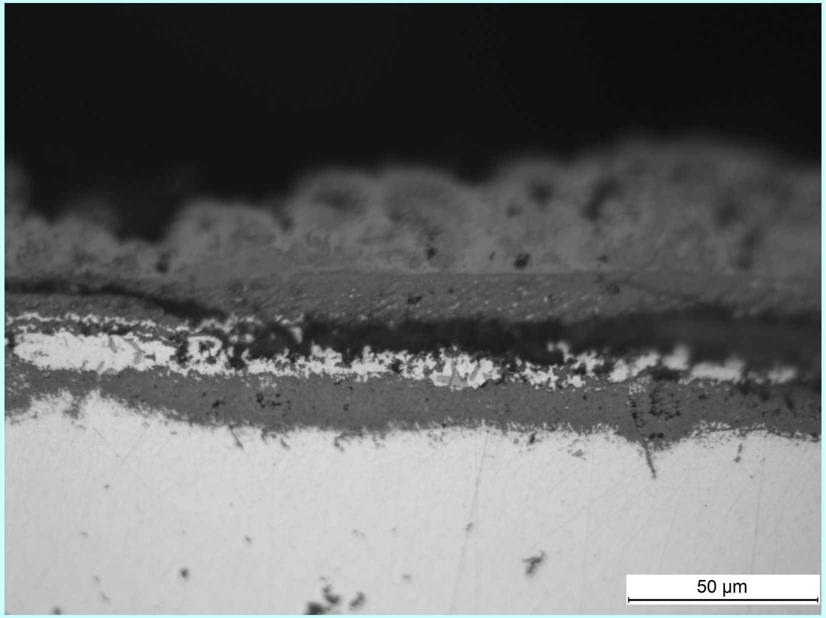
Cross sectional view of the front side (optical micrograph)



Probe 1, material SAN 28; (T_{mat} 488…527°C)

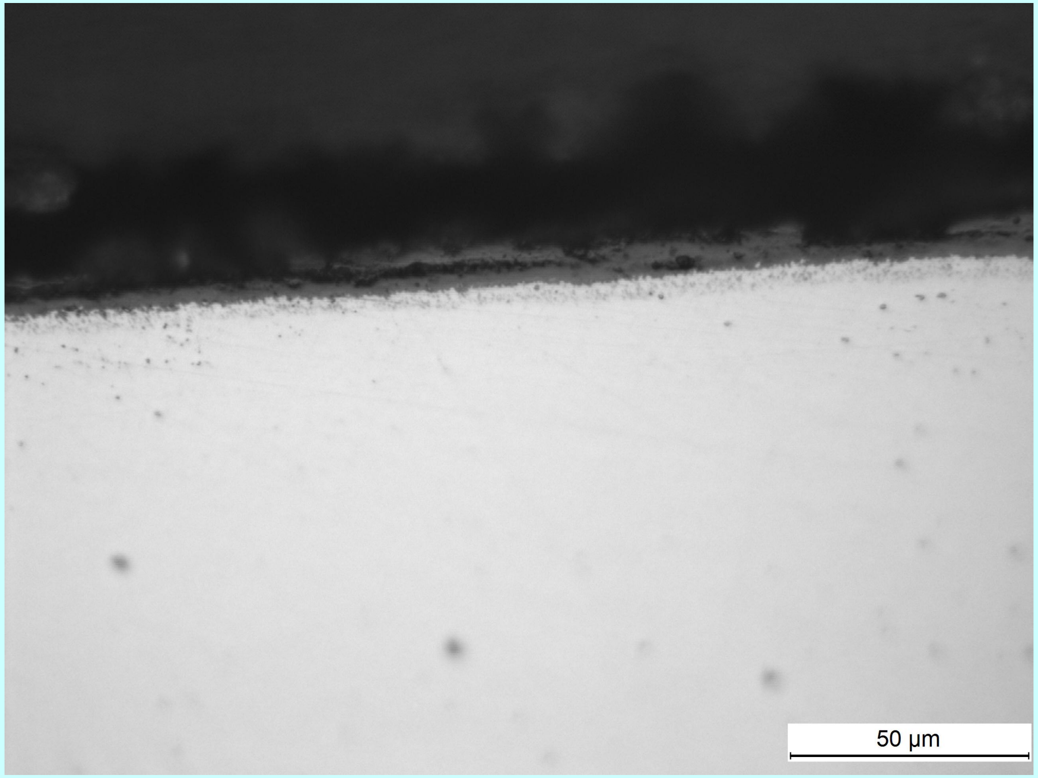
Cross sectional views of the leeward side (optical micrographs)





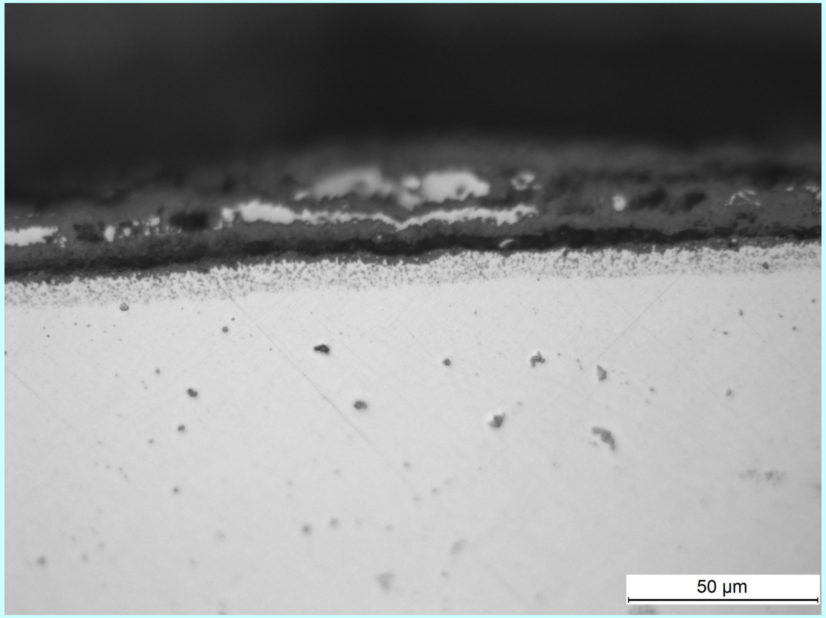
Probe 1, material Super 625: T_{mat} ~ 527^{o}C

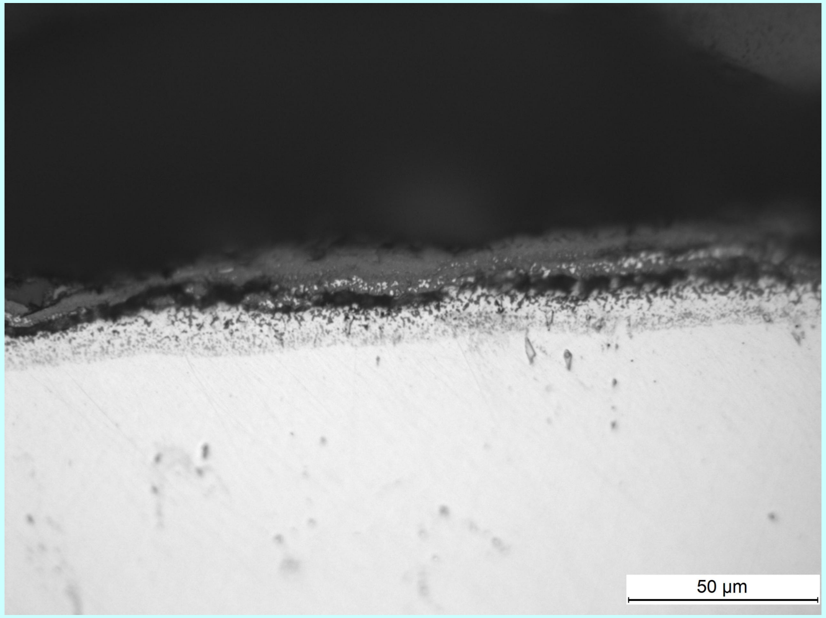
Some cross sectional views of the windward side (optical micrograph)



Probe 1, material Super 625: (T_{mat} max > 527^{o}C)

