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VTT, Characterisation of probe test samples exposed to BLRB lower furnace environments – draft report 26.11.2012

RESEARCH REPORT

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Characterisation of probe test samples exposed to BLRB lower furnace environments

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Abstract

Current trend to increase electricity generation of recovery boilers possess new demands for the tube materials, when the material temperatures are increased due to higher steam values. Operational experiences from current boilers have shown that the AISI 304 L compound tubes suffer from accelerated corrosion in furnace wall, when the material temperatures are increased from normal values due to the internal surfaces scales. This indicates that the AISI 304L might be unsuitable cladding material for the future high pressure boilers.

The goal of this study was to test different potential cladding materials in actual recovery boiler lower furnace conditions, but at higher than current temperatures, in order to determine what materials could be suitable for future high pressure recovery boilers. The work was divided so that specimen manufacturing and probe tests were conducted by Boildec Oy, whereas the sample characterisation was performed by VTT. The test materials were carbon steel; austenitic stainless steels 3R12, 3RE28 and 3XRE28; high nickel alloys Sanicro 28, HR11N and Sanicro 38 and two nickel base alloys Super 625 and Sanicro 67. The test temperature was 440°C and test duration varied from 1000 to 2700 hours.

The results show that materials with superior corrosion resistance to AISI 304L exist and hence corrosion in lower furnace can be managed by proper material selection. According to the wall thickness measurements the test materials can be put in following order based on increased resistance: C-steel << 3R12 < HR11N ~ Sanicro 38 (~ Sanicro 28 ~ 3RE28/3XRE28) < Super 625 < Sanicro 67.

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1 Introduction

Increasing boiler pressure induces a corresponding increase in tube temperature in steam generator. Operational experiences from current boilers indicate that AISI 304L (3R12), which has been the most commonly used cladding material, suffers from accelerated corrosion at higher than normal operation temperatures, which are sometimes encountered when internal surfaces in furnace wall tubes are covered with thick scale. These temperatures would be normal at high pressure boilers, and thus AISI 304L appears non-suitable cladding material for high pressure boilers. Currently few alternative materials are used, such as Sanicro38 (mod. UNS N08825) and HR11N, but their corrosion resistance at high temperatures has not been thoroughly studied and operational experiences are still limited. Also other highly alloyed materials are available, but data on their corrosion resistance are lacking.

2 Goal

The goal of this study was to test different potential cladding materials in actual recovery boiler lower furnace conditions, but at higher than current temperatures, in order to determine what materials could be suitable for future high pressure recovery boilers. The work was divided so that specimen manufacturing and probe tests were conducted by Boildec Oy, whereas the sample characterisation was performed by VTT.

3 Experimental

3.1 Test materials, specimens and evaluation procedures

The test materials were carbon steel (P265GH), three austenitic stainless steels 3R12 (AISI 304L), 3RE28 (AISI 310) and 3XRE28, three austenitic high nickel alloys Sanicro 28 (UNS N08028), Sanicro 38 (mod. UNS N08825) and HR11N and two austenitic nickel base alloys Sanicro 67 (UNS N06690) and Super 625. Chemical compositions of the test materials are shown in Table 1.

After exposure the material performance was assessed with wall thickness measurements and metallographic analysis. Before measurements, after cutting from the probe, the samples were thoroughly washed under water with nylon brush and rinsed with ethanol to remove deposits. The wall thickness profiles of the test samples were measured before and after testing with coordinate measurement machine as a function of circumference from three axial locations (Z = 15, 25 and 32 mm) so that from each location 100 points were measured, Figure 1.

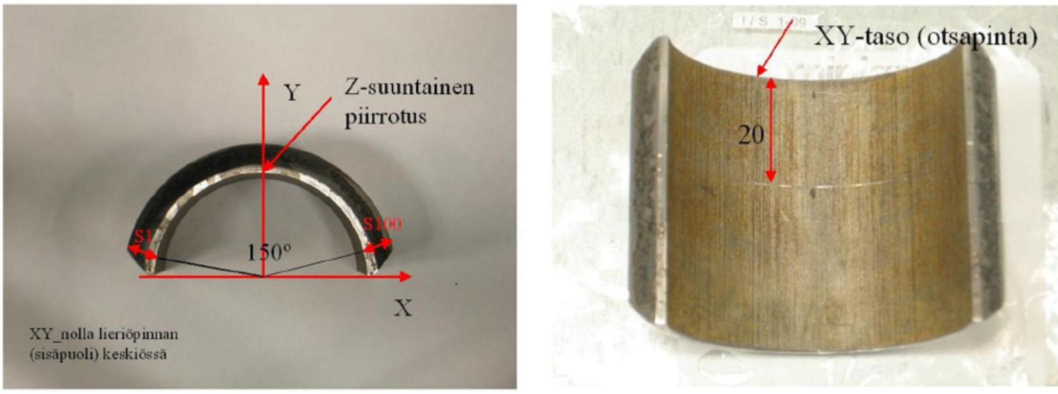
In tests No.1 - 3 the 3R12, 3RE28, 3XRE28, Sanicro 28, Sanicro 38 and Sanicro 67 specimens were cut from composite tubes and tested in as received condition, whereas the HR11N and Super 625 specimens were machined from lager solid pieces and tested in as machined condition. In tests No.4 and 5 the outer and inner surfaces of all specimens were machined and hand grinded/polished prior assembly to the probe (Figure 2) to improve the accuracy of wall thickness measurements. The average corrosion rates were calculated on the basis of average wall thickness loss at the specimen apex (ca. 35…50 points/30…45° angle at apex). The maximum corrosion rates were calculated from the wall thinning curved derived from the wall thickness measurements.

For metallographic analysis one cross-section per sample (Z = 15 mm) was prepared and analysed with scanning electron microscope (SEM). The composition of oxide layers and deposits was determined with energy dispersive spectroscopy (EDS).

Table 1. Nominal composition of the test materials if not otherwise mentioned.

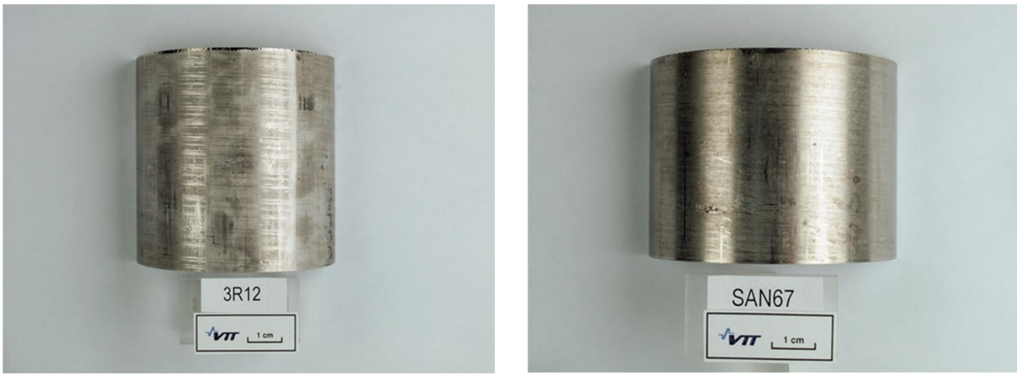
Material	%C	%Mn	%Si	%Cr	%Ni	%Mo	%Fe	%Cu	Other
Carbon steel									
P265GH	≤0.2	0.80 - 1.40	≤0.40	≤0.30	≤0.30	≤0.08	bal.	≤0.30	
Austenitic stainless steels									
3R12 [304L]	≤0.02	1.3	0.4	18.5	10.5	...	bal.	...	
3RE28[A)] [310]	0.023	1.77	0.39	25.6	21.0	0.06	bal.	0.06	
3xRE28 [A)]	0.012	1.63	0.35	25.2	21.3	0.25	bal.	0.14	
High nickel alloys									
Sanicro 28 [UNS N08028]	≤0.02	≤2.0	≤0.6	27	31	3.5	bal.	1.0	
Sanicro 38 [mod. 825]	≤0.03	0.8	≤0.5	20	38.5	2.6	bal.	1.7	Ti: 0.8
HR11N	0.03	2.0	0.6	27.0	38	0.5 - 1.5	bal.		N: 0.1
Nickel base alloys									
Sanicro 67 [Alloy 690]	0.02	≤0.5	≤0.5	30	60	...	bal.	...	Co: <0,05
Super 625	0.1	≤0.5	≤0.5	20 - 23	bal.	...	≤5.0	...	W: 3.15-4.15 Al: 0.4 Co ≤ 1.0

A) Tube samples analysed by VTT

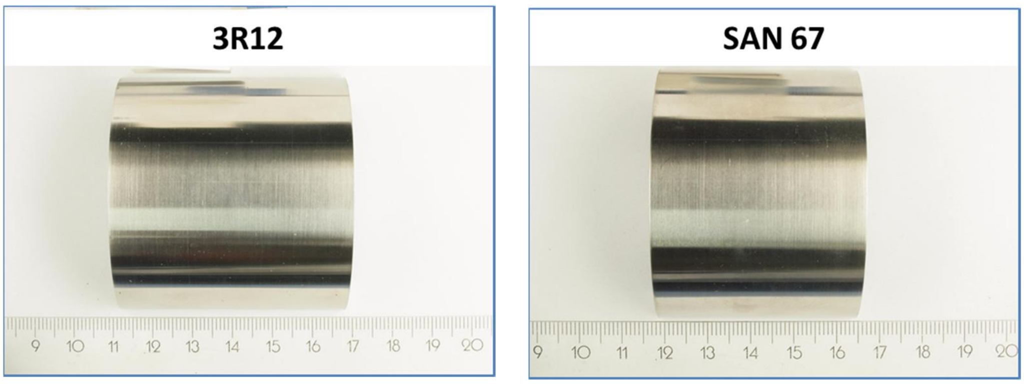


a) *b)*

Figure 1. The wall thickness profiles were measured before and after testing with coordinate measurement machine a) as a function of circumference b) from three axial locations (Z = 15, 25 and 32 mm).



a)



b)

Figure 2. Examples of sample surfaces prior exposure: a) in as received condition for the probe No. 2 and b) after machining and hand grinding for the probe No. 7.

3.2 Test conditions

The probe tests were conducted in Metsä Fibre Joutseno mill by Boildec Oy. The test matrix and test conditions are summarised in Table 2 and Table 3, more detailed information from the test set-up and parameters can be obtained from the probe test reports /1...5/. Maximum cladding temperatures in a high pressure boiler are about 400°C, when internal surfaces are clean. With scaling, cladding temperatures may become higher and, consequently, the test temperature was selected to be 440°C. The exposure durations varied from 1006 to 2700 hours so that target duration of 1000 h was applied in the first three tests and it was extended to above 2000 h in the last two tests to ensure the validity of the results.

Table 2. Test matrix.

Test No.	Materials	Total test duration
1	3R12, 3RE28, Sanicro 28, Sanicro38	1006
2	3R12, 3XRE28, HR11N, Sanicro 67	1023
3	3R12, HR11N, Sanicro 38, Super 625	1250
4	3R12, carbon steel, Sanicro 67, Super 625	2700
5	3R12, Sanicro 28, HR11N, Sanicro 38	2630

Table 3. Summary of the test conditions during exposure tests.

Test No.	Test duration [h]		Effective temperature [°C]
	Total	Effective[A)]	
1	1006	906 (pressure over 9 bar)	~440
2	1023	744 (pressure over 8 bar)	~440
3	1250	750 (pressure over 7 bar)	~430
4	2700	2154 (pressure over 9 bar)	~440
5	2630	2157 (pressure over 9 bar)	ca. 440°C

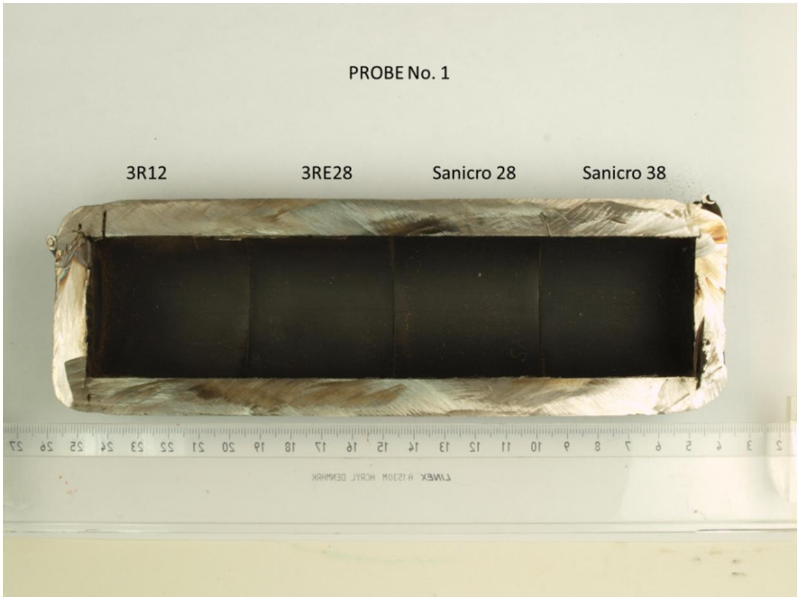
[A)] Used in corrosion rate calculations

4 Results

4.1 Probe test No.1

Total test duration of the test No. 1 was 1006 hours from which 906 hours at the target temperature of 440 °C. The test materials in this exposure were 3R12, 3RE28, Sanicro 28 and Sanicro 38, Figure 3. According to visual inspection all samples were in good condition after testing i.e. neither marked general or localised corrosion nor deposits or oxide scales were observed either on outer or inner surfaces.

a)



b)

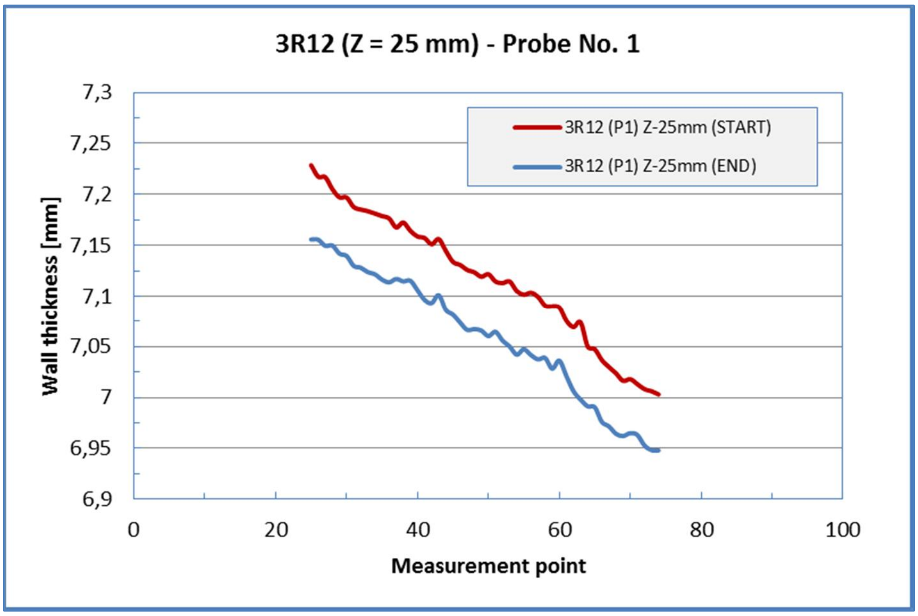
Figure 3. Macrographs taken from the probe No. 1 head after exposure: a) outer surface exposed to the furnace side and b) inner surface exposed to the cooling liquid.