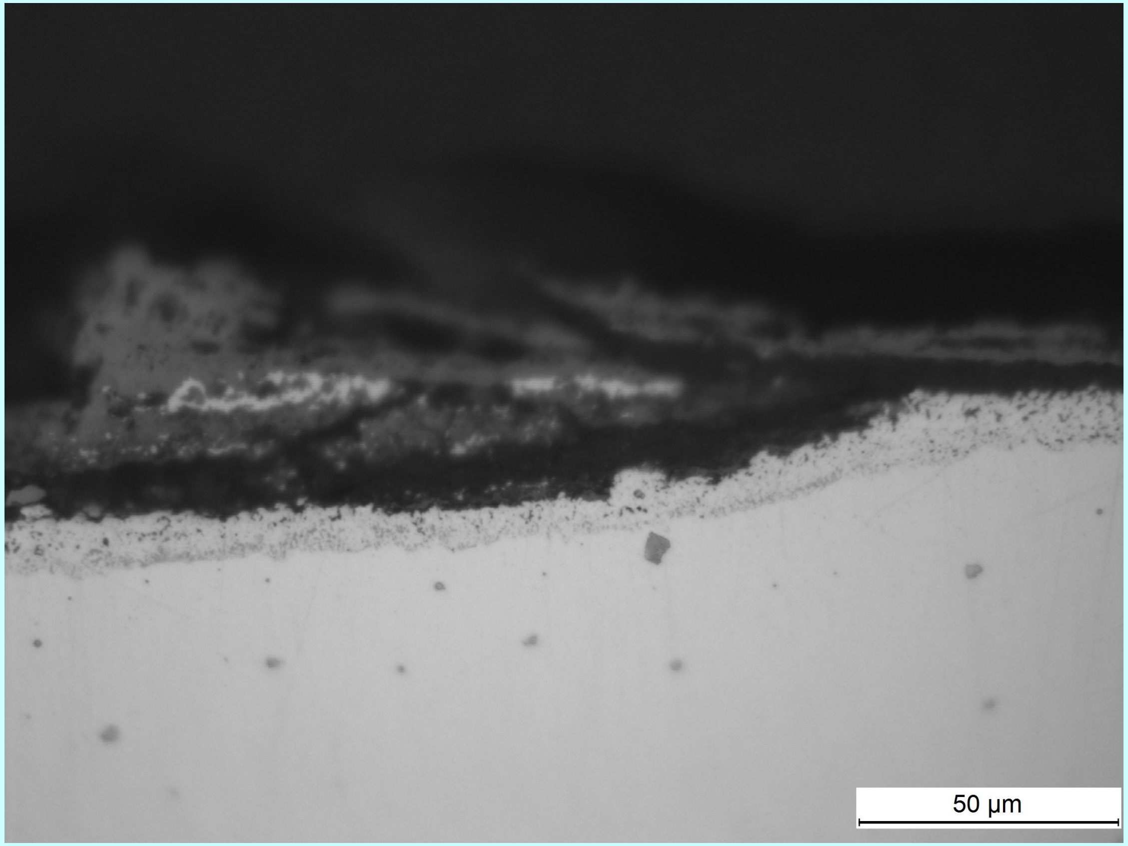
Cross sectional view ~ 30^{o} up and ~ 30^{o} down from the windward side





Probe 1, material Super 625: T_{mat} 488-527°C

Cross sectional view of the leeward side (optical micrograph)

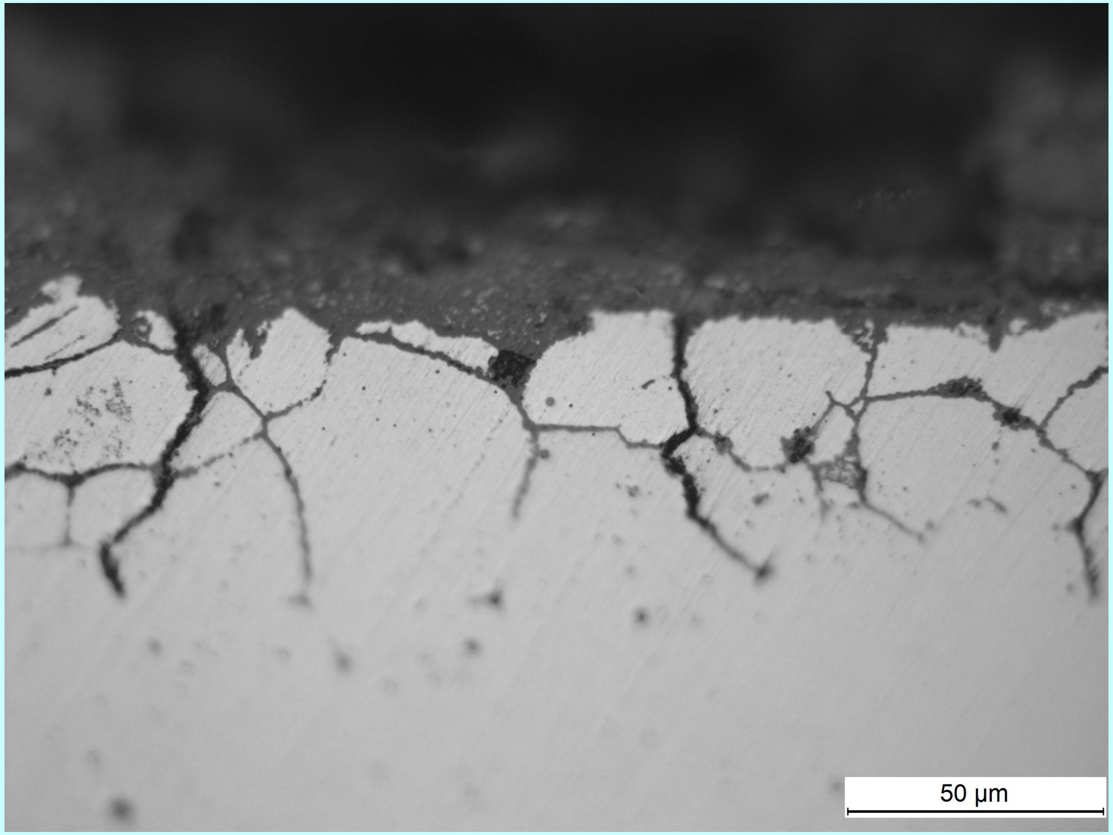


Probe 1, material 347 H: T_{mat} ~ 527^{o}C

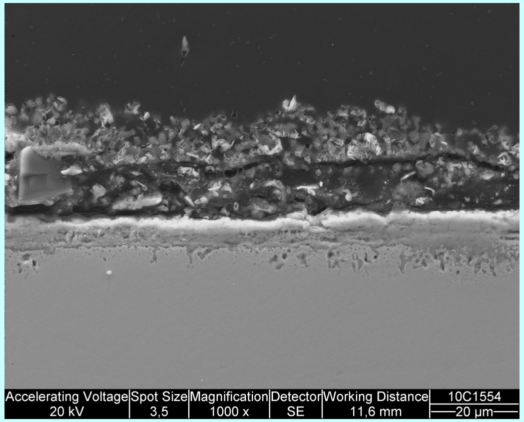
Cross sectional view of the windward side (optical micrograph)

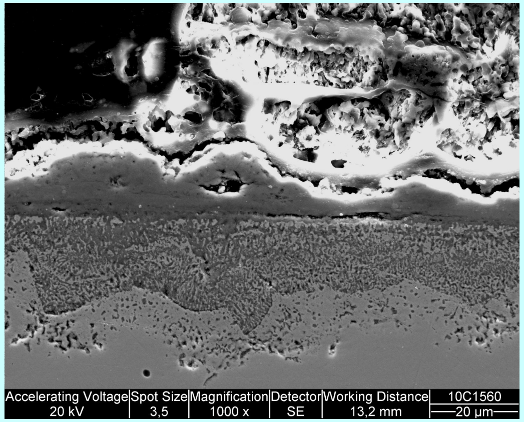
Probe 1, material 347 H: T_{mat} ~ 488-527°C

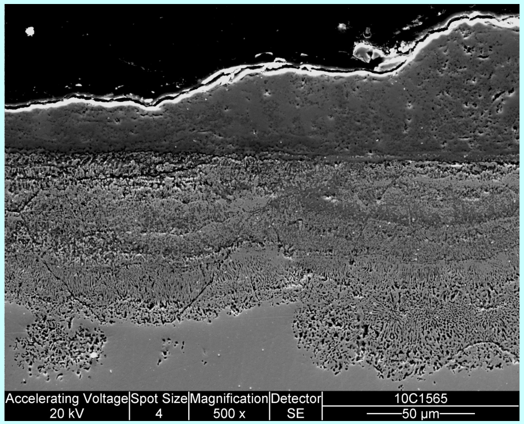
Cross sectional view of the leeward side (optical micrograph)

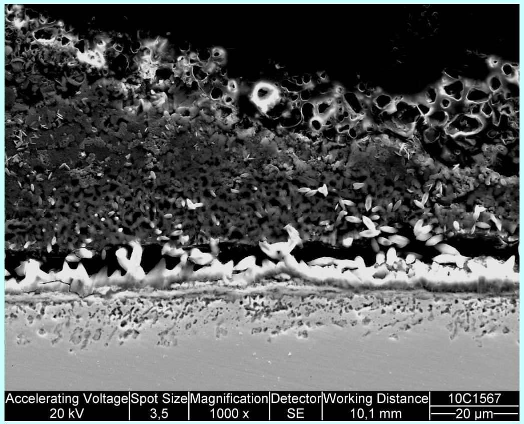


Probe 2: S2.1, Sanicro 28 (0, 90, 180, 270)