4.1.1 Corrosion rates

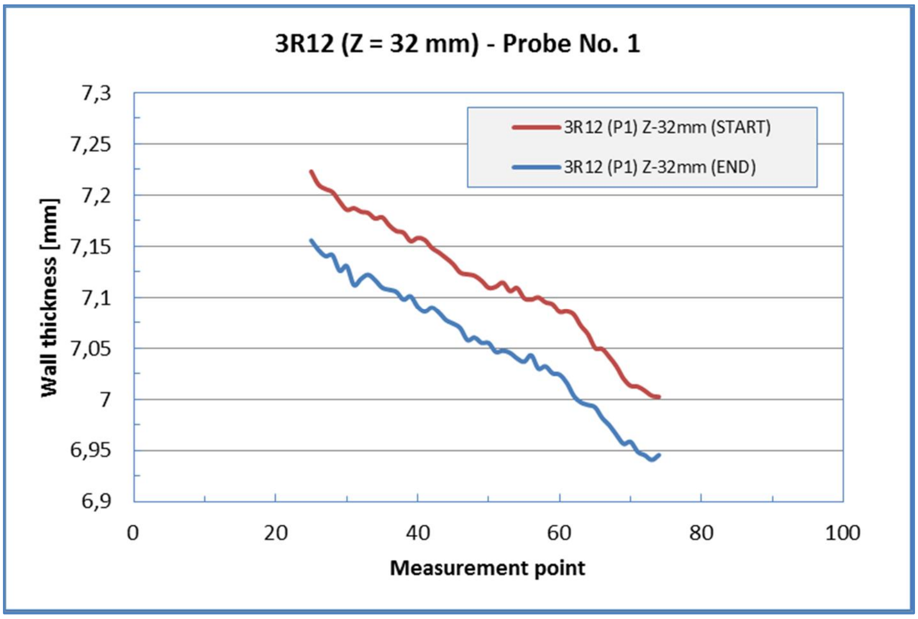
The results of the wall thickness profile measurements and the wall thinning curves derived from them are presented in Figures 4...11. The results showed that marked wall thinning had taken place on the 3R12 specimen. For the other materials the data was more scattered showing that wall thinning and deposit formation (increase in wall thickness) had taken place locally. Measurements showed also that tube wall thicknesses varied a lot as a function of circumference.

The average and maximum corrosion rates calculated on the basis of the wall thickness measurements are presented in Figure 12. In this test highest corrosion rate, order of 0.7 mm/a, was measured for the 3R12 material. Corrosion rate was next highest in the Sanicro 38, for which a maximum corrosion rate of ca. 0.2 mm/a was determined. The maximum corrosion rates of Sanicro 28 and 3RE28 materials were in the order of 0.1 mm/a and they were best performing materials in this test.

The reason to the negative values in average corrosion rates is that the washing and brushing with nylon brush was not effective enough to remove all deposits from the surfaces prior wall thickness measurements, indicating that average corrosion rates may give too optimistic result. Respectively the maximum corrosion rates may give too conservative results, if there are some problems in specimen alignment during WT measurements; this is a specific concern of samples with scratches or dents.

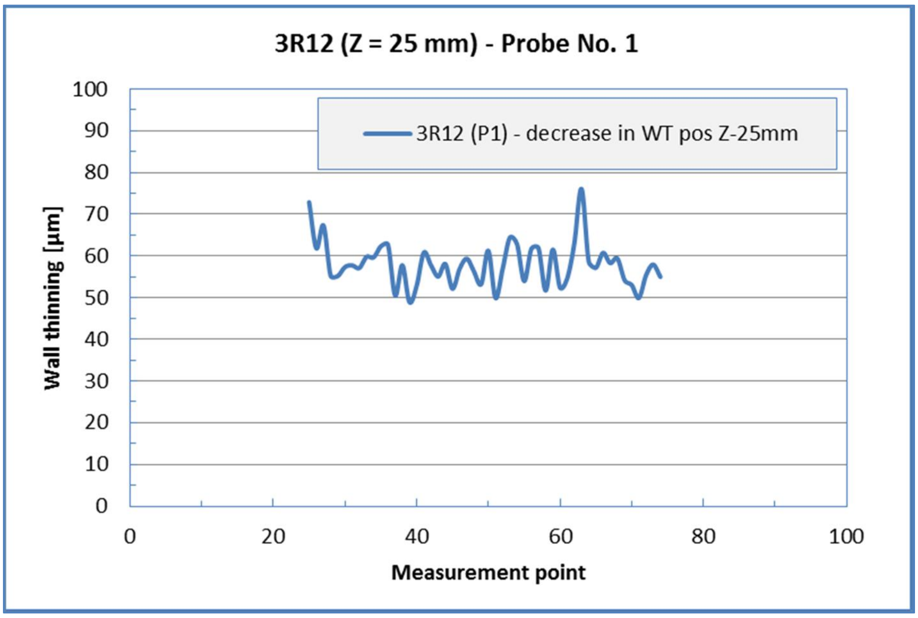


a)

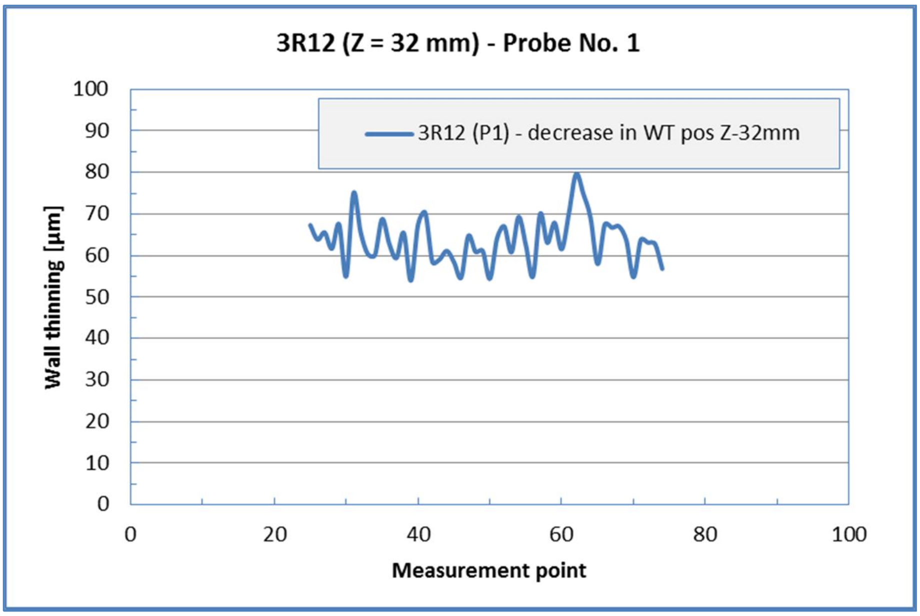


b)

Figure 4. Circumferential wall thickness profiles from 3R12 specimen (Probe No. 1): a) axial location Z = 25 mm and b) axial location Z = 32 mm.

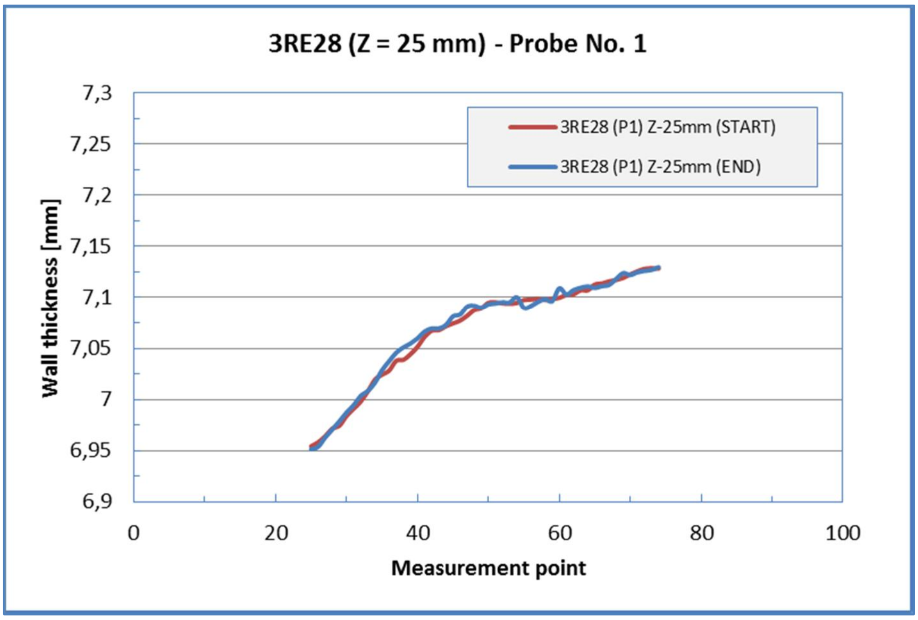


a)

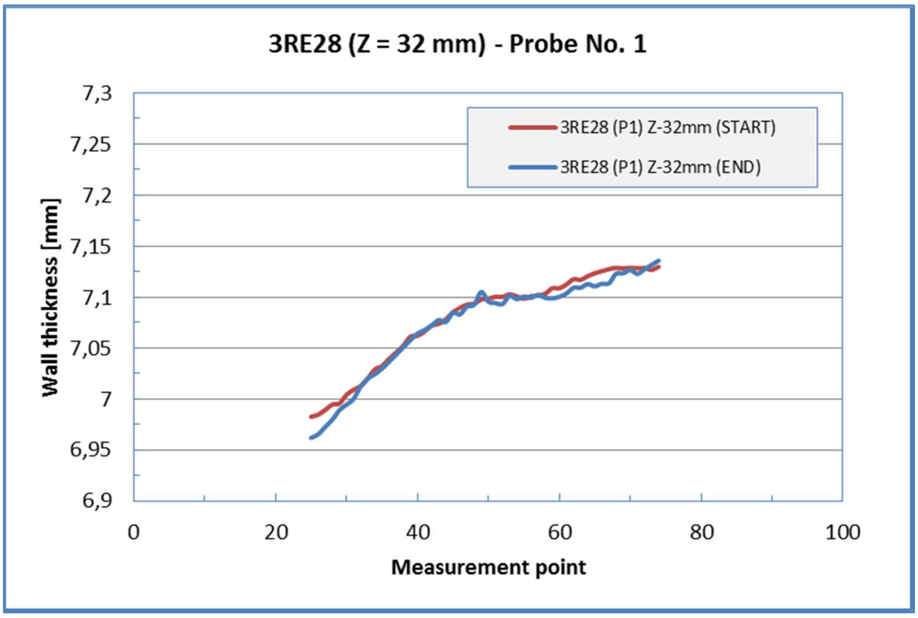


b)

Figure 5. Circumferential wall thinning curves from 3R12 specimen (Probe No. 1): a) axial location Z = 25 mm and b) axial location Z = 32 mm.

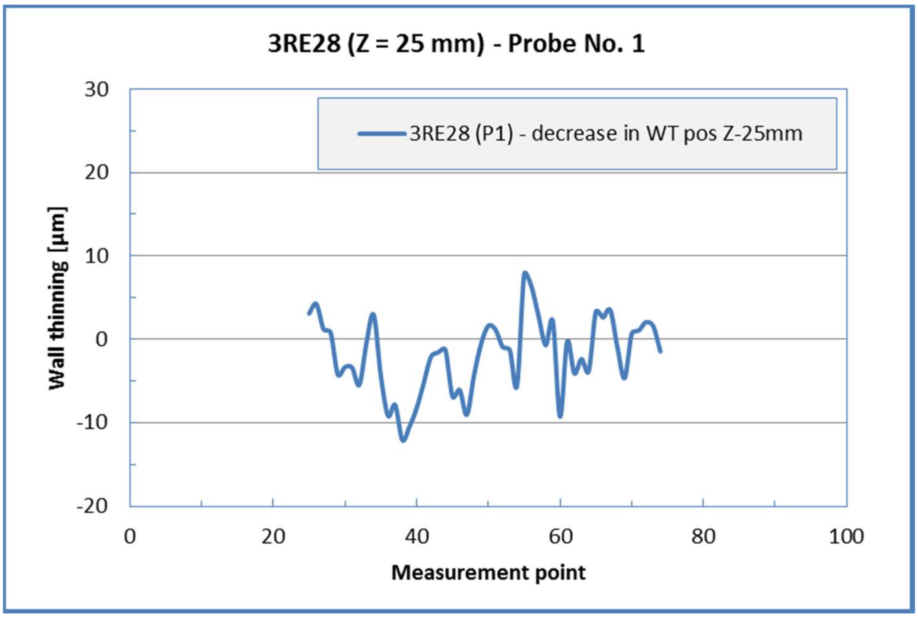


a)

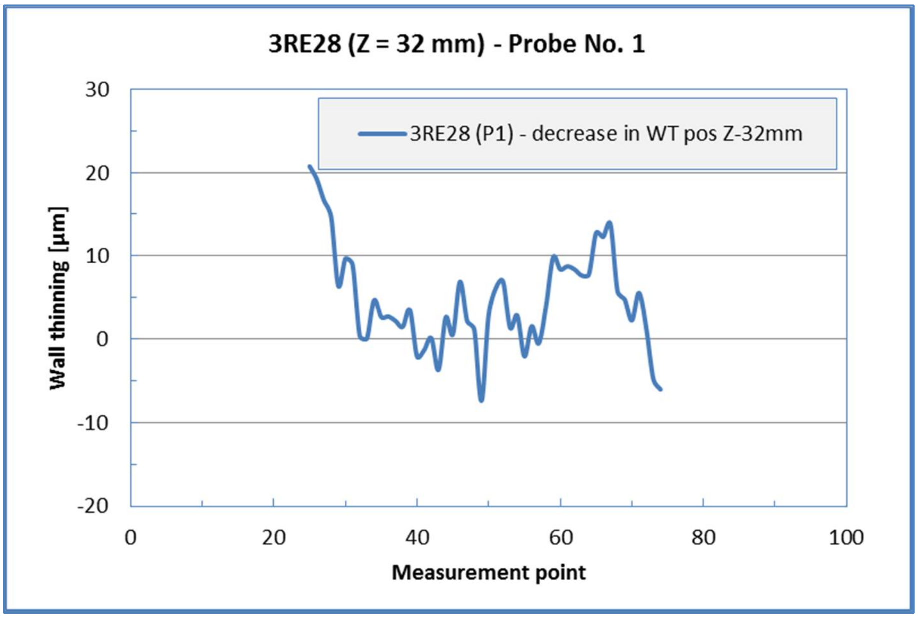


b)

Figure 6. Circumferential wall thickness profiles from 3RE28 specimen (Probe No. 1): a) axial location Z = 25 mm and b) axial location Z = 32 mm.

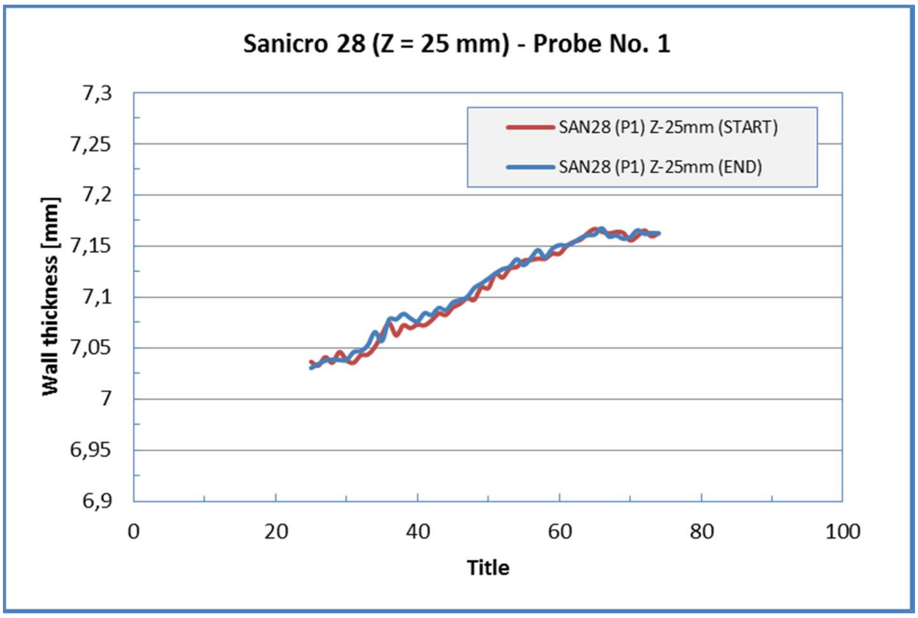


a)

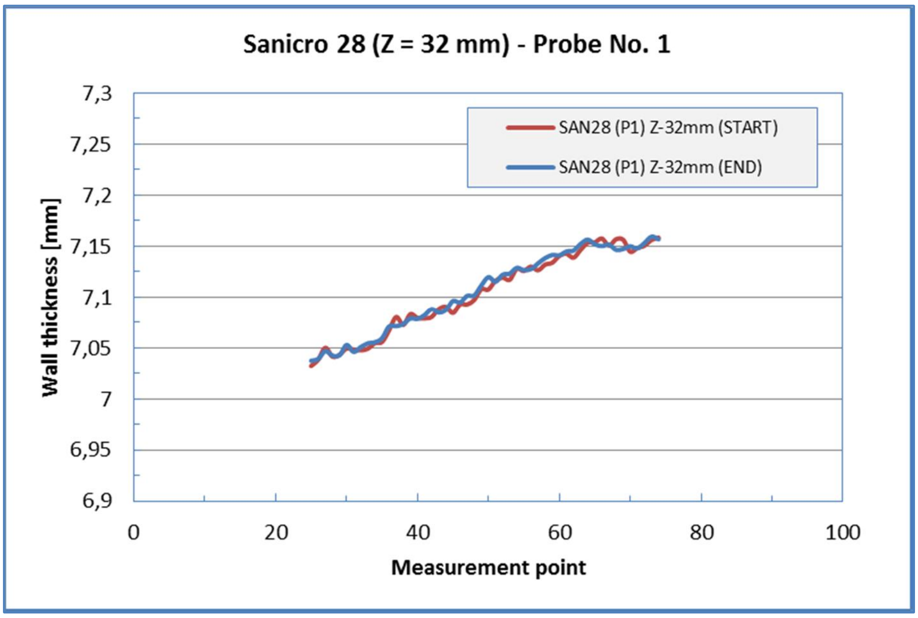


b)

Figure 7. Circumferential wall thinning curves from 3RE28 specimen (Probe No. 1): a) axial location Z = 25 mm and b) axial location Z = 32 mm.