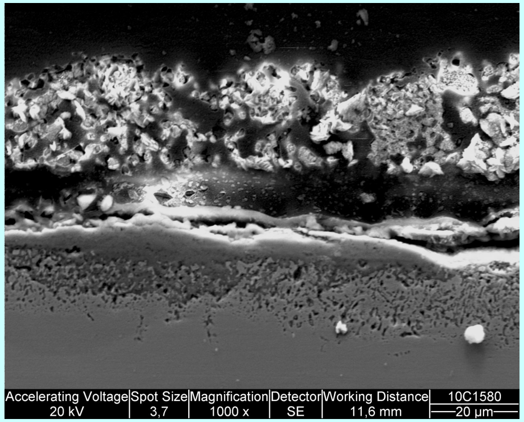


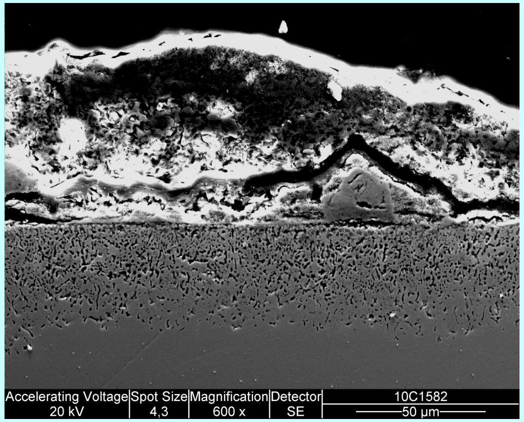


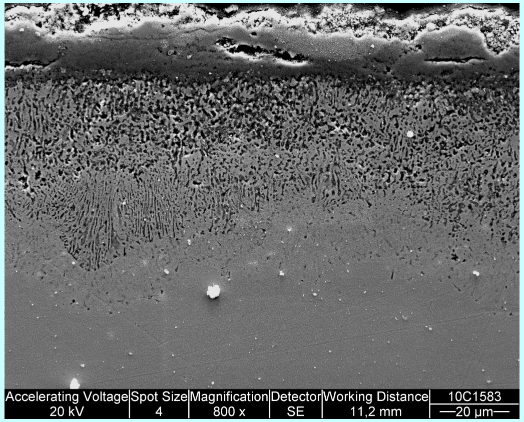


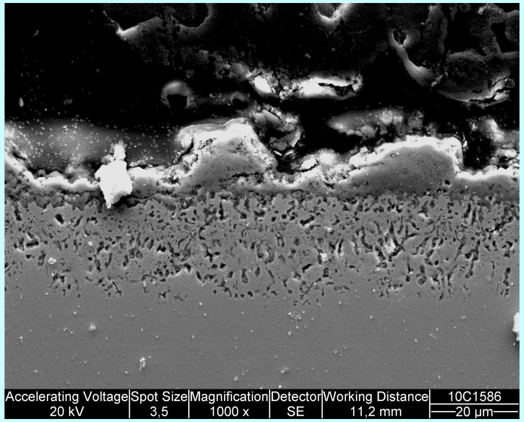


Probe 2: S2.2, HR 11 N (0, 90, 180, 270)

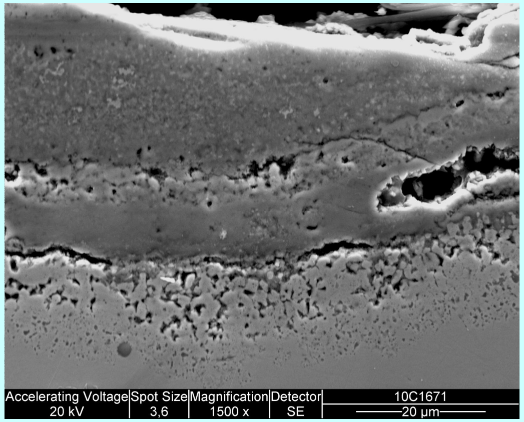


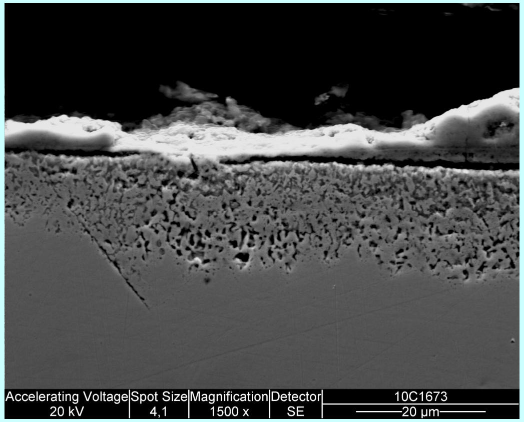


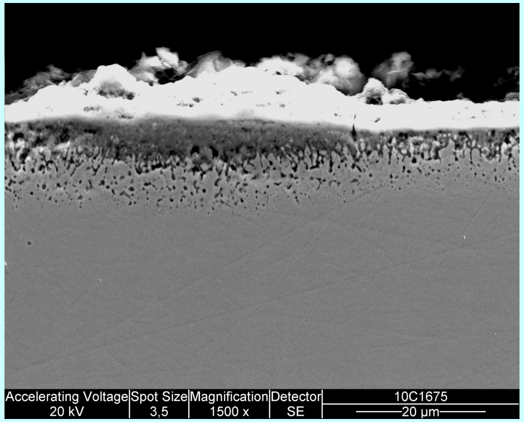


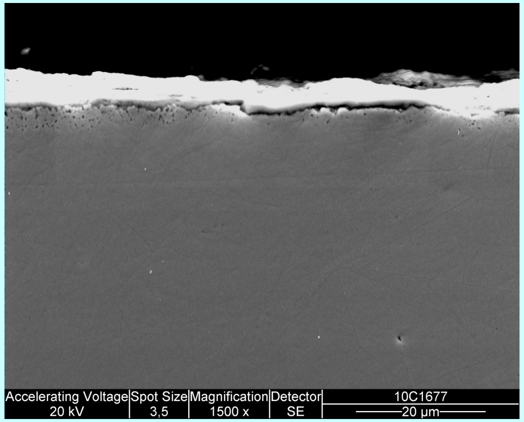


Probe 2; S2.3 Super 625 (60, 90, 180, 270)

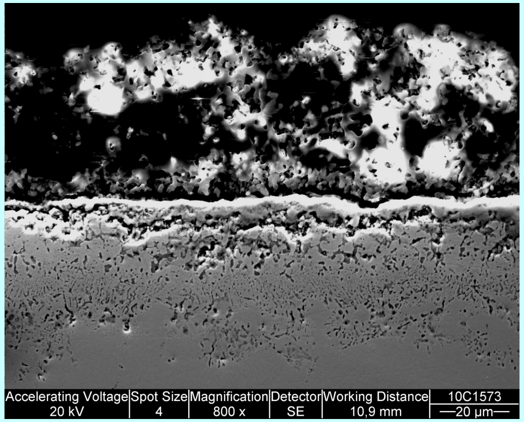


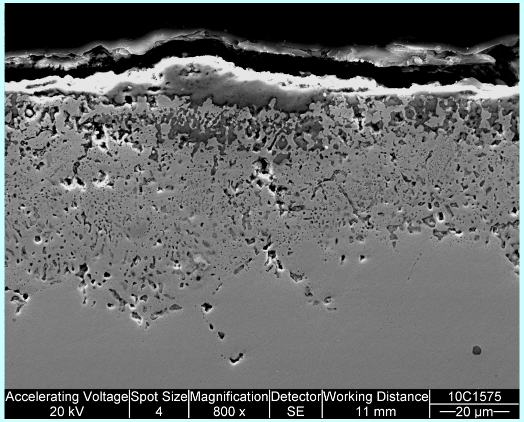


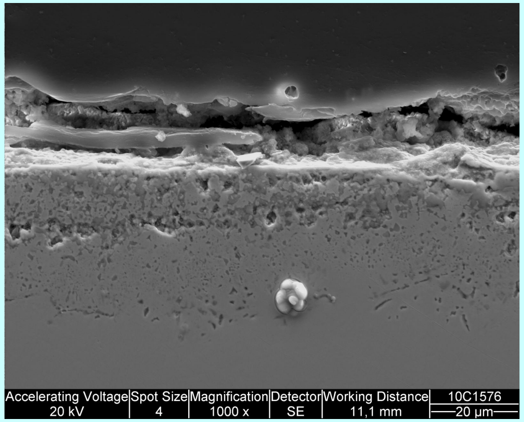


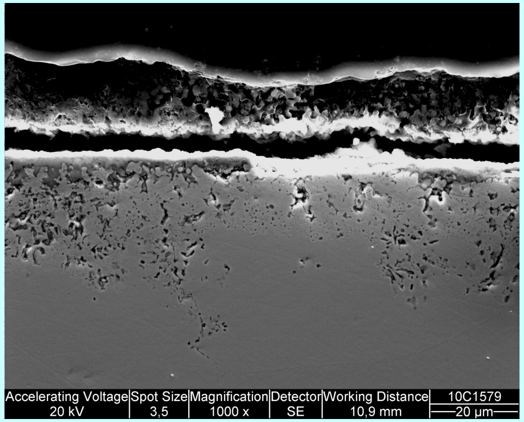


SAN 69 (0, 90, 180, 270)

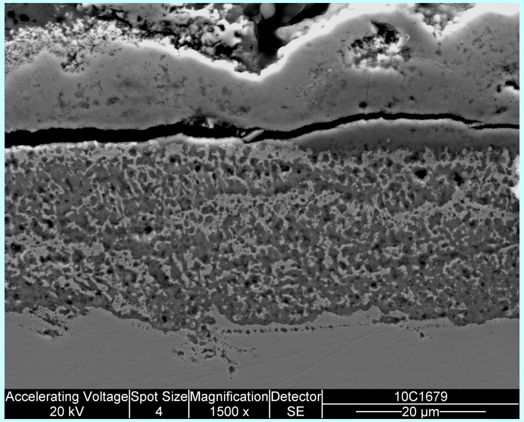


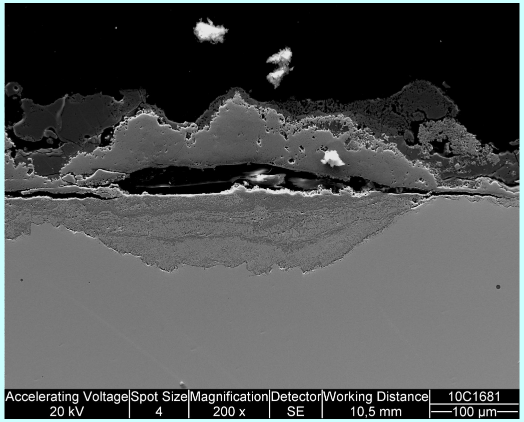


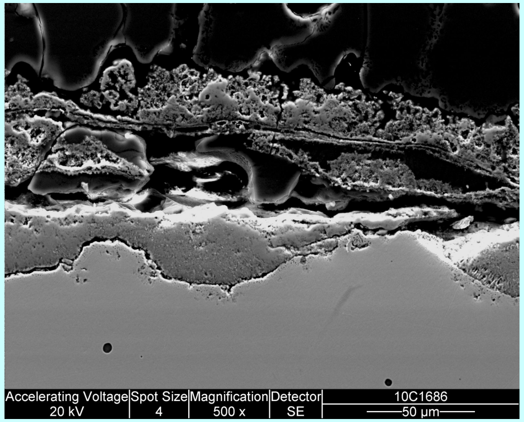


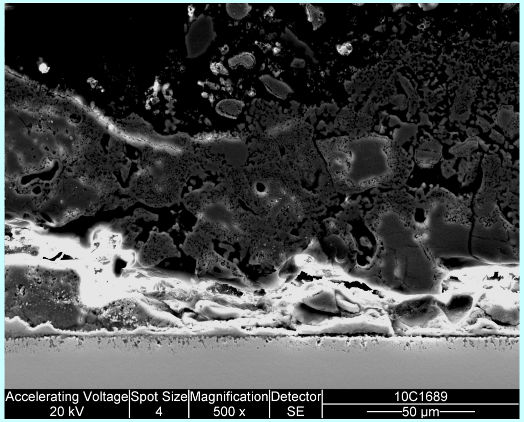


S2.5 AISI 310 (0, 90, 180, 270)

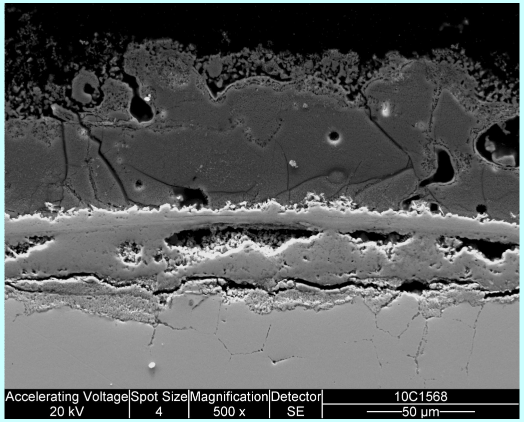


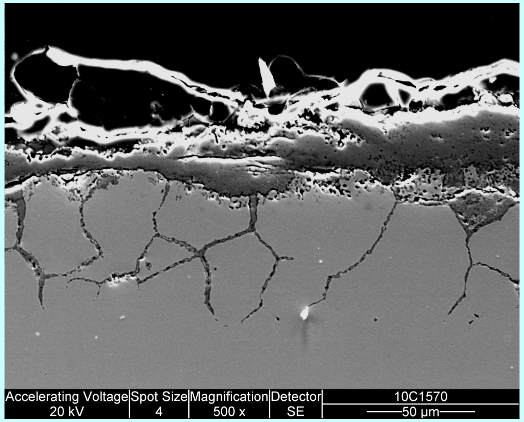


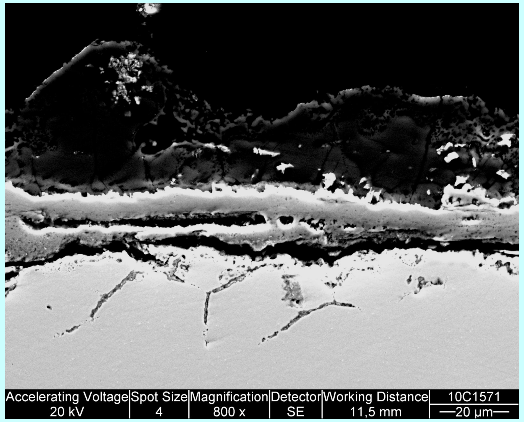


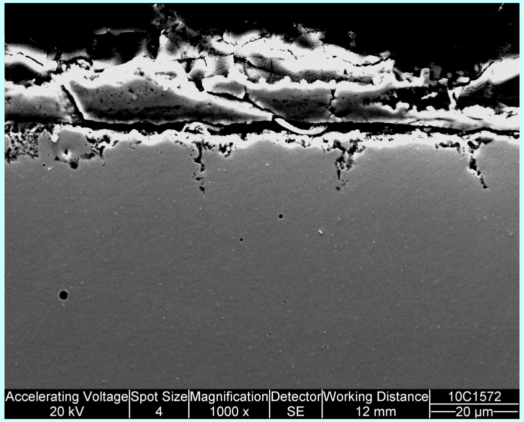


S2.6 AISI 347 H (0, 90, 180, 270)