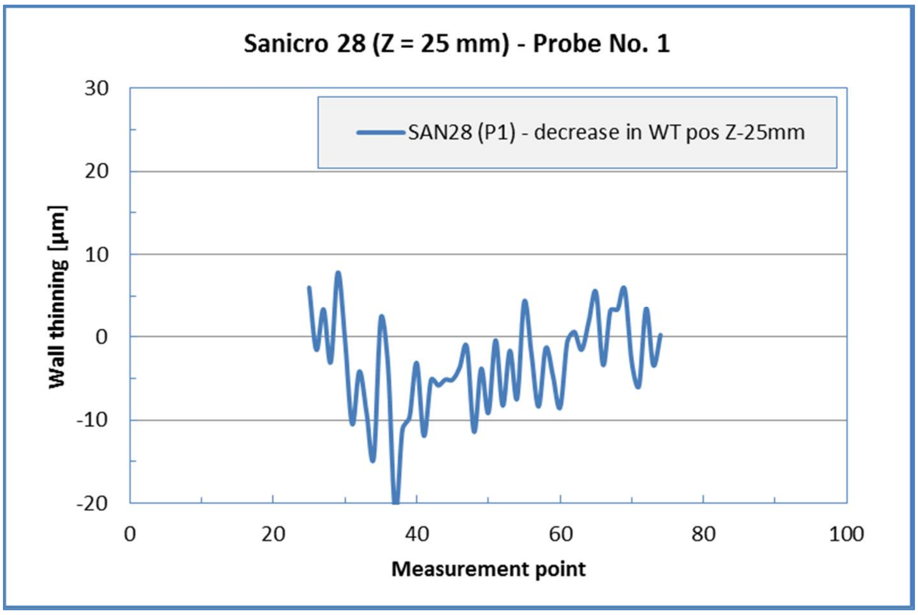


a)

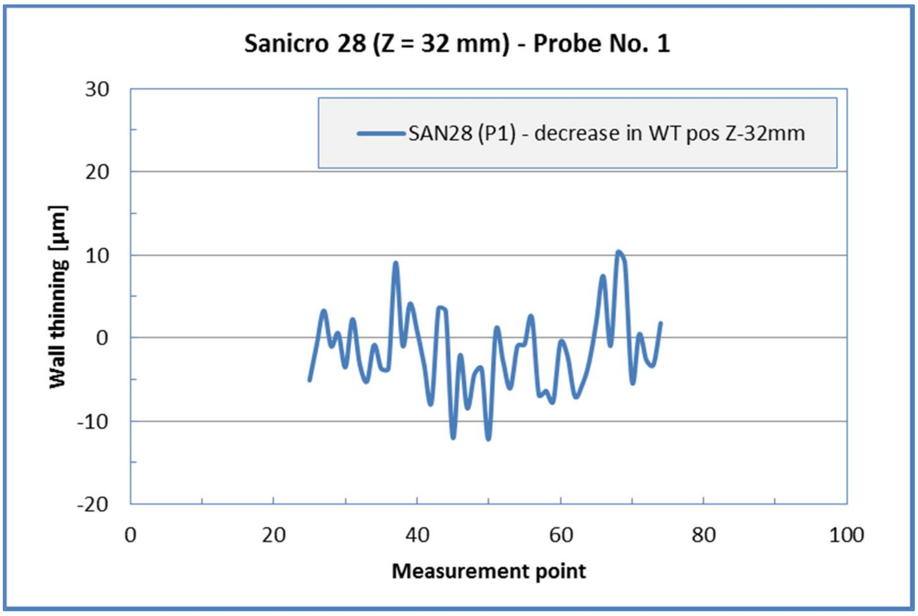


b)

Figure 8. Circumferential wall thickness profiles from Sanicro 28 specimen (Probe No. 1): a) axial location Z = 25 mm and b) axial location Z = 32 mm.

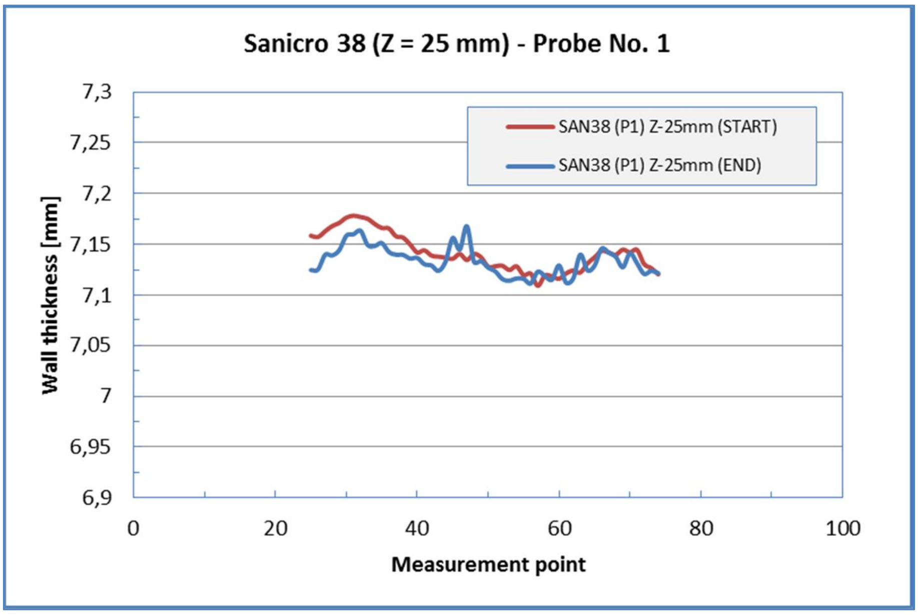


a)

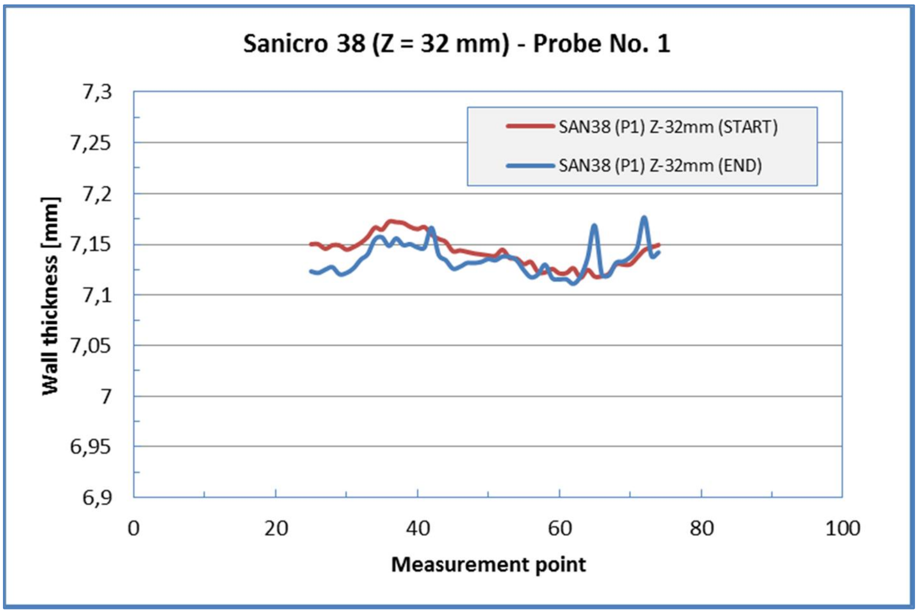


b)

Figure 9. Circumferential wall thinning curves from Sanicro 28 specimen (Probe No. 1): a) axial location Z = 25 mm and b) axial location Z = 32 mm.

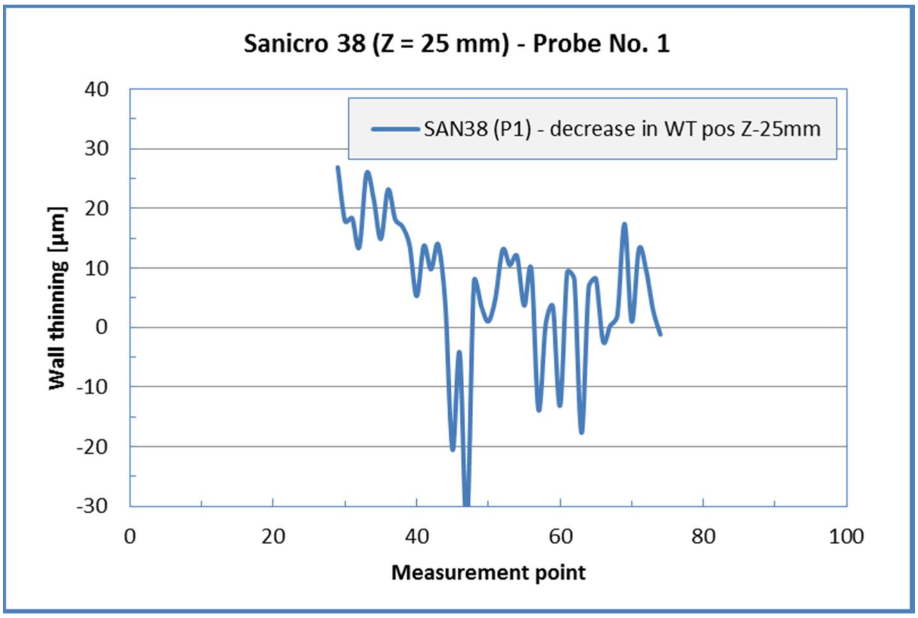


a)

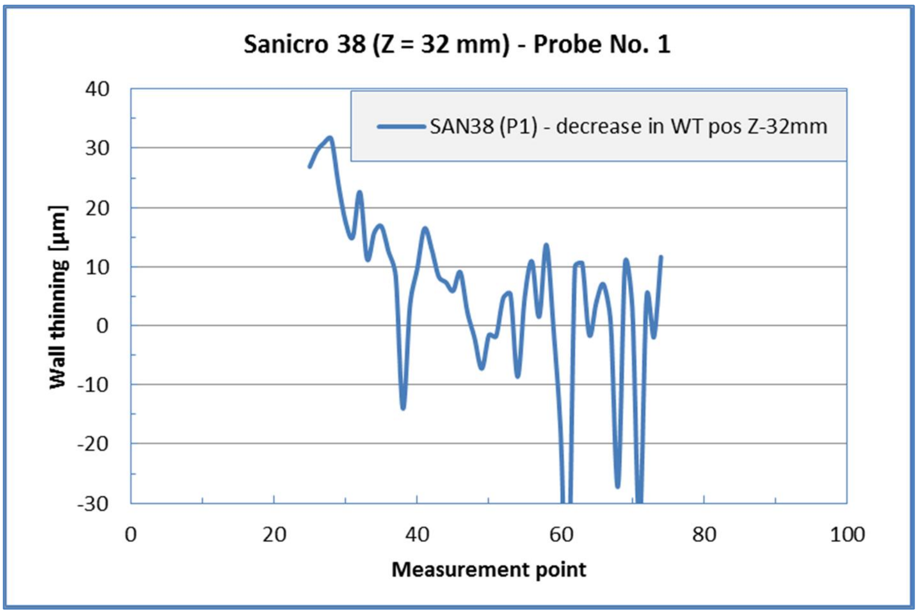


b)

Figure 10. Circumferential wall thickness profiles from Sanicro 38 specimen (Probe No. 1): a) axial location Z = 25 mm and b) axial location Z = 32 mm.

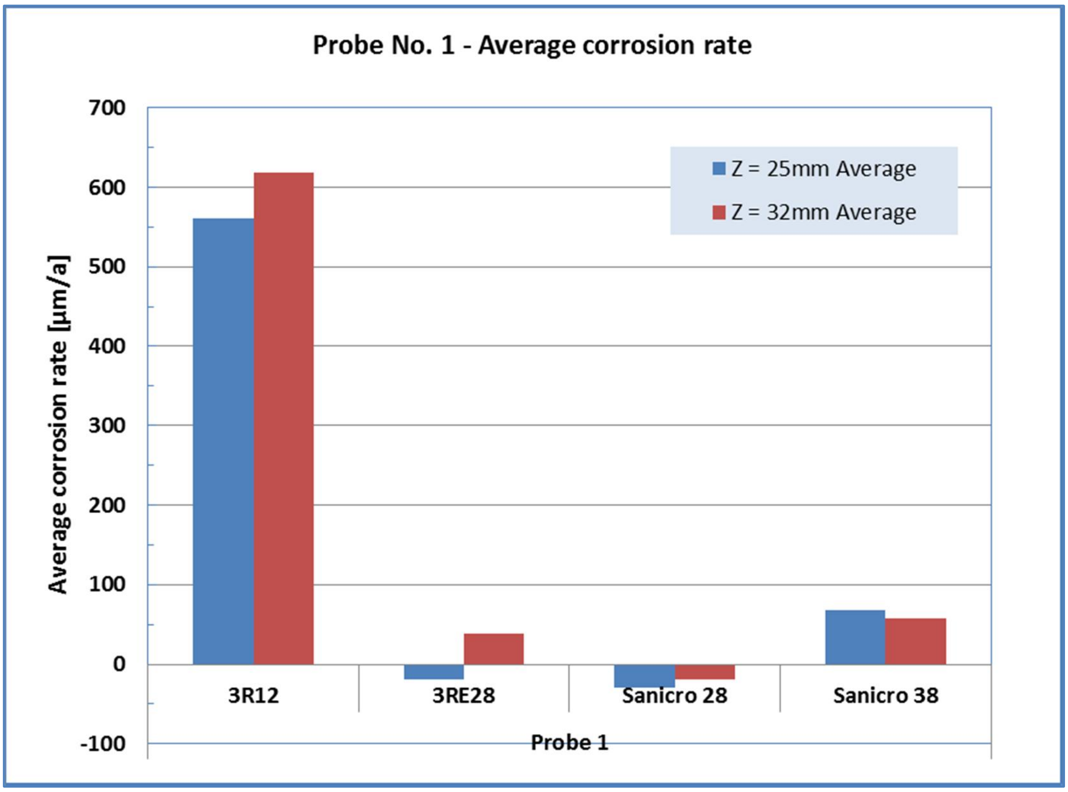


a)