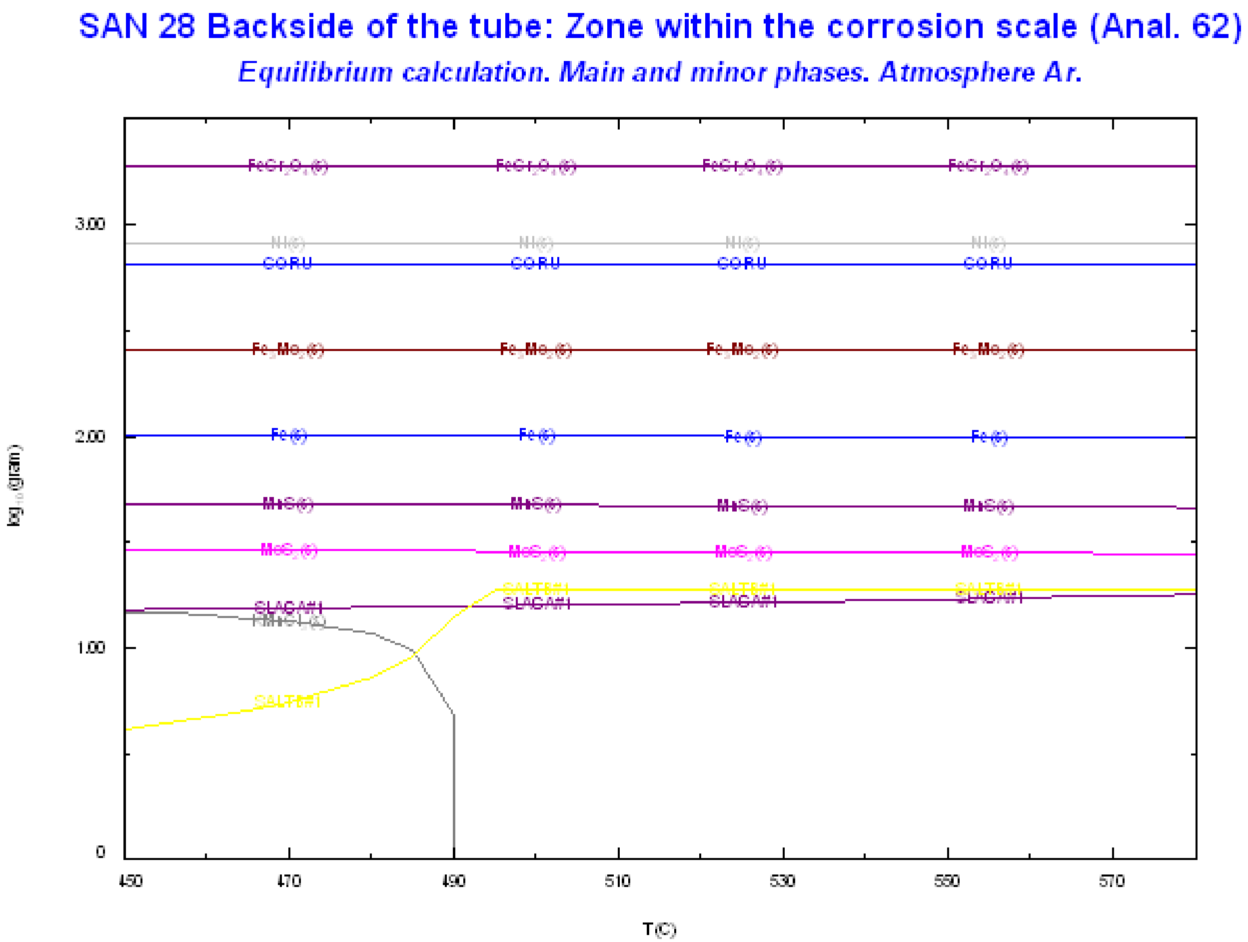




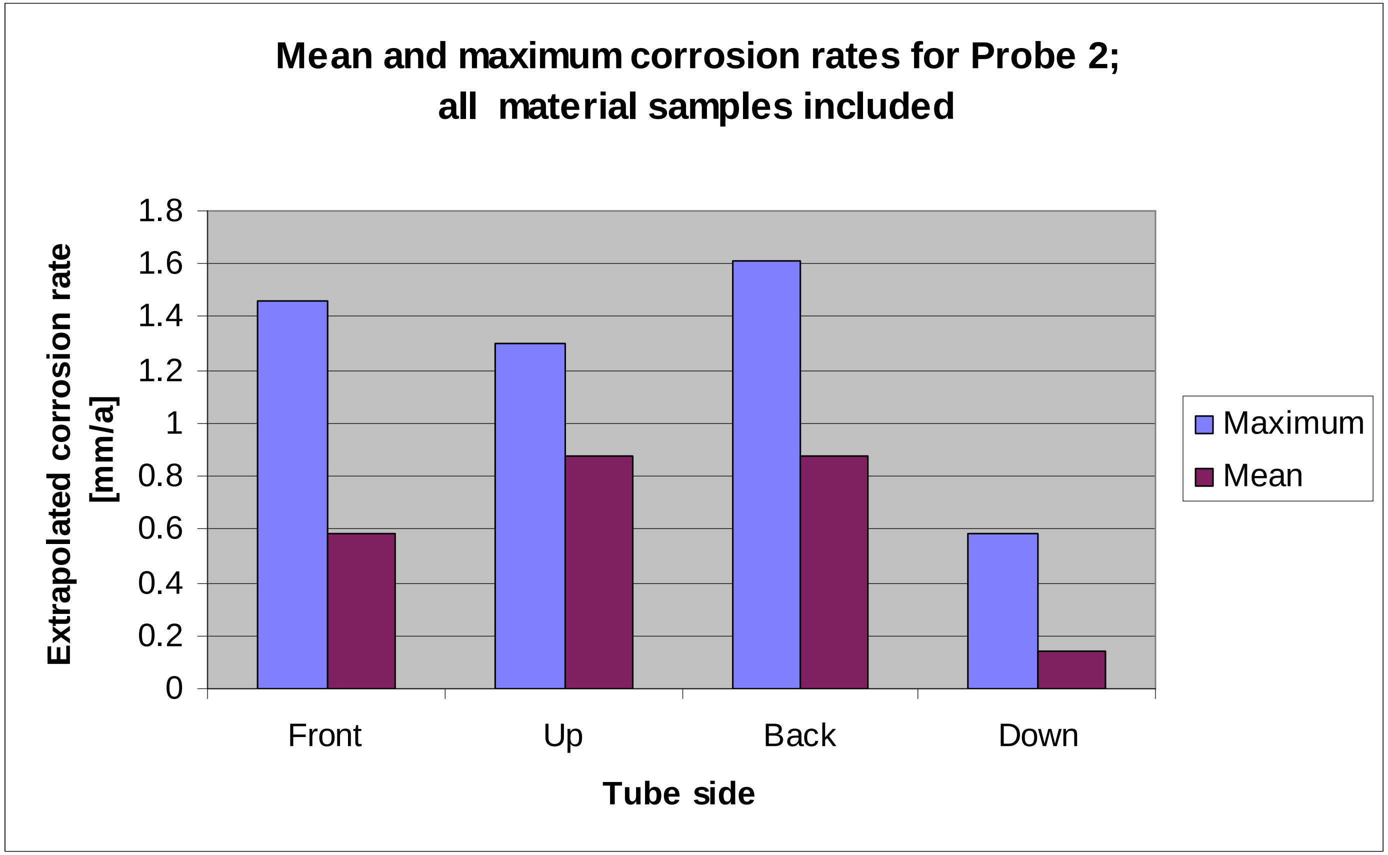




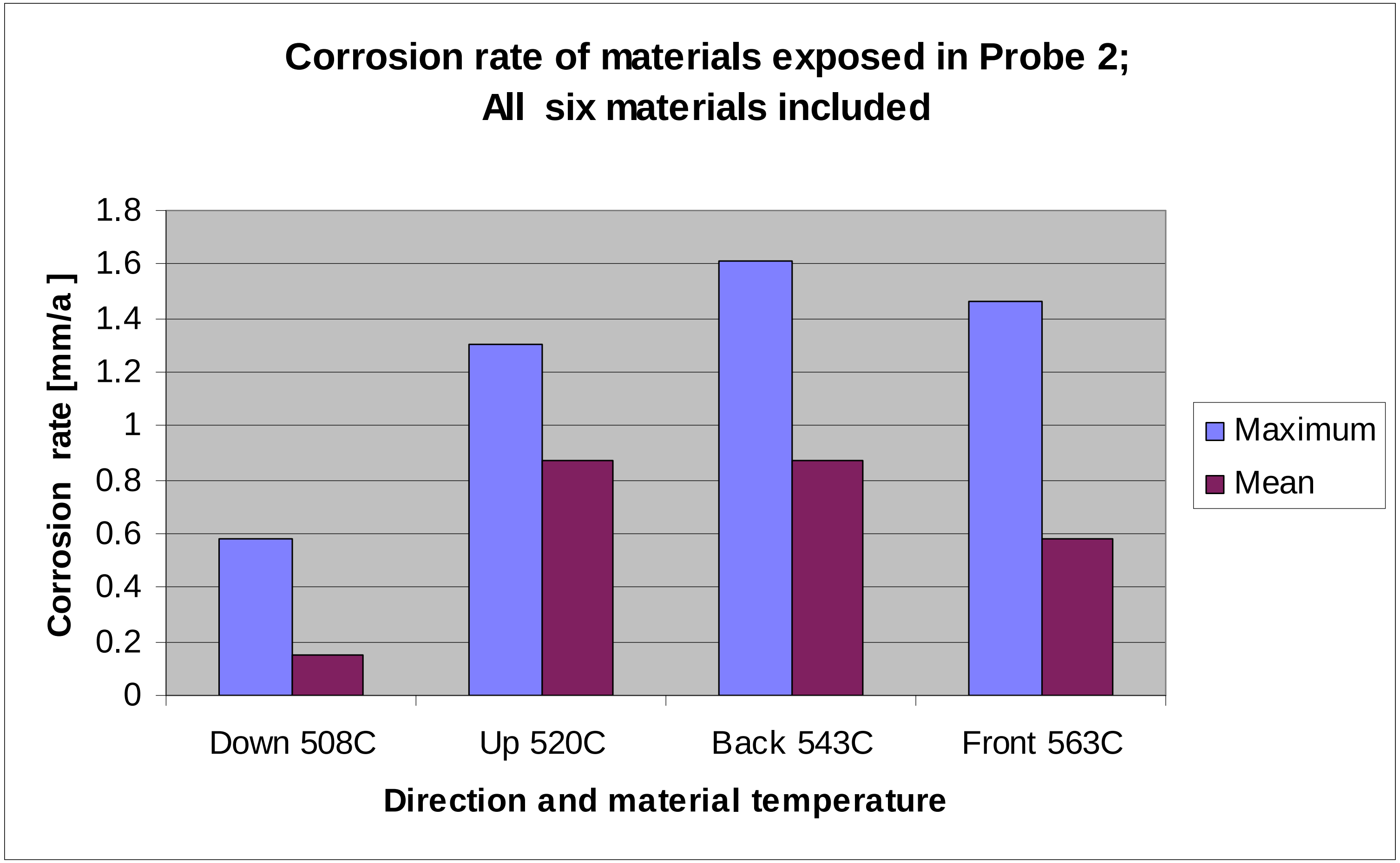
SAN 28 Leeward-side: Calculated phase composition of a zone within the corrosion scale



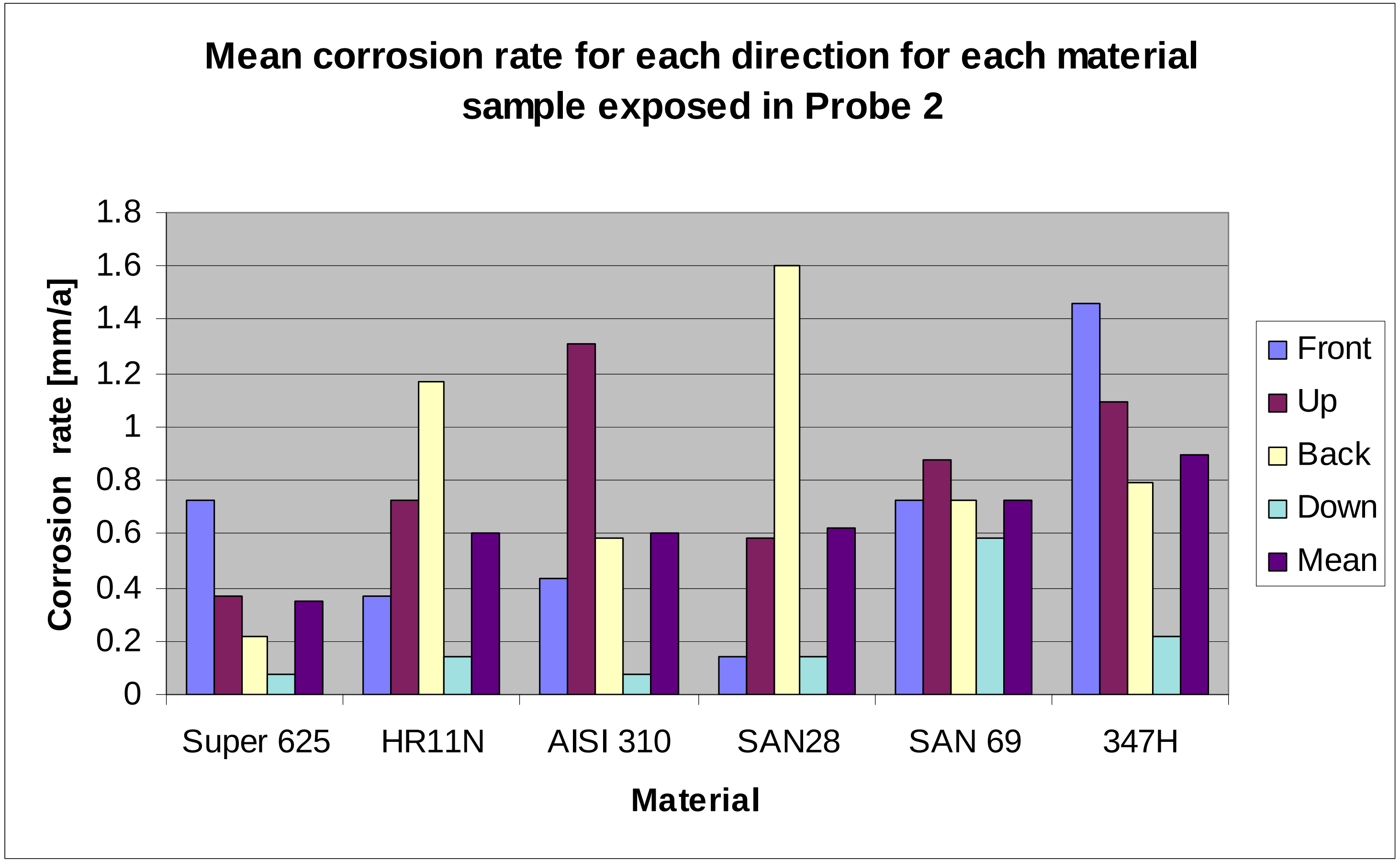
Corrosion rates: All samples in Probe 2



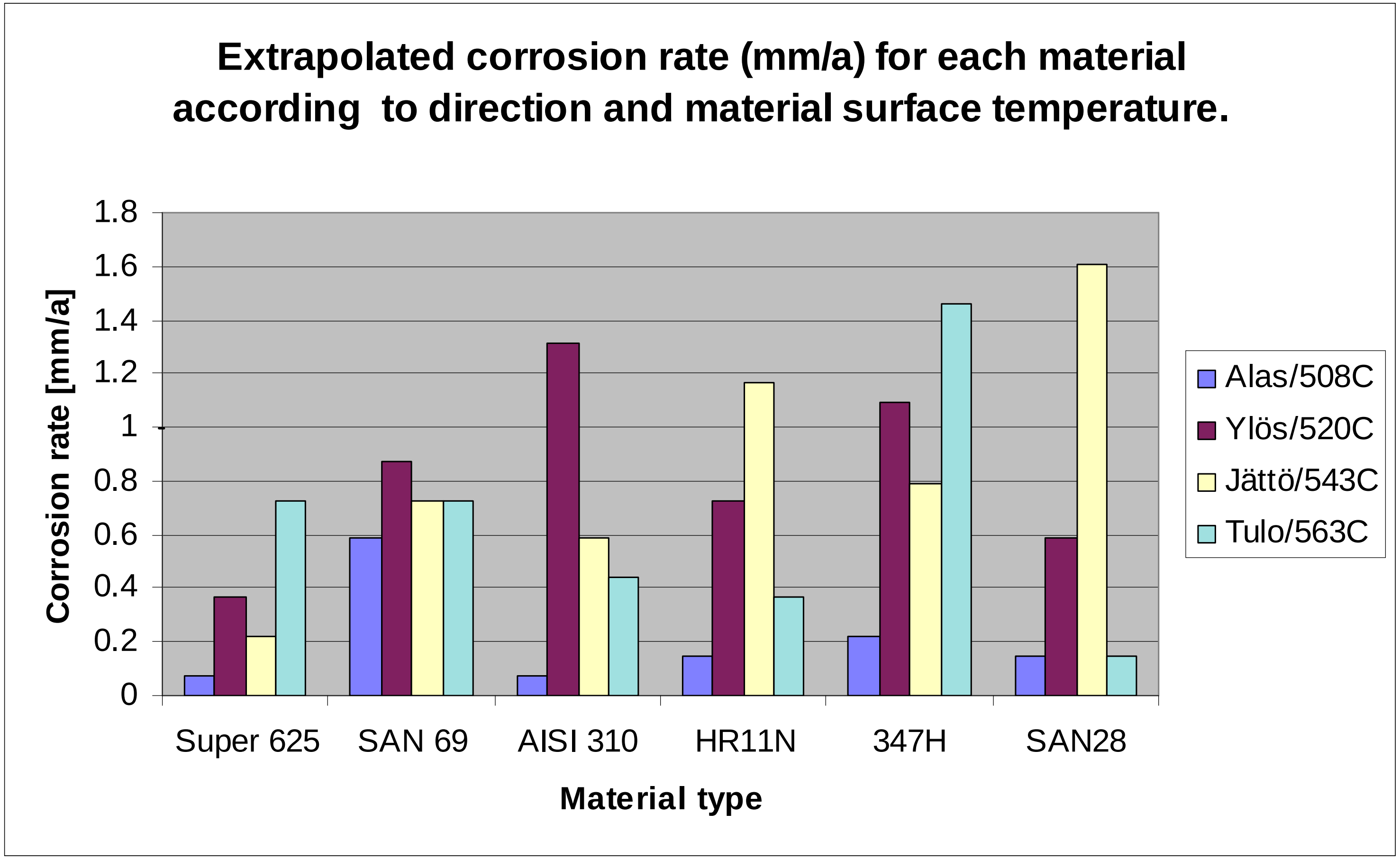
Corrosion rates: All samples in Probe 2



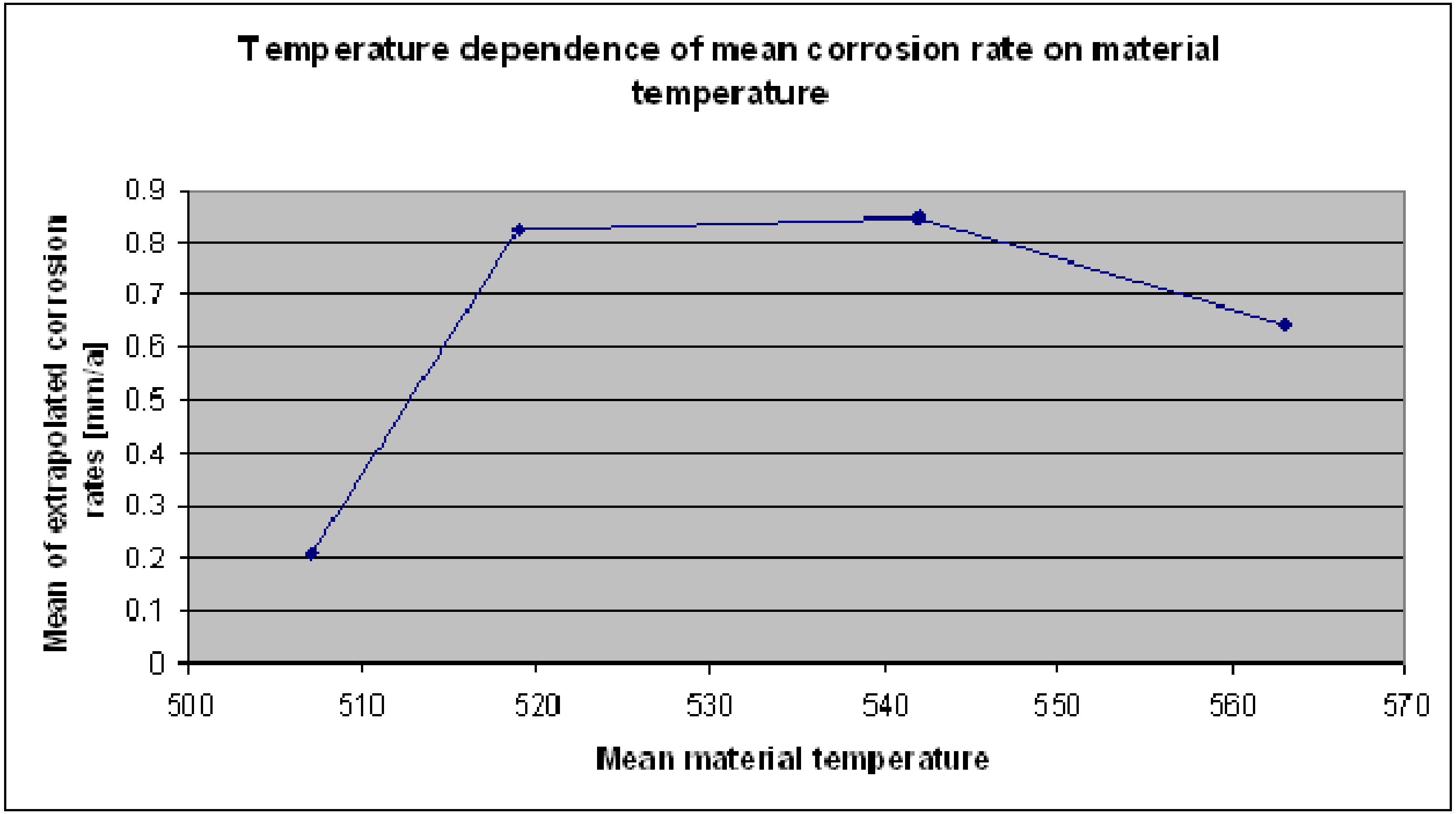
Corrosion rates for each material in Probe 2



Corrosion rates for each material (arranged in the ranking order accepted)



Metal loss observed according to mean measured temperature



Discussion

Deposits types ?