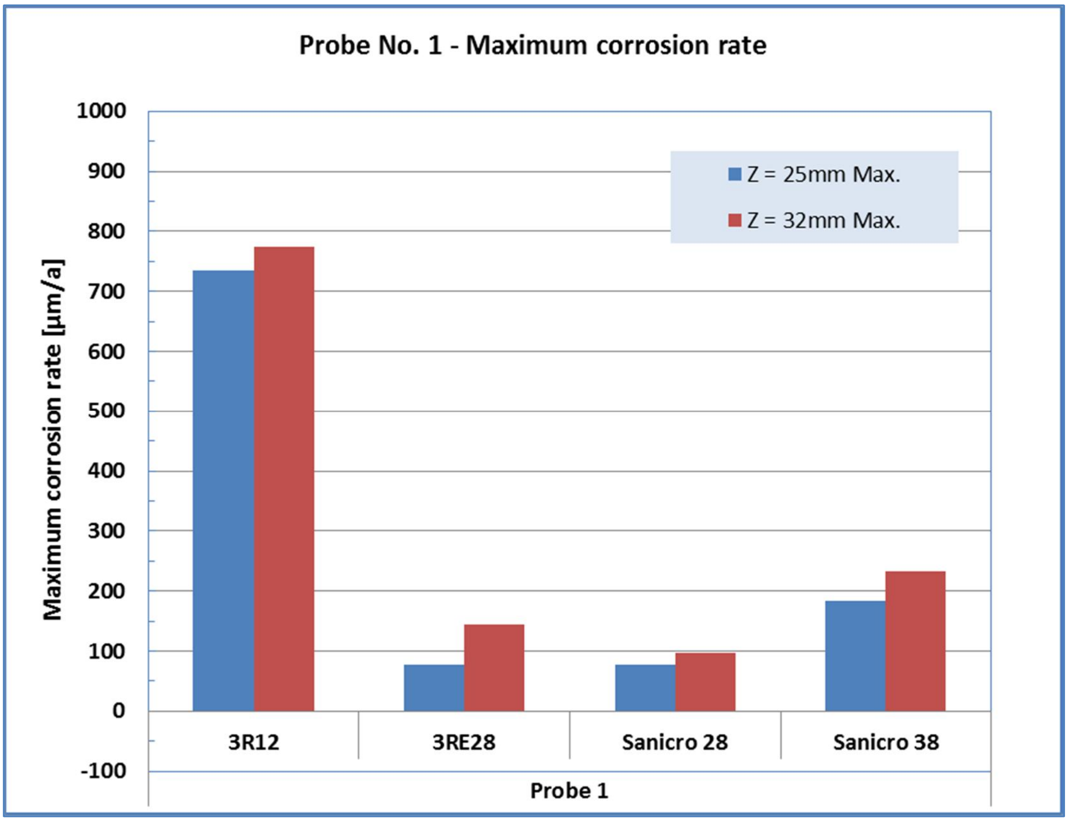


b)

Figure 11. Circumferential wall thinning curves from Sanicro 38 specimen (Probe No. 1): a) axial location Z = 25 mm and b) axial location Z = 32 mm.



a)

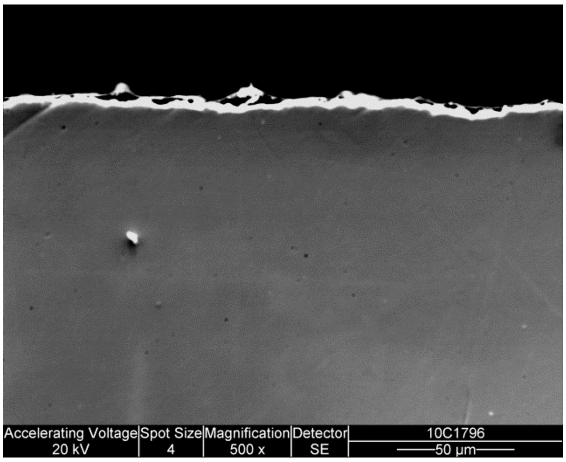


b)

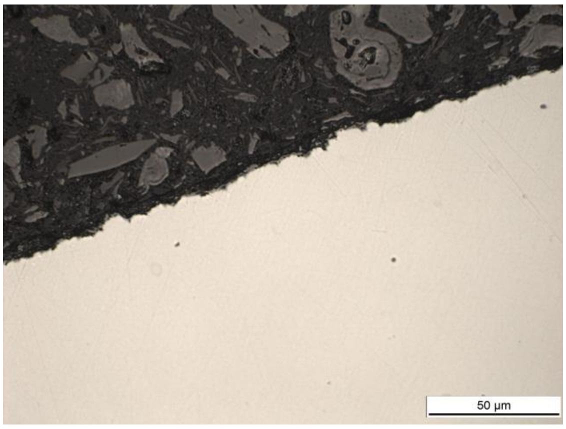
Figure 12. a) Average and b) maximum corrosion rates of the test materials calculated on the basis of the wall thickness measurements after after 906 h exposure in lower furnace at 440 °C (Probe test No. 1).

4.1.2 Metallography

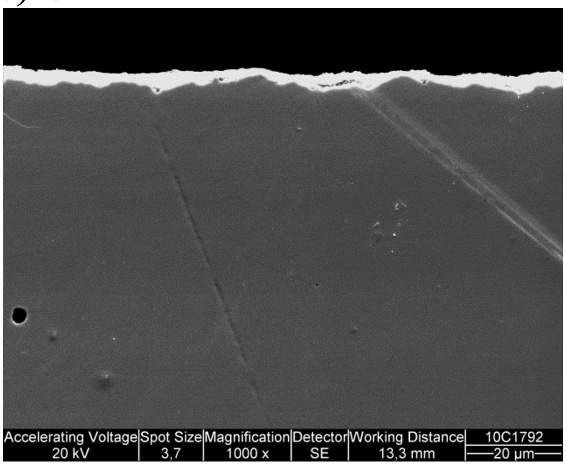
After the tests the samples were examined with optical microscope and/or SEM to determine the type of the corrosion attack. All samples had suffered from general thinning and no marked deposits or oxide/sulphide scales were observed, Figure 13. According to the EDS (Figure 14) analysis the thin layers (thickness ca. 5 µm) on 3RE28 and Sanicro 28 were depleted in iron and nickel and enriched in chromium and contained also high amounts of sulphur. Whereas the composition of thin layer on 3R12 was similar to the base material and no sulphur was detected.



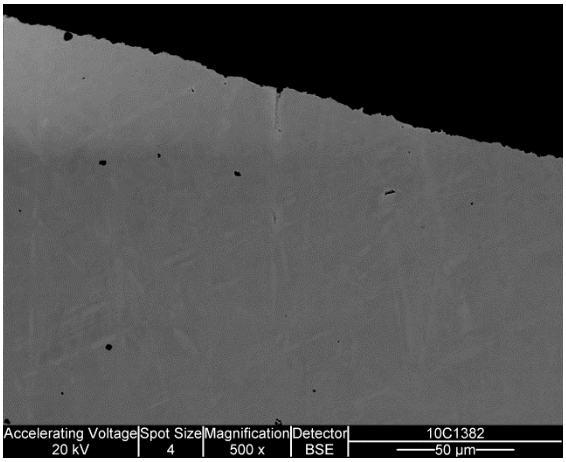
a) 3R12



b) 3RE28



c) *Sanicro 28*



d) *Sanicro 38*

Figure 13. Cross sections from a) 3R12, b) 3RE28, c) Sanicro 28 and d) Sanicro 38 after 906 h exposure in lower furnace at 440 °C (Probe test No. 1)

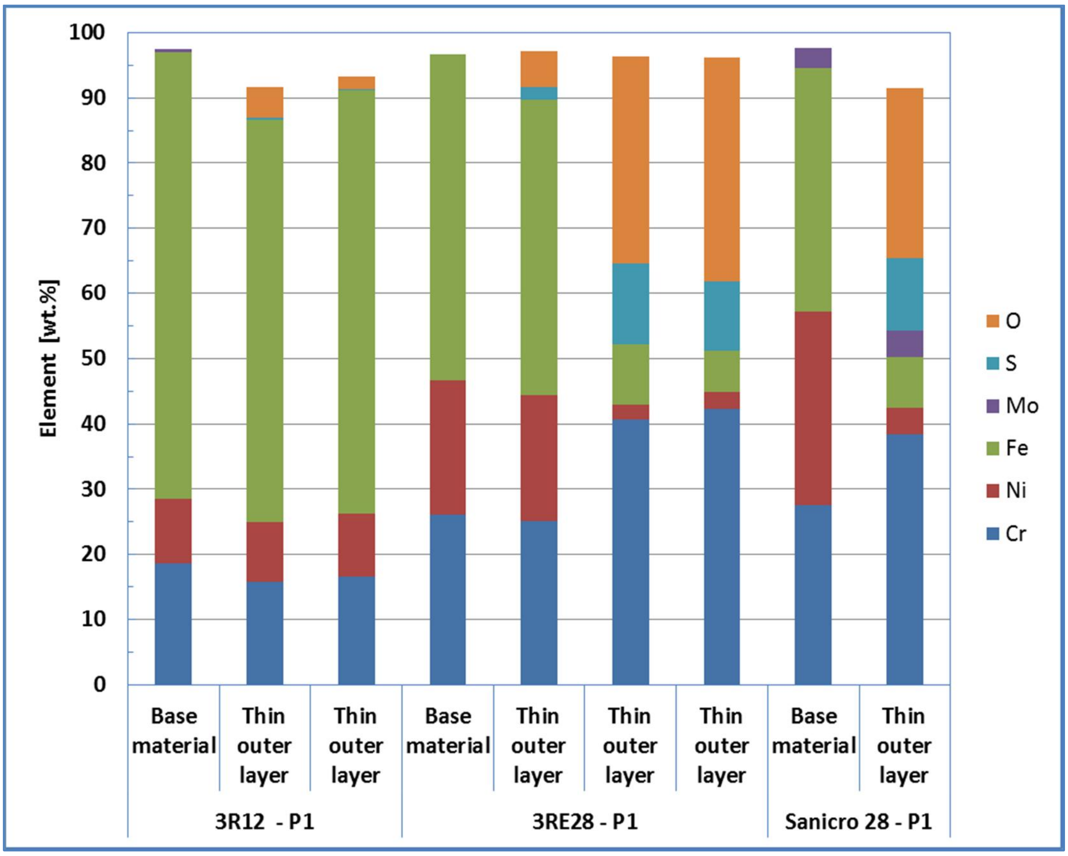


Figure 14. Results from the EDS analysis performed for the 3R12, 3RE28 and Sanicro 28 specimens after 906 h exposure in lower furnace at 440 °C (Probe test No. 1). Note: Quantitative results from cross sections, carbon excluded. Data from layers are from point analysis, whereas area analysis was used for base materials.

4.2 Probe test No.2

Total test duration of the test No. 2 was 1023 hours from which 744 hours at the target temperature of 440 °C. The test materials in this exposure were 3R12, 3XRE28, HR11N and Sanicro 67, Figure 15. According to visual inspection the inner surfaces of the specimens were in good condition after testing i.e. neither marked general or localised corrosion nor deposits or oxide scales were observed. The outer surfaces of the specimens appeared to be in good condition but the thin dark and white deposits on the surfaces hindered accurate examinations.

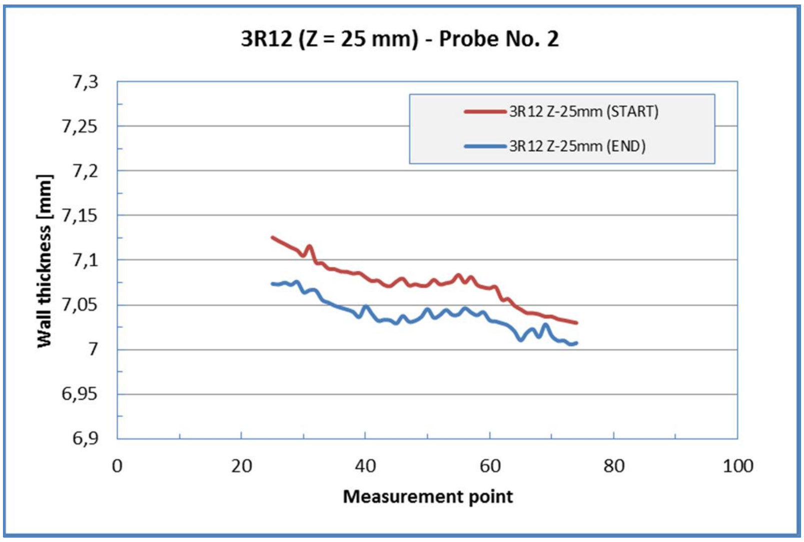
a)

b)

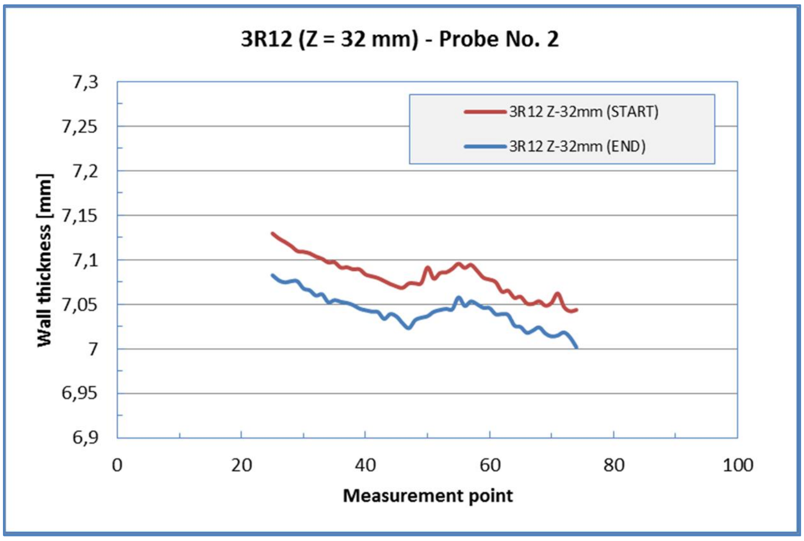
Figure 15. Macrographs taken from the probe No. 2 head after exposure: a) outer surface exposed to the furnace side and b) inner surface exposed to the cooling liquid.

4.2.1 Corrosion rates

The results of the wall thickness profile measurements and the wall thinning curves derived from them are presented in Figures 16...23. The results showed that marked wall thinning had taken place on the 3R12 specimen and lesser degree also on the HR11N specimen. The data of the 3XRE28 and Sanicro 67 materials was more scattered showing that wall thinning and deposit formation (increase in wall thickness) had taken place locally. Measurements showed also that the wall thickness variations were smaller in the machined HR11N specimen than in the other specimens tested in as received condition. The average and maximum corrosion rates calculated on the basis of the wall thickness measurements are presented in Figure 12. In this test highest corrosion rate in the order of 0.6 mm/a was measured for the 3R12 material. The corrosion resistance of the 3XRE28, HR11N and Sanicro 67 was practically at the same level.

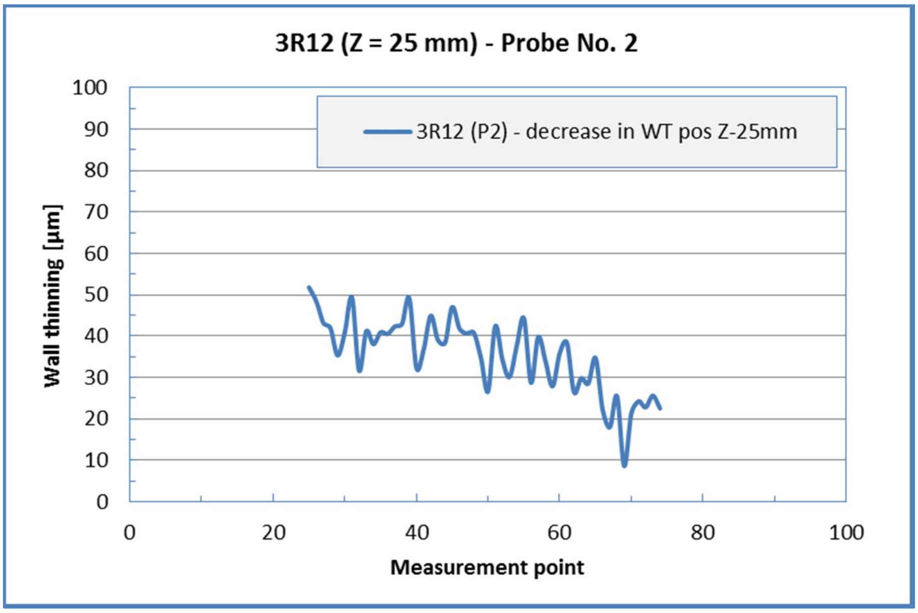


a)

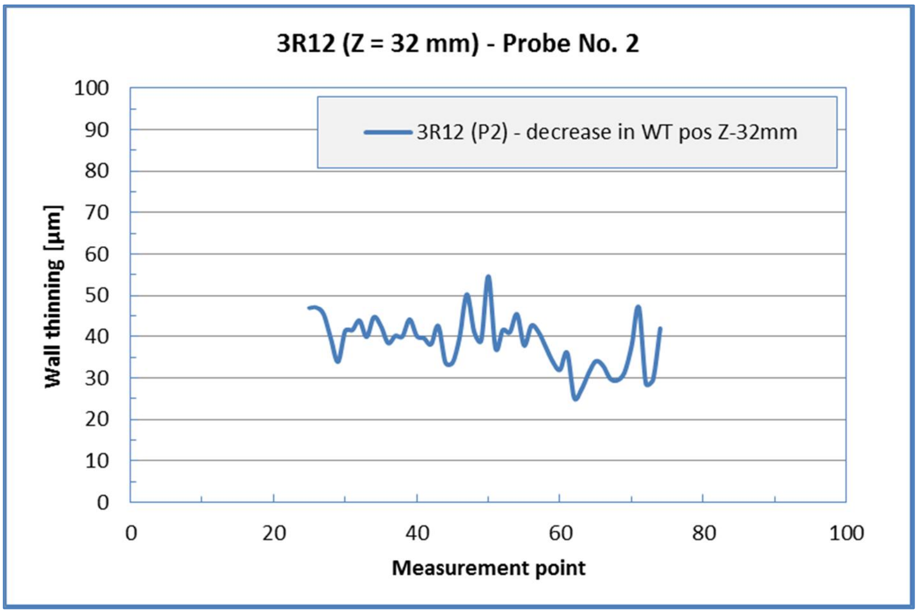


b)

Figure 16. Circumferential wall thickness profiles from 3R12 specimen (Probe No. 2): a) axial location Z = 25 mm and b) axial location Z = 32 mm.

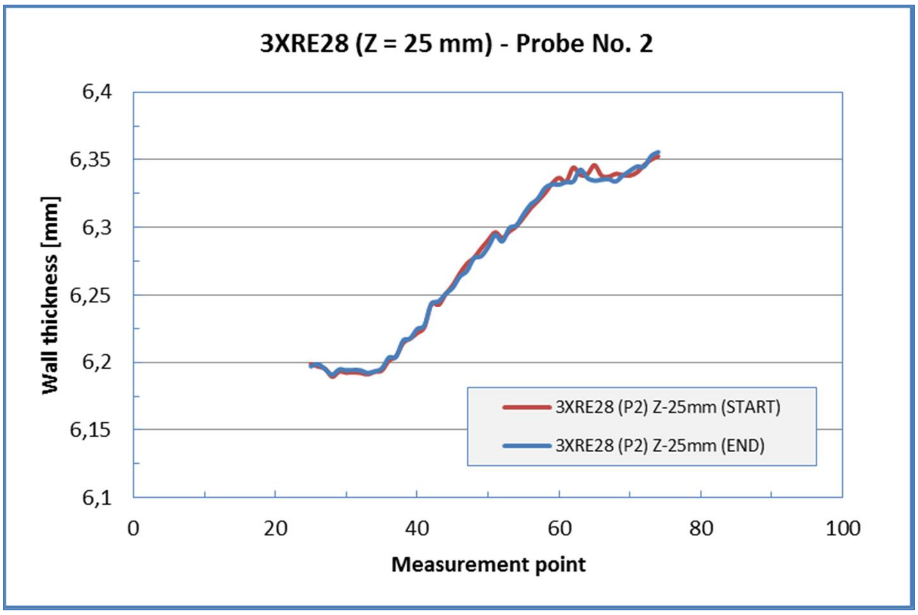


a)

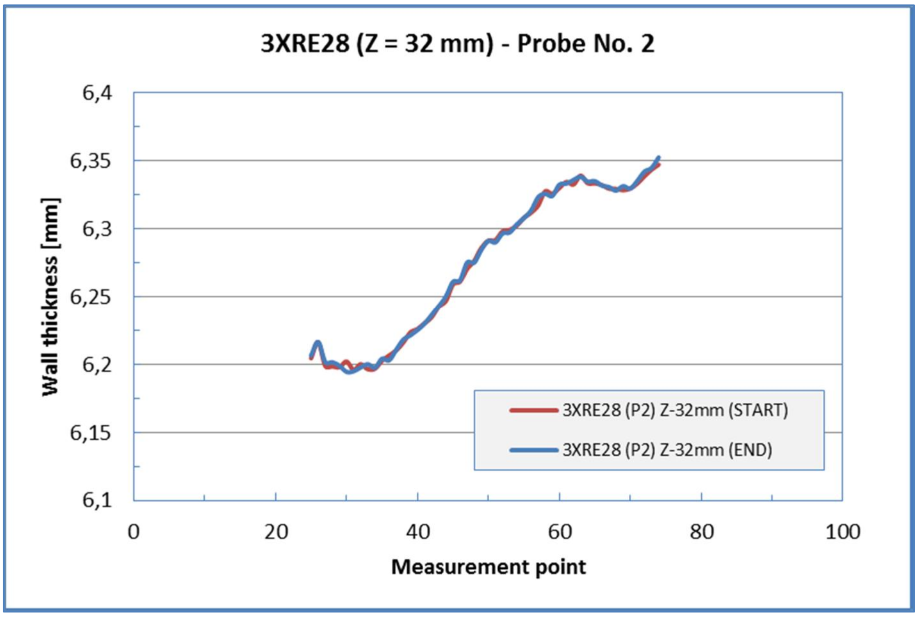


b)

Figure 17. Circumferential wall thinning curves from 3R12 specimen (Probe No. 2): a) axial location Z = 25 mm and b) axial location Z = 32 mm.

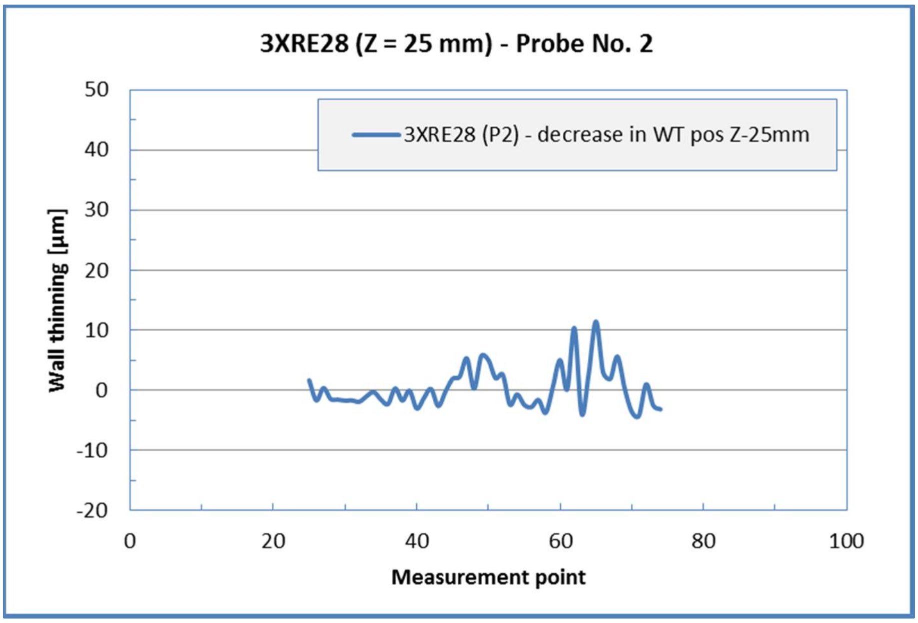


a)

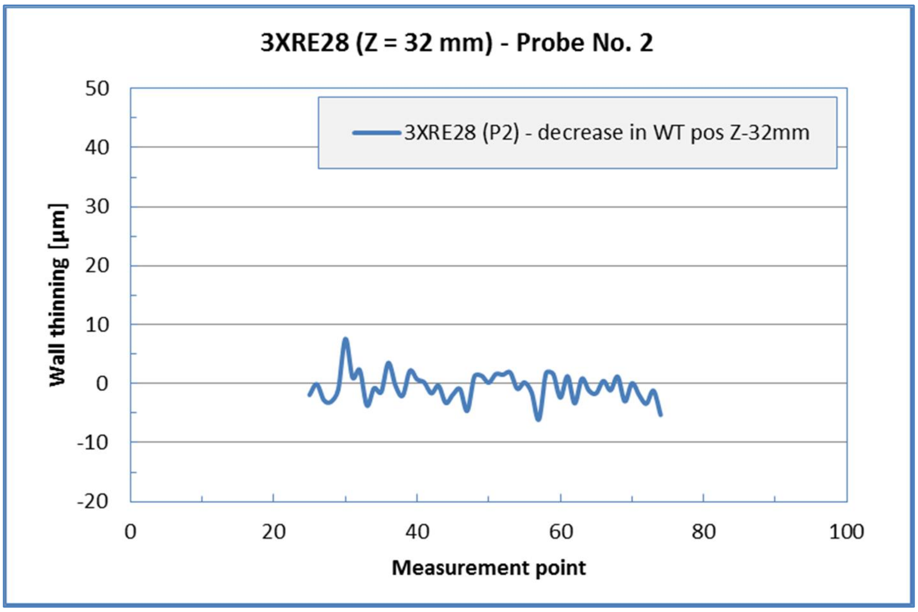


b)

Figure 18. Circumferential wall thickness profiles from 3XRE28 specimen (Probe No. 2): a) axial location Z = 25 mm and b) axial location Z = 32 mm.

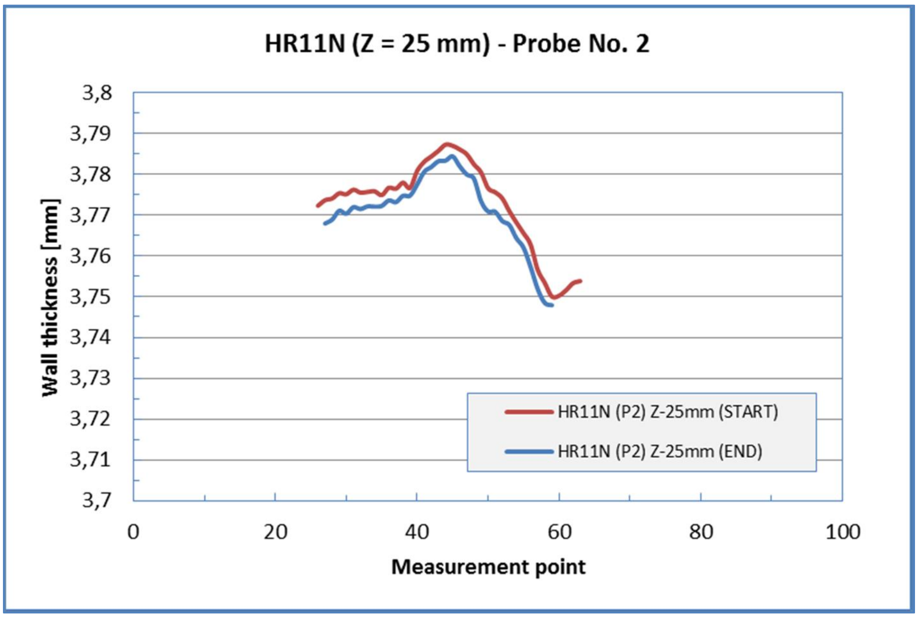


a)

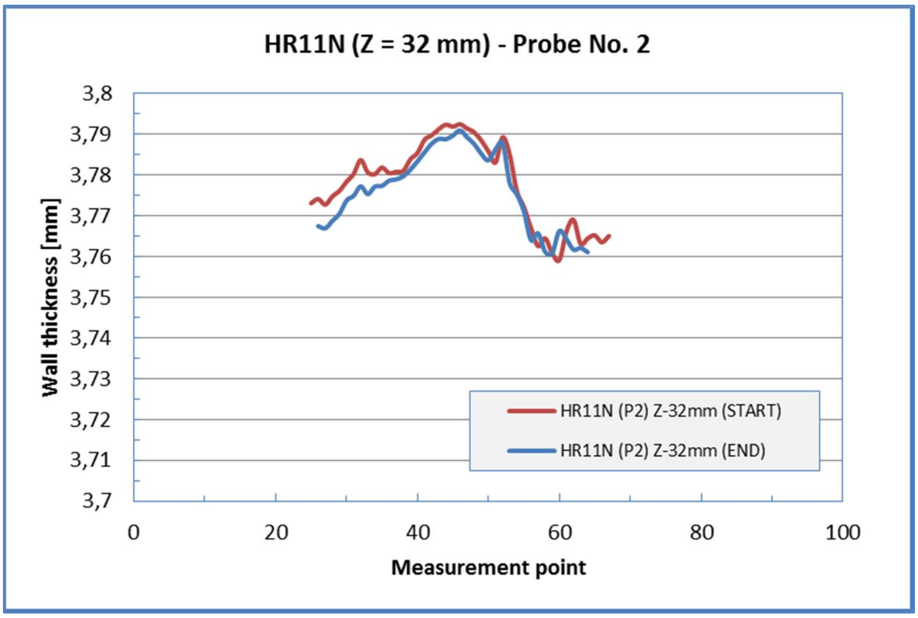


b)

Figure 19. Circumferential wall thinning curves from 3XRE28 specimen (Probe No. 2): a) axial location Z = 25 mm and b) axial location Z = 32 mm.

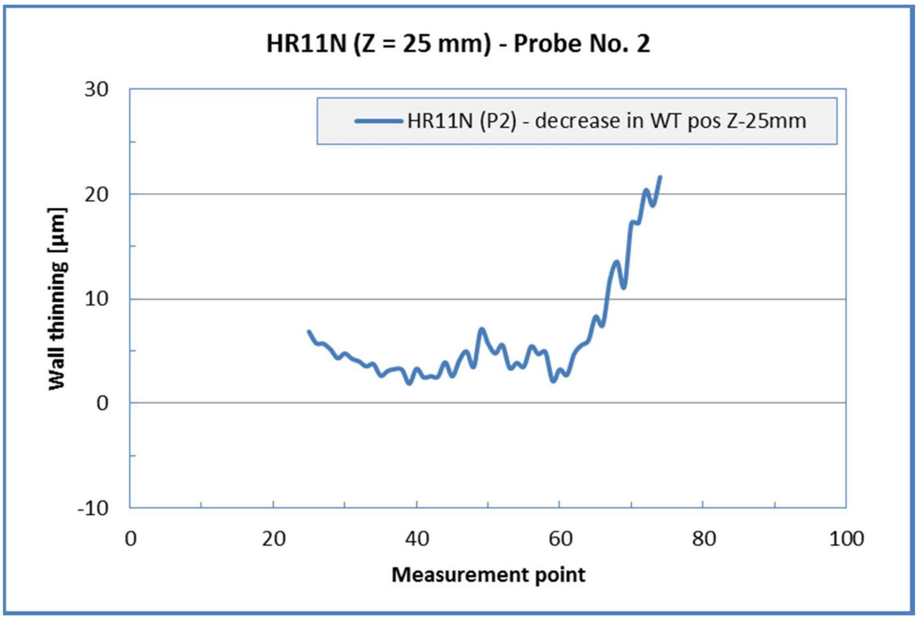


a)

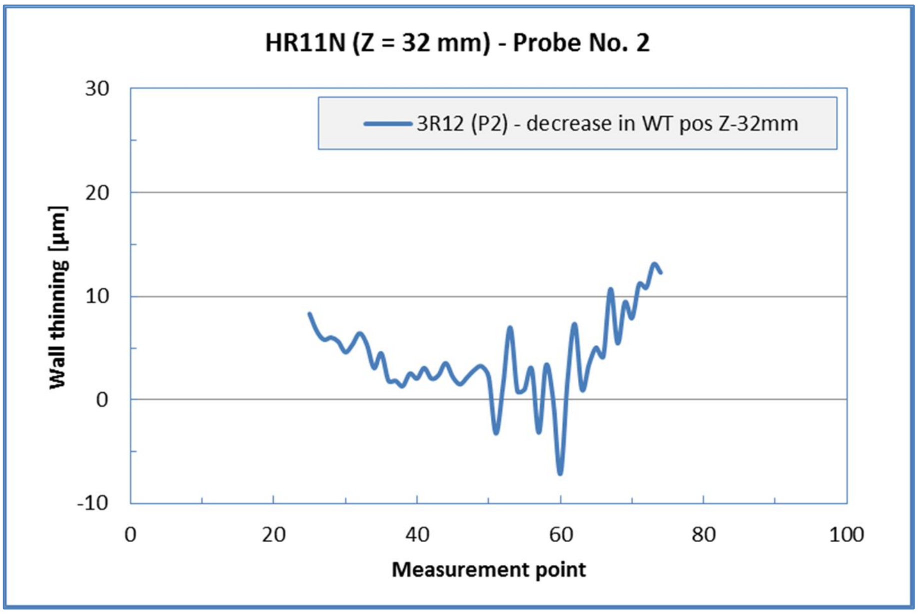


b)

Figure 20. Circumferential wall thickness profiles from HR11N specimen (Probe No. 2): a) axial location Z = 25 mm and b) axial location Z = 32 mm.