Black liquor analysis submitted by Joutseno staff shows chloride 0.1 wt-% Cl

S/(Na+K) and Cl/(Na+K) analysed for various directions in samples exposed in Probe 2

Cl content from nil (below analysis limit) to few tens of per cent (maximum ~2.5 wt-% Cl)

CO_3 content in the probe deposits not actually known

-> Following data (ref. Joutseno RB!) acceptable for discussions:

Wm. James. Frederick Jr., Esa K. Vakkilainen, Sintering and Structure Development in Alkali Metal Salt Deposits Formed in Kraft Recovery Boilers, Energy & Fuels 2003, 17, 1501-1509

Wm. James. Frederick Jr., Esa K. Vakkilainen, The Conditions for Boiler Bank Plugging by Submicrometer Sodium Salt (Fume) Particles in Kraft Recovery BoilersEnergy & Fuels 2004, 18, 795-803

Discussion

High alloyed steels have shown to suffer from pitting attack when exposed in half immersion to eutectic sulphate-chloride melts at 525^{o}C in air[1)]

The pitting attack is most severe at the melt(-air) borderline. This pitting attack may lead to unacceptably high rate of localized corrosion.

Then, corrosion morphology and material wastage rates are found to correspond closely to those observed for high austenitic stainless steel specimens (AISI 310, HRC) experiencing high material temperatures during recovery boiler exposures (duration 1055 h).

Ref. 1: Superheater Tube Corrosion in Changing Operation Conditions of Recovery Boilers, Martti Mäkipää, Maria Oksa and Lasse Koivisto, Paper NACE 01424-01-T-5H.

Discussion

Pitting resistance of various high-chromium alloys (e.g., Super 625, SAN 28, AC66) is rather good when exposed to sulphate-chloride melt in laboratory.

However, under sulphate-chloride-carbonate melt exposures, heavy material wastage is observed for the same steels at locations at or above the melt surface, where oxygen potential is high favoring basic fluxing of chromium and iron.

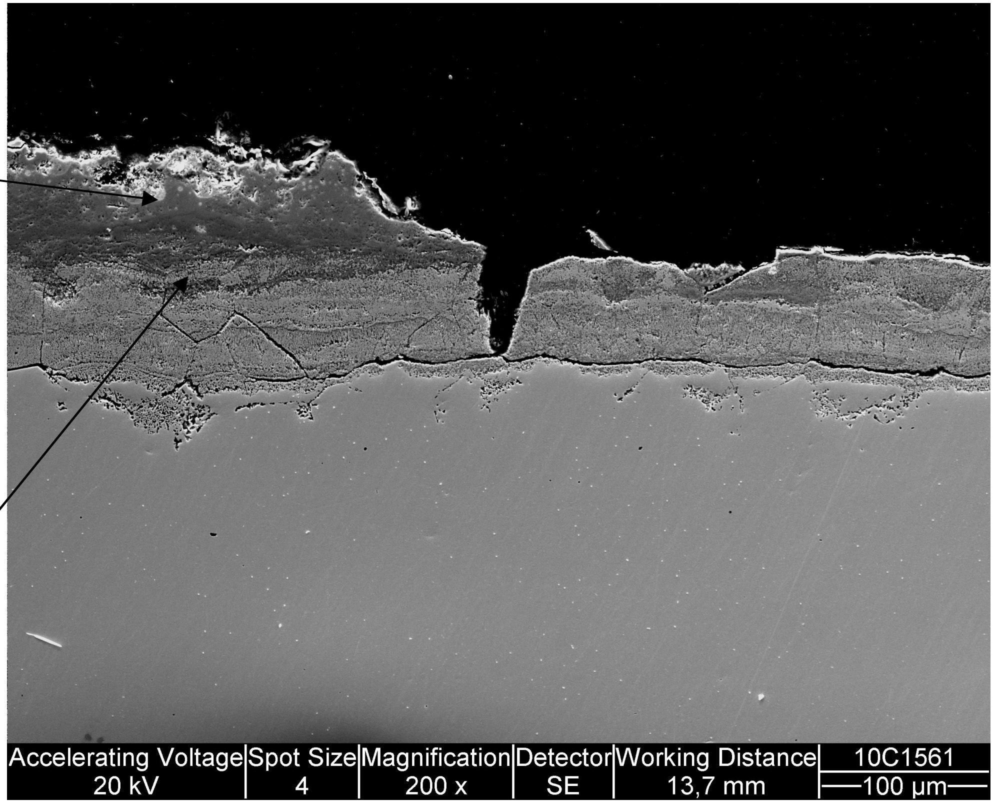
Probe 2: S2.1, SAN 28: Leeward-side (172 degrees) Material temperature: T_{mean} 544^{o}C, T_{max} 595^{o}C

Quantitative Results for: S2-1, Analysis 59

Element	Weight %	Weight % Error	Atom %	Atom % Error
O	47.36	+/- 0.38	60.48	+/- 0.48
Na	26.80	+/- 0.14	23.82	+/- 0.12
S	20.40	+/- 0.10	13.00	+/- 0.07
Cl	0.35	+/- 0.05	0.20	+/- 0.03
K	3.94	+/- 0.06	2.06	+/- 0.03
Cr	0.48	+/- 0.07	0.19	+/- 0.03
Mn	0.29	+/- 0.05	0.11	+/- 0.02
Fe	0.39	+/- 0.05	0.14	+/- 0.02
Total	100.00		100.00	

Quantitative Results for: S2-1, Analysis 60

Element	Weight %	Weight % Error	Atom %	Atom % Error
O	21.80	+/- 1.46	46.69	+/- 3.12
Na	5.24	+/- 0.14	7.81	+/- 0.21
Al	0.13	+/- 0.03	0.16	+/- 0.03
Si	0.14	+/- 0.02	0.18	+/- 0.03
S	1.09	+/- 0.02	1.16	+/- 0.03
K	0.37	+/- 0.02	0.32	+/- 0.02
Cr	7.05	+/- 0.11	4.65	+/- 0.07
Mn	12.14	+/- 0.20	7.57	+/- 0.13
Fe	45.78	+/- 0.29	28.08	+/- 0.18
Cu	6.26	+/- 0.24	3.38	+/- 0.13
Total	100.00		100.00	