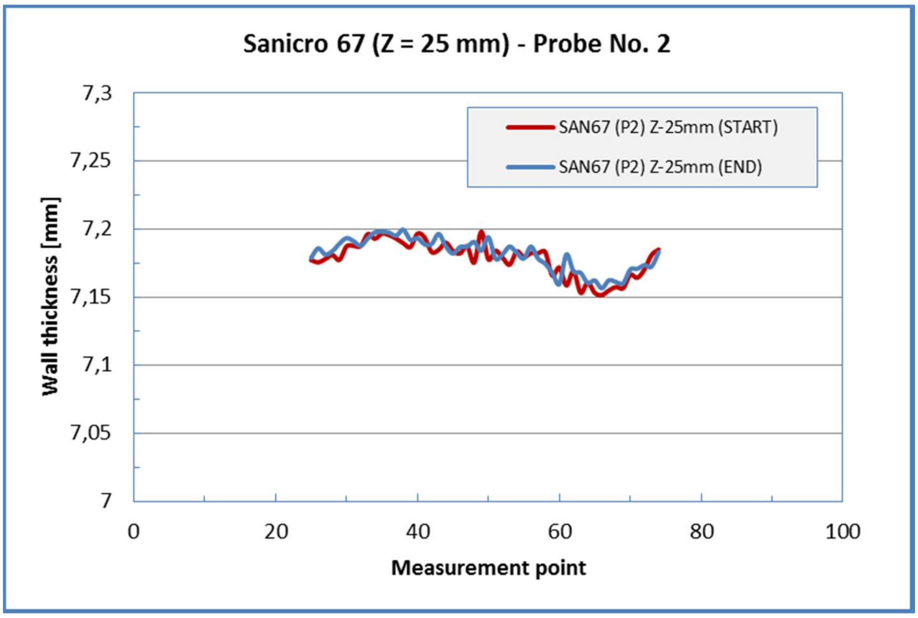


a)

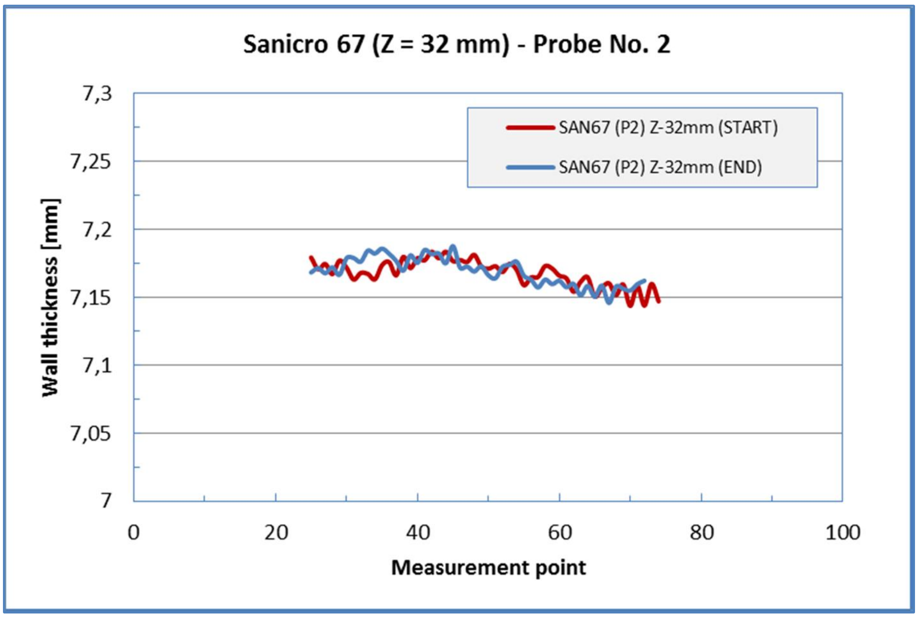


b)

Figure 21. Circumferential wall thinning curves from HR11N specimen (Probe No. 2): a) axial location Z = 25 mm and b) axial location Z = 32 mm.

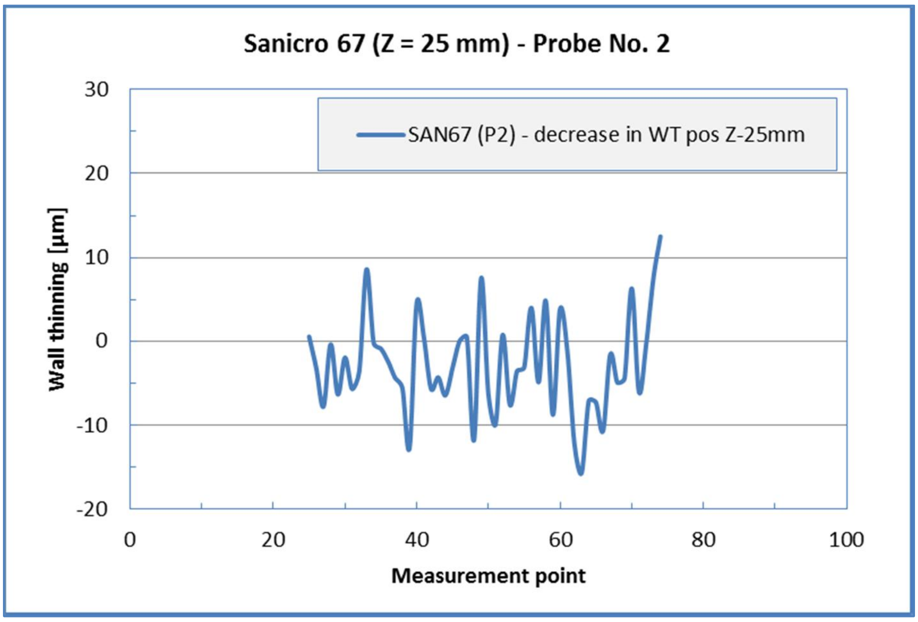


a)

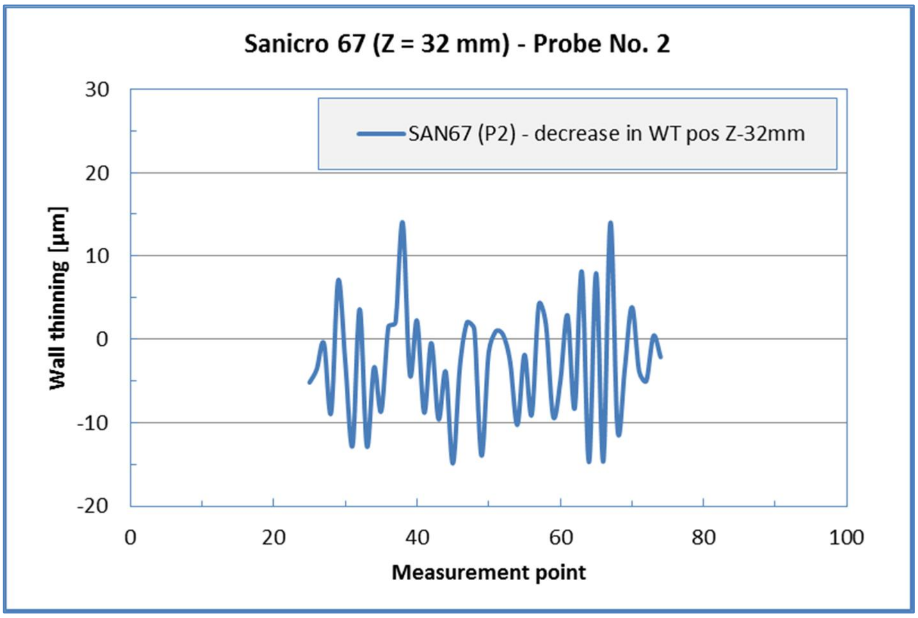


b)

Figure 22. Circumferential wall thickness profiles from Sanicro 67 specimen (Probe No. 2): a) axial location Z = 25 mm and b) axial location Z = 32 mm.

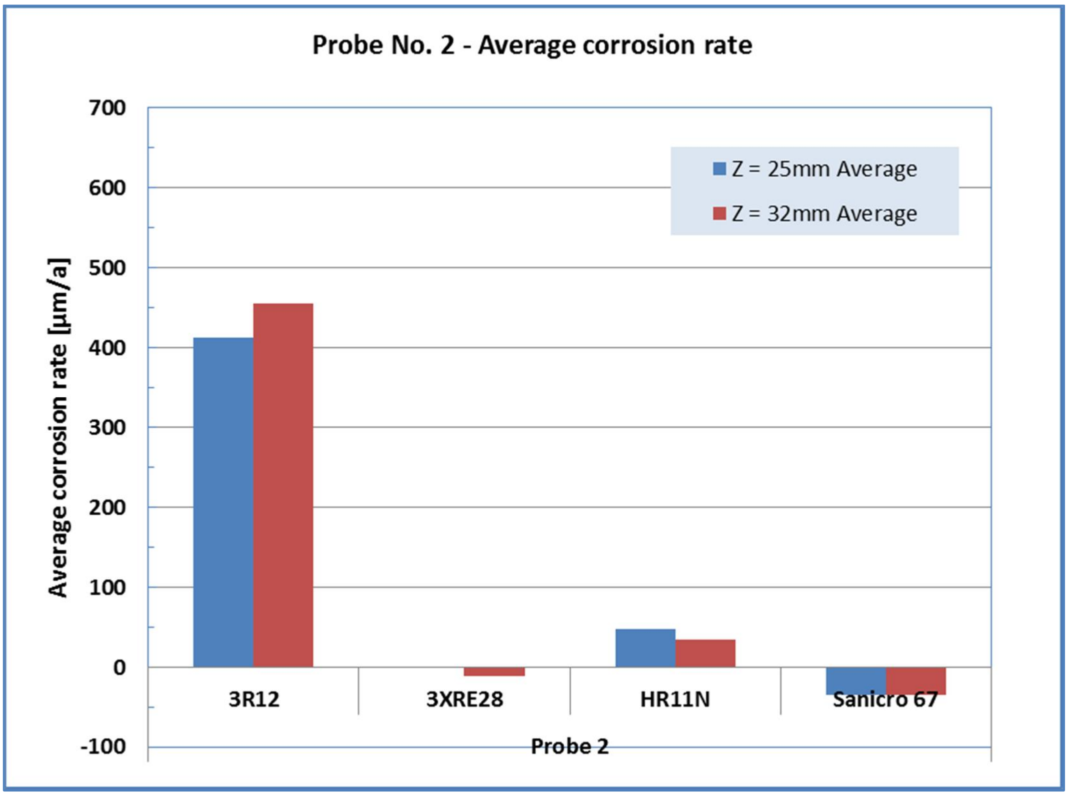


a)

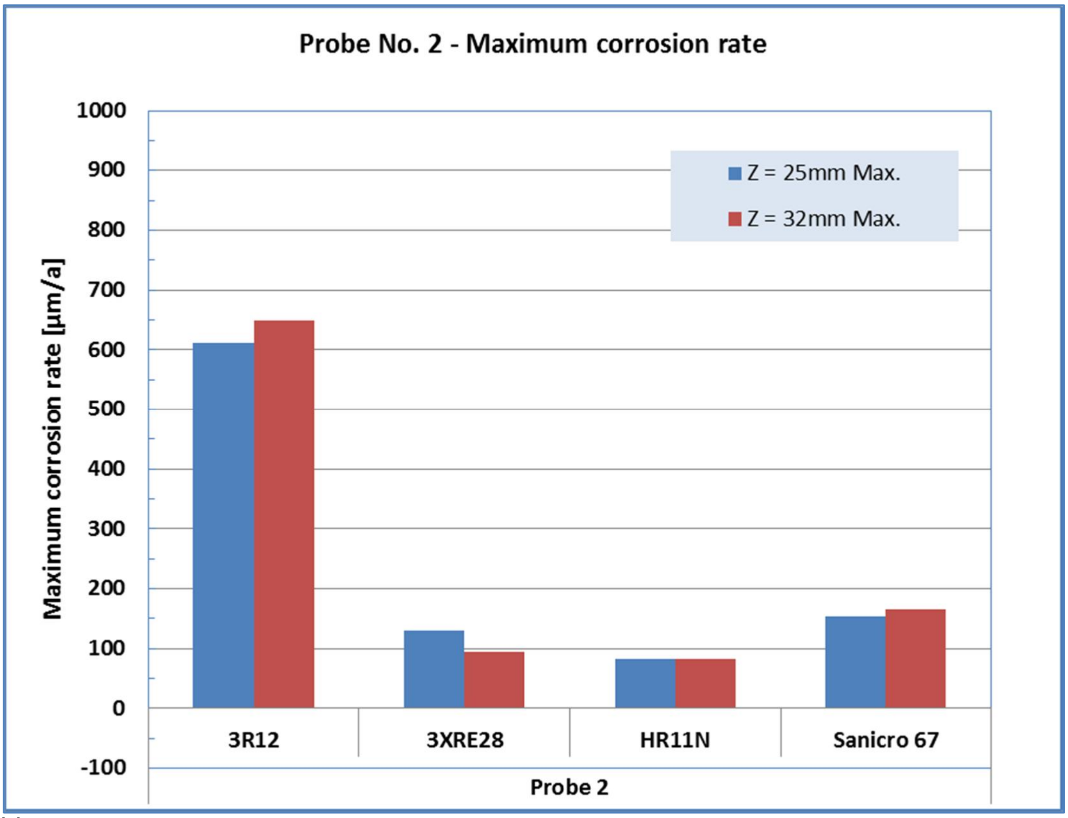


b)

Figure 23. Circumferential wall thinning curves from Sanicro 67 specimen (Probe No. 2): a) axial location Z = 25 mm and b) axial location Z = 32 mm.



a)

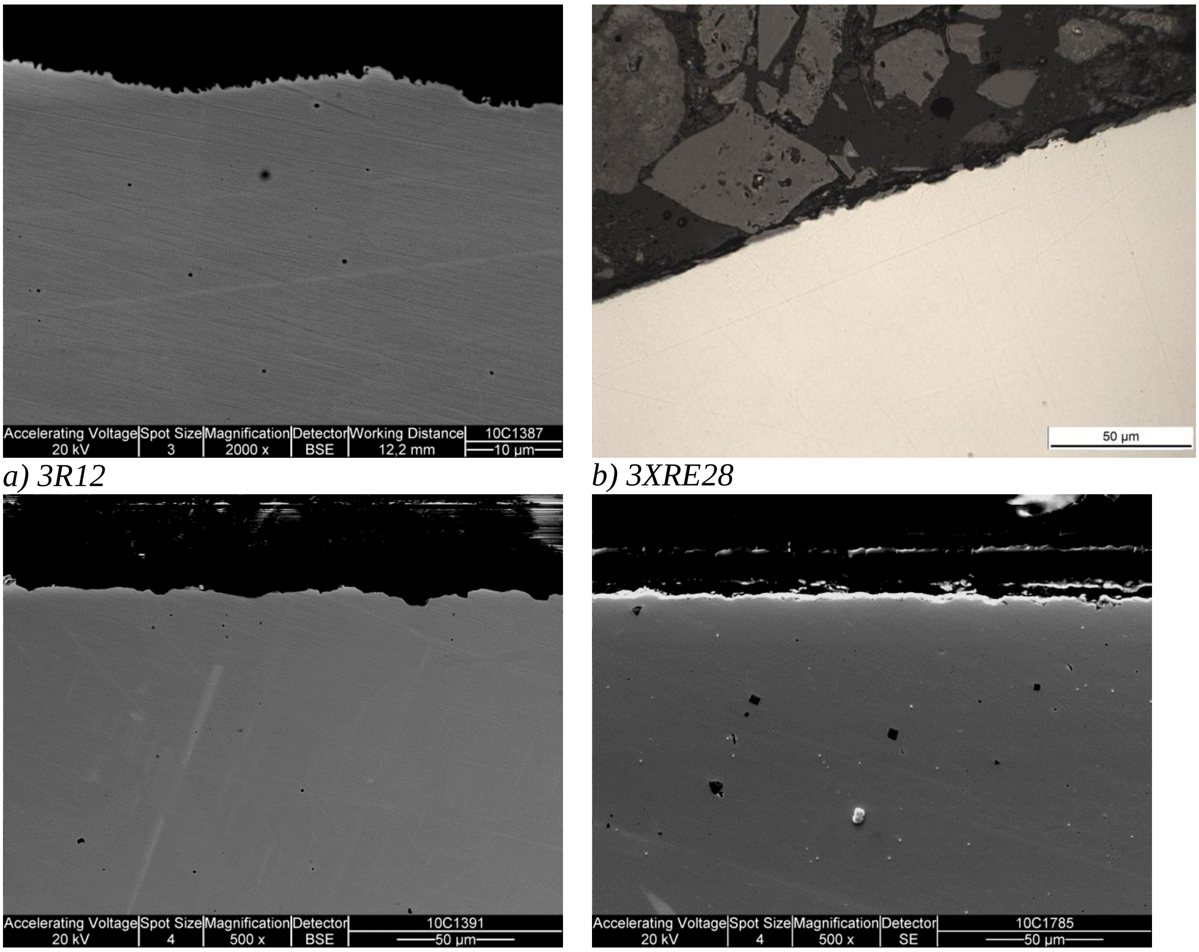


b)

Figure 24. a) Average and b) maximum corrosion rates of the test materials calculated on the basis of the wall thickness measurements after 744 h exposure in lower furnace at 440 °C (Probe test No. 2).