Materials ranking according to FactSage 6.1 predictions

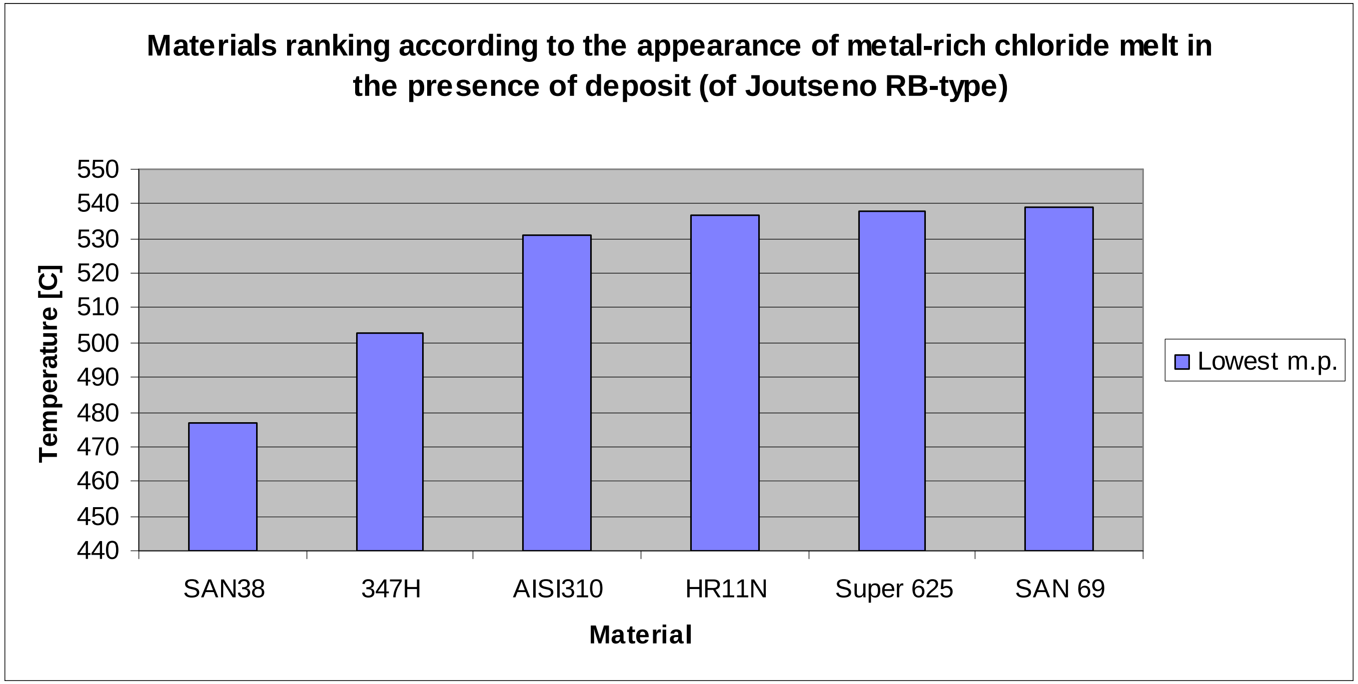
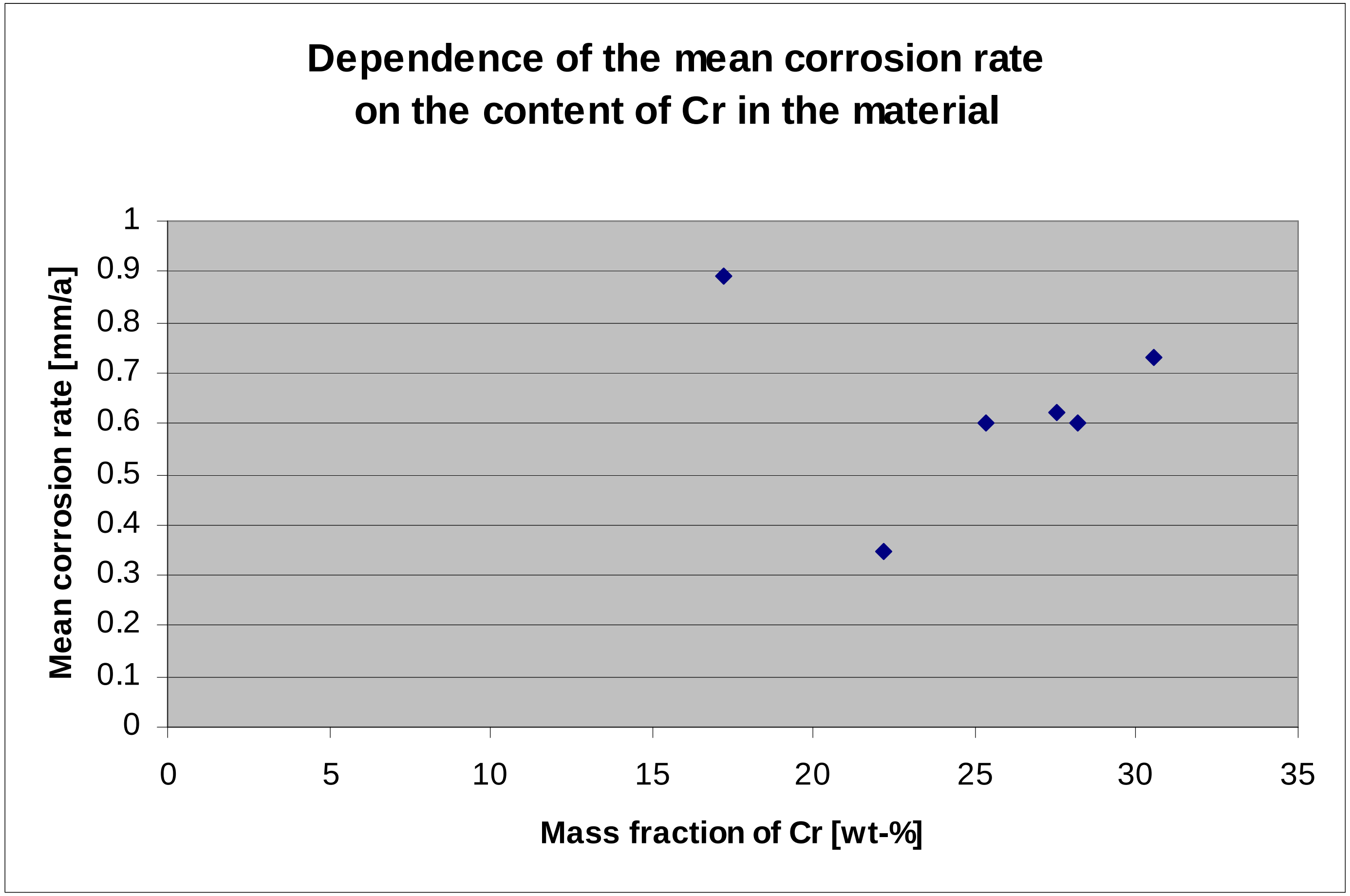


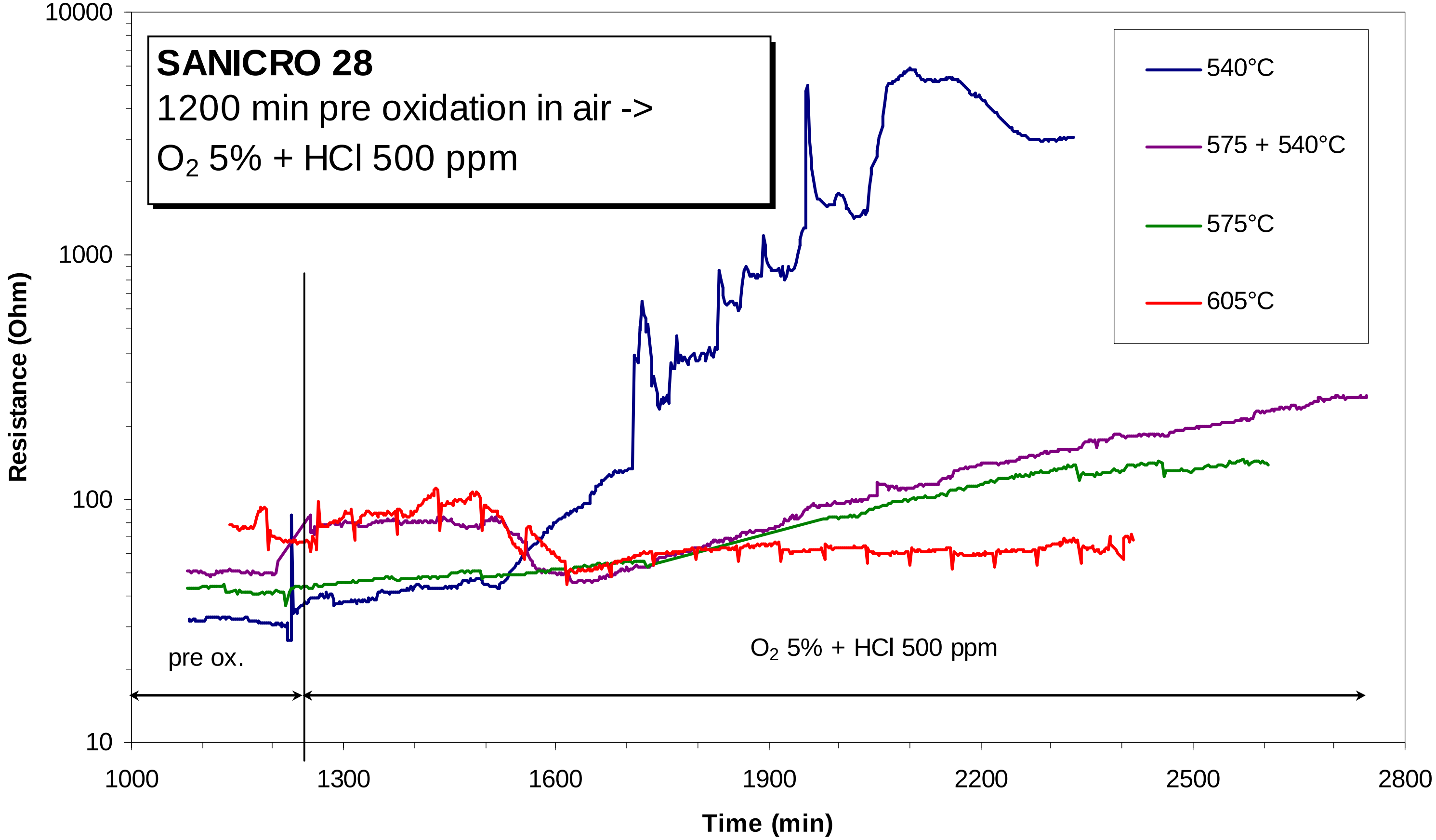
Table of measure metal losses

		180	90	270	0		Rank		Rank	(mm/a)	
Model		**Back**	**Up**	**Down**	**Front**	**MEAN**	**MEAN**	**MAX**	**MEAN**	**MAX**	
VI	**SAN28**	0.110	0.040	0.010	0.010	0.043	**III**	**VI**	0.62	1.61	VI
III	**HR11N**	0.080	0.050	0.010	0.025	0.041	**II**	**III**	0.60	1.17	III
II	**625**	0.015	0.025	0.005	0.050	0.024	**I**	**I**	0.35	0.73	I
I	**SAN 69**	0.050	0.060	0.040	0.050	0.050	**IV**	**III**	0.73	0.88	II
IV	**AISI 310**	0.040	0.090	0.005	0.030	0.041	**II**	**IV**	0.60	1.31	IV
V	**347H**	0.05	0.08	0.02	0.10	0.061	**VI**	**V**	0.89	1.46	V
	Mean	0.06	0.06	0.01	0.04	0.043			0.63		

The effect of alloying with chromium



Historic data



Conclusions

- According to maximum metal loss materials ranking was:
  SAN28 < 347H < AISI310 < HR11N < SAN69 ~ Super 625 (paras)

- According to model calculations reffing to deposits with about 0.5 % and Cl and some carbonate ranking is:
  SAN28 << 347H << AISI310 < HR11N < Super 625 ~ SAN 69 (best)

- The role of alloying with chromium should be scrutinised in continuation (alternative optimised alloy types with moderate Cr and Ni contents ?)

- Super 625 and possibly SAN 625 are the most promising SH material candidates for high material temperatures

- There is still no proof that material temperatures > 524^{o}C are attainable

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