4.2.2 Metallography

After the tests the samples were examined with optical microscope and/or SEM to determine the type of the corrosion attack. All samples had suffered from general thinning and no marked deposits or oxide/sulphide scales were observed on the surfaces, Figure 25. According to the EDS analysis (Figure 26) the thin, a few µm thick layer, observed on 3XRE28 was depleted in iron and nickel and enriched in chromium and contained also high amounts of sulphur. The similar thin layer on Sanicro 67 contained high amounts of sulphur and was depleted in nickel and iron whereas chromium content was at the same level than in the base material.



a) 3R12 *b) 3XRE28* *c) HR11N* *d) Sanicro 67*

Figure 25. Cross sections from a) 3R12, b) 3XRE28, c) HR11N and d) Sanicro 67 after 744 h exposure in lower furnace at 440 °C (Probe test No. 2)

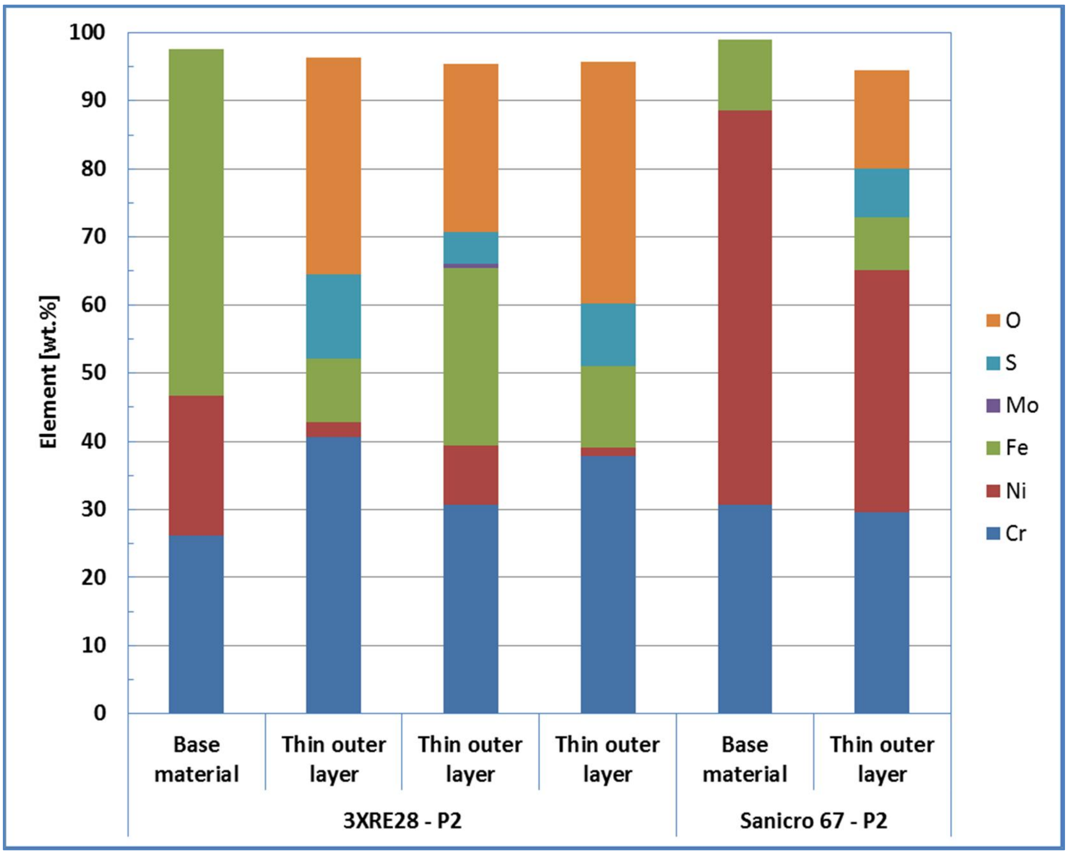


Figure 26. Results from the EDS analysis performed for the 3XRE28 and Sanicro 67 specimens after 744 h exposure in lower furnace at 440 °C (Probe test No. 2). Note: Quantitative results from cross sections, carbon excluded. Data from layers are from point analysis, whereas area analysis was used for base materials.

4.3 Probe test No. 3

Total test duration of the test No. 3 was 1250 hours from which 750 hours at the target temperature of 430 °C. The test materials in this exposure were 3R12, HR11N, Sanicro 38 and Super 625, Figure 27.

According to visual inspection the inner surfaces of the specimens were in good condition after testing. Some deposits were observed on the inner surfaces but based on their appearance they originate from the probe cutting conducted after the probe has been removed from the boiler. The outer surfaces of the specimens were covered with dark and brown deposits but appeared to be in good condition.

a)

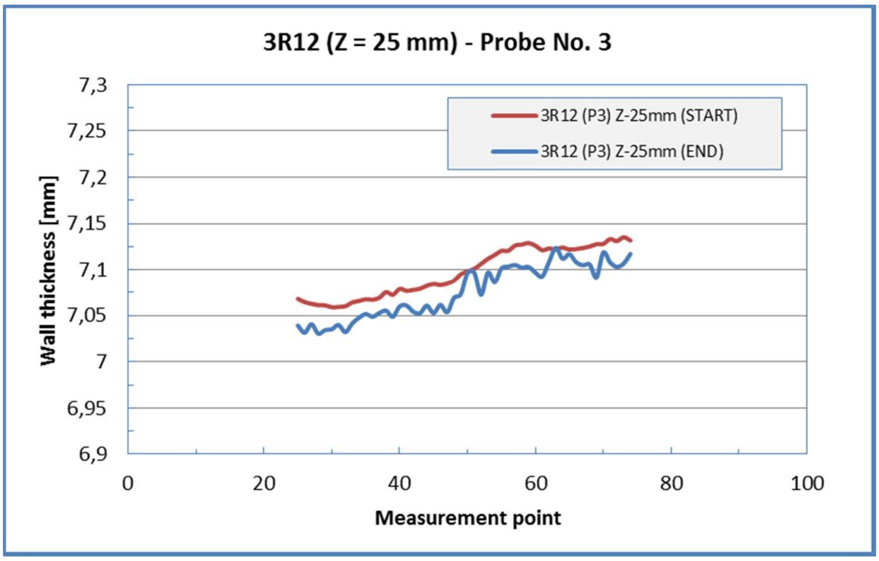
b)

Figure 27. Macrographs taken from the probe No. 3 head after exposure: a) outer surface exposed to the furnace side and b) inner surface exposed to the cooling liquid.

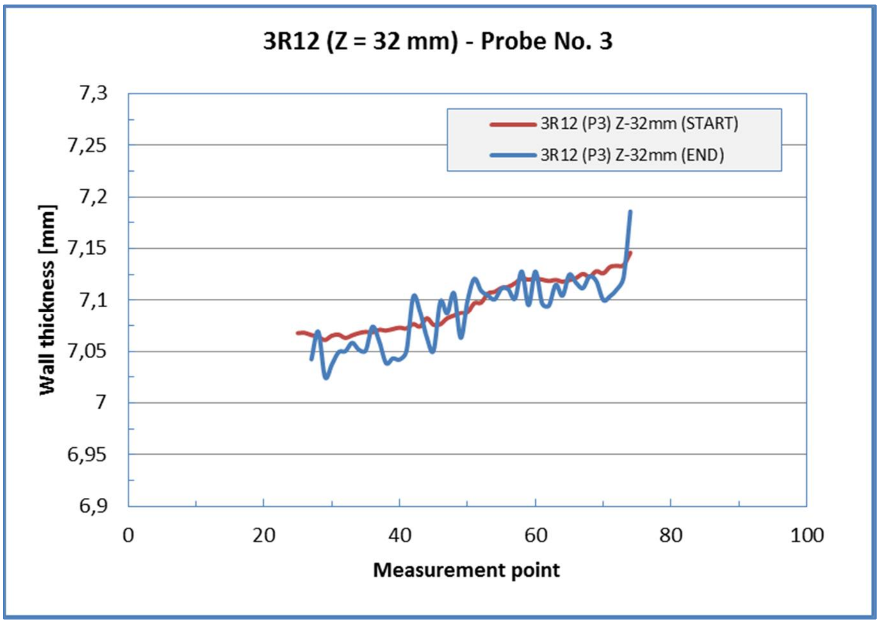
4.3.1 Corrosion rates

The results of the wall thickness profile measurements and the wall thinning curves derived from them are presented in Figures 28...35. The results showed that marked wall thinning had taken place only on the 3R12 specimen. Some wall thinning was observed also on the Super 625 specimen. The data of the HR11N and Sanicro 38 was more scattered showing that wall thinning and deposit formation (increase in wall thickness) had taken place locally. In addition the data in this test was more scattered than in the previous test indicating that all deposits were not removed from the surfaces in washing performed for the specimens' prior measurements.

The average and maximum corrosion rates calculated on the basis of the wall thickness measurements are presented in Figure 36. In this test the corrosion rate of 3R12 was in the order 0.4 mm/a, i.e. about 0.2 mm/a lower than in the first two tests, most probably due the lower probe temperature. The corrosion rate of the Super 625 was unexpectedly high ca. 0.3...0.4mm/a. The maximum corrosion rates of HR11N and Sanicro 38 were in the order of 0.1 mm/a, and they were best performing materials in this test.

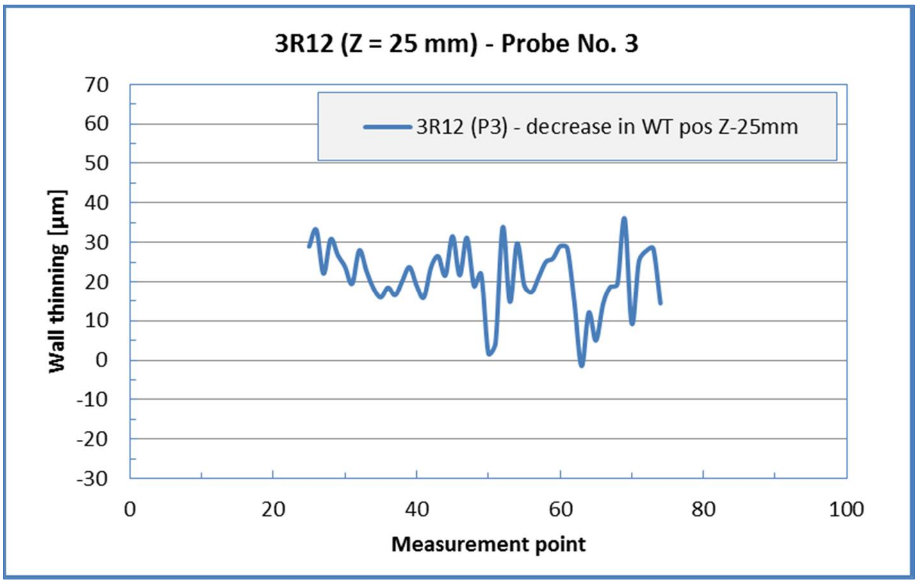


a)

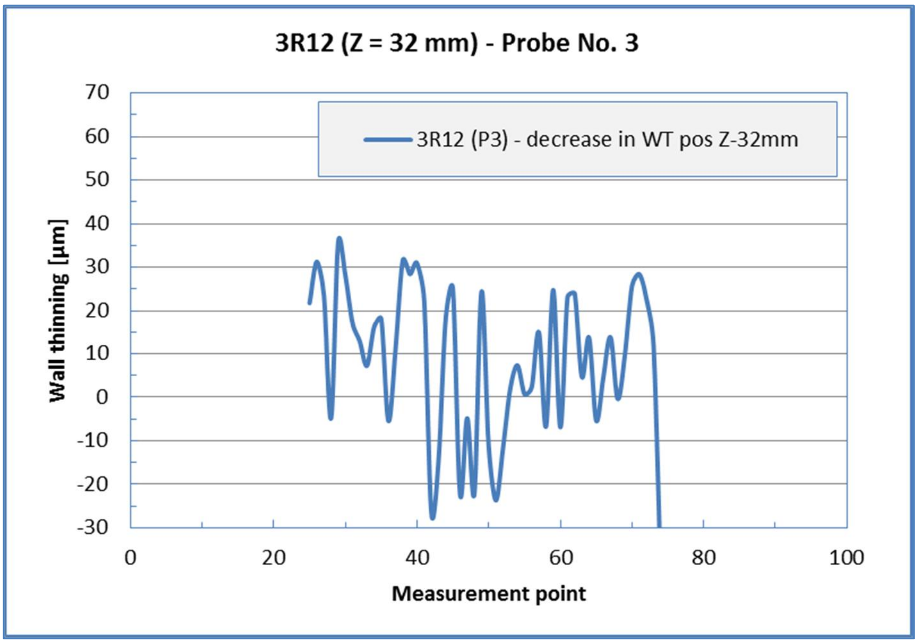


b)

Figure 28. Circumferential wall thickness profiles from 3R12 specimen (Probe No. 3): a) axial location Z = 25 mm and b) axial location Z = 32 mm.

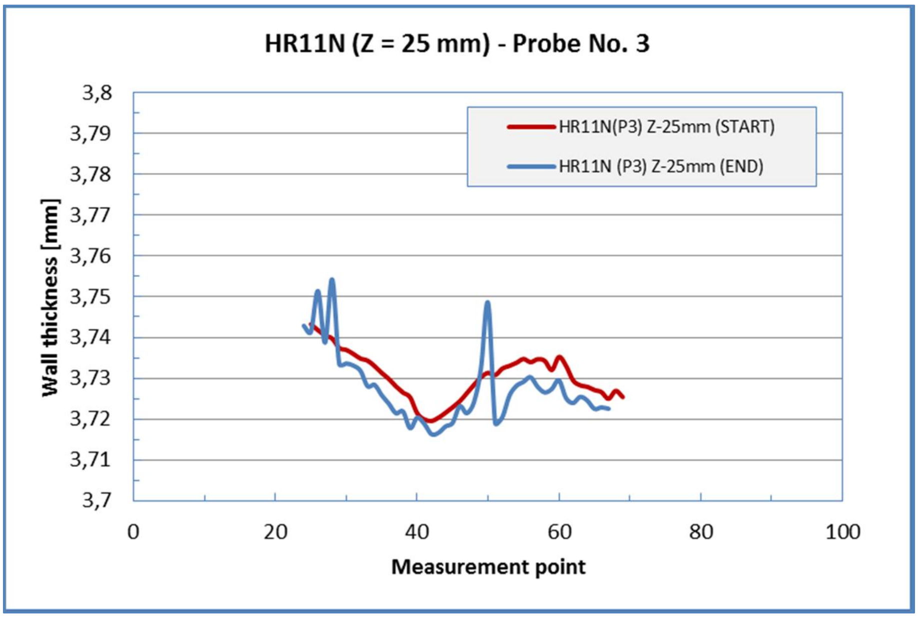


a)

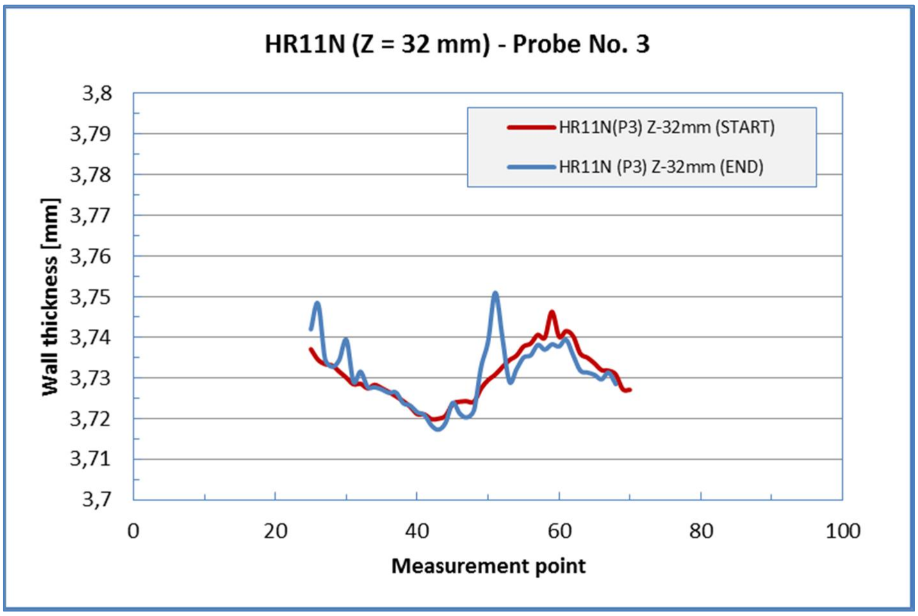


b)

Figure 29. Circumferential wall thinning curves from 3R12 specimen (Probe No. 3): a) axial location Z = 25 mm and b) axial location Z = 32 mm.

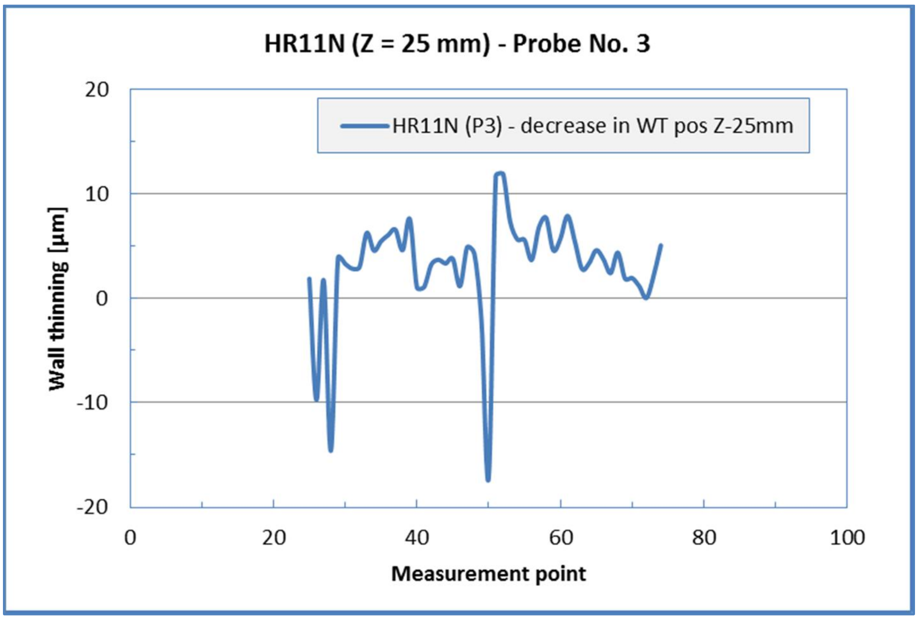


a)

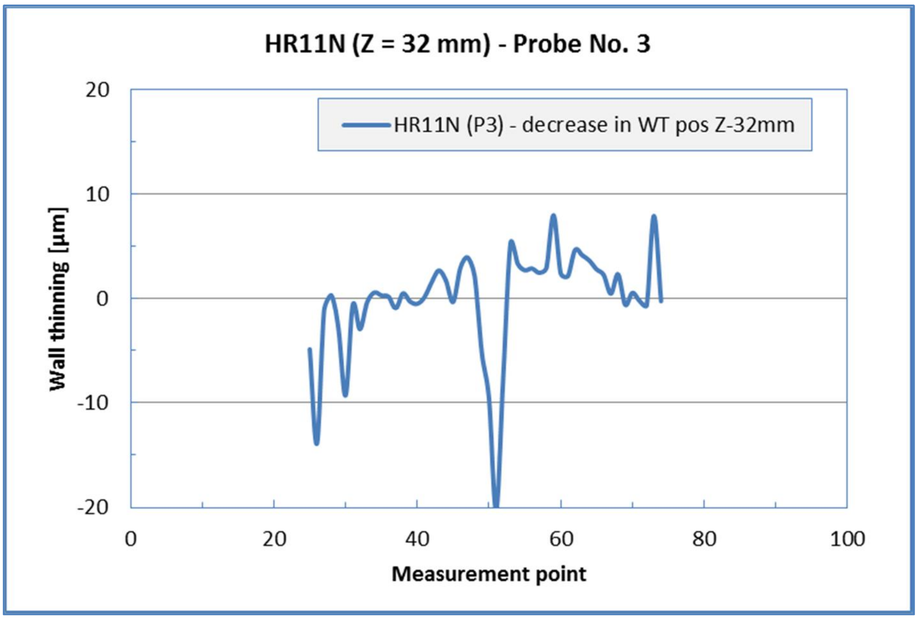


b)

Figure 30. Circumferential wall thickness profiles from HR11N specimen (Probe No. 3): a) axial location Z = 25 mm and b) axial location Z = 32 mm.

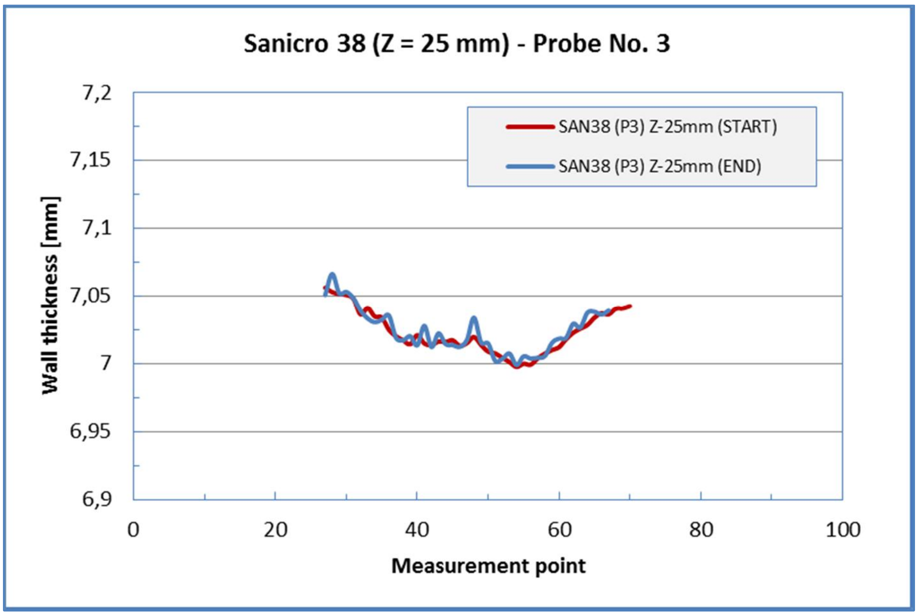


a)

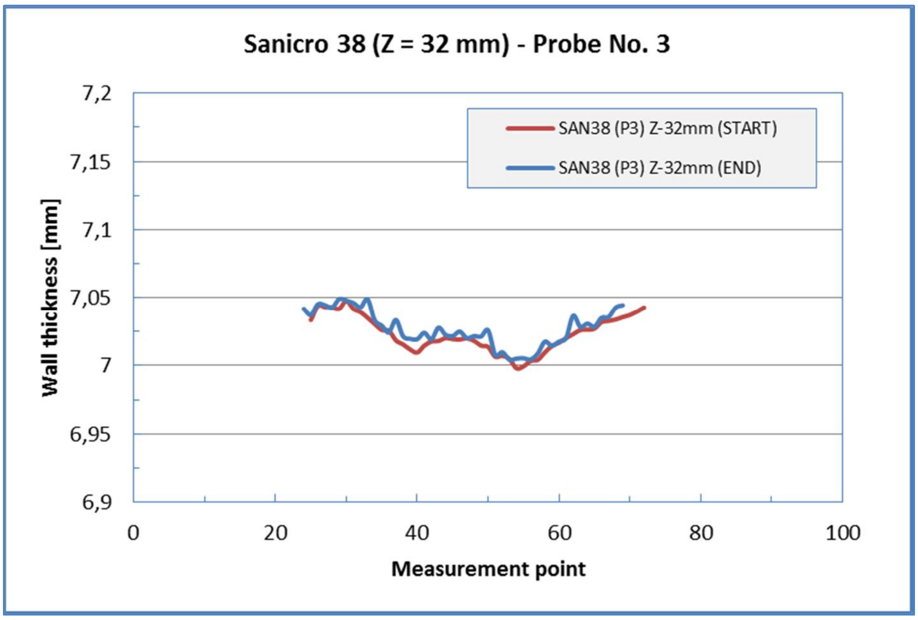


b)

Figure 31. Circumferential wall thinning curves from HR11N specimen (Probe No. 3): a) axial location Z = 25 mm and b) axial location Z = 32 mm.

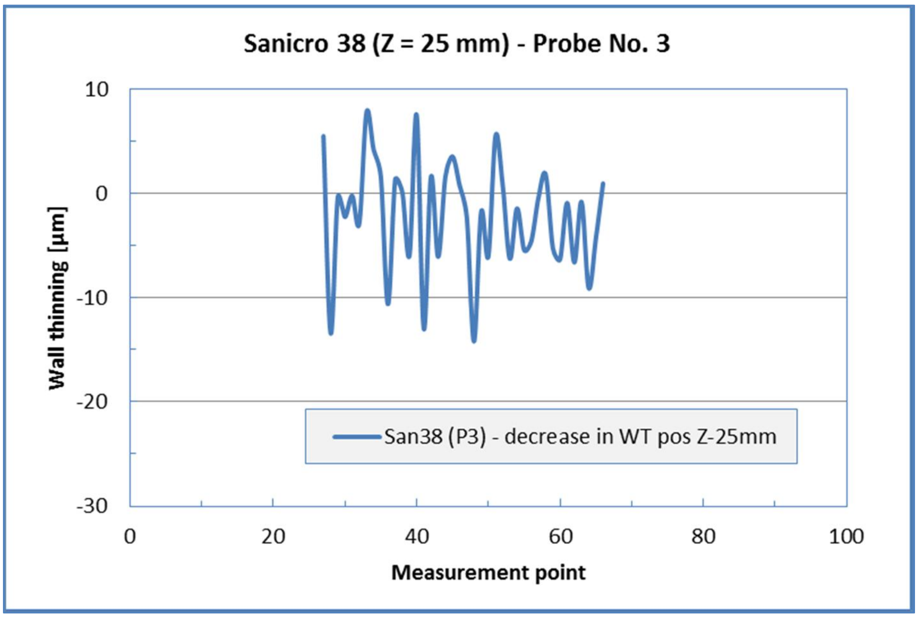


a)

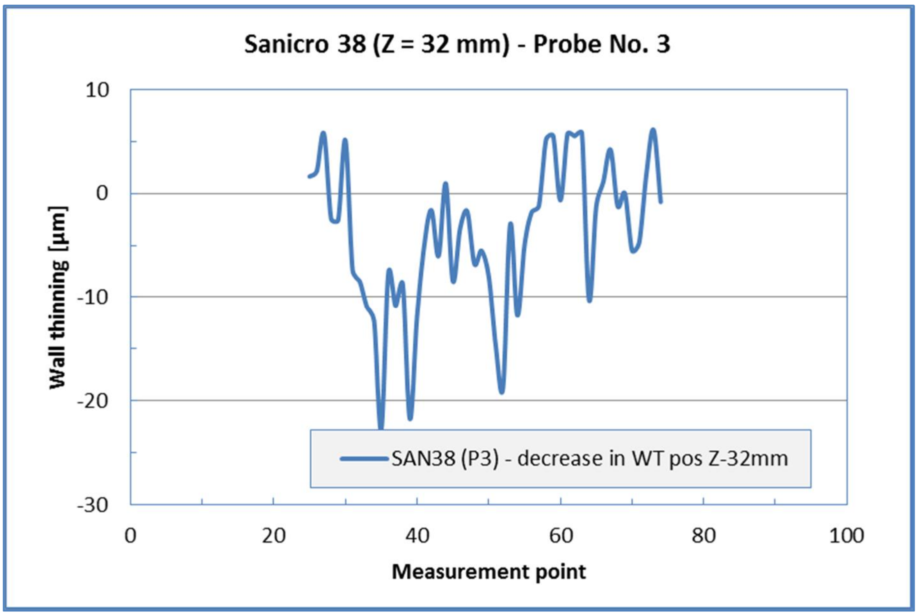


b)

Figure 32. Circumferential wall thickness profiles from Sanicro 38 specimen (Probe No. 3): a) axial location Z = 25 mm and b) axial location Z = 32 mm.

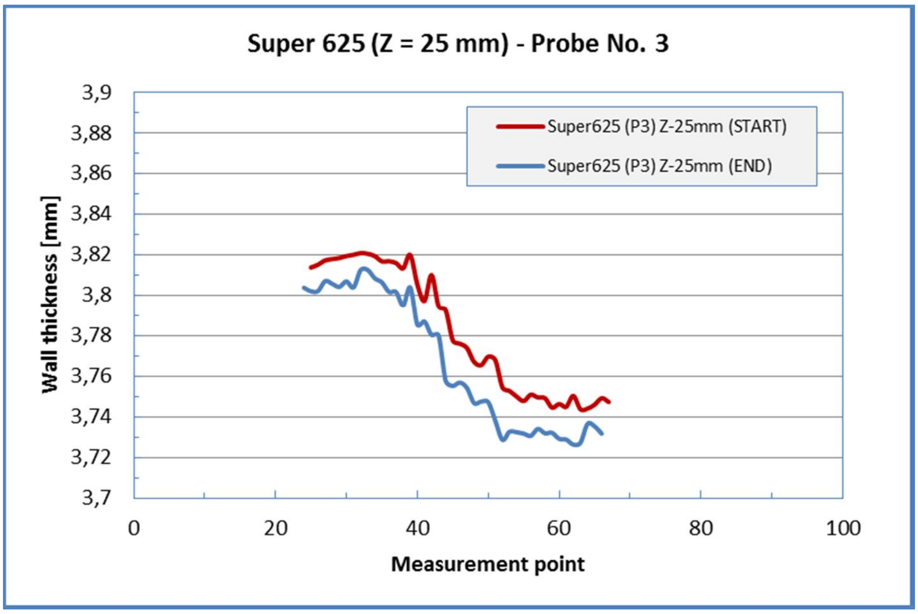


a)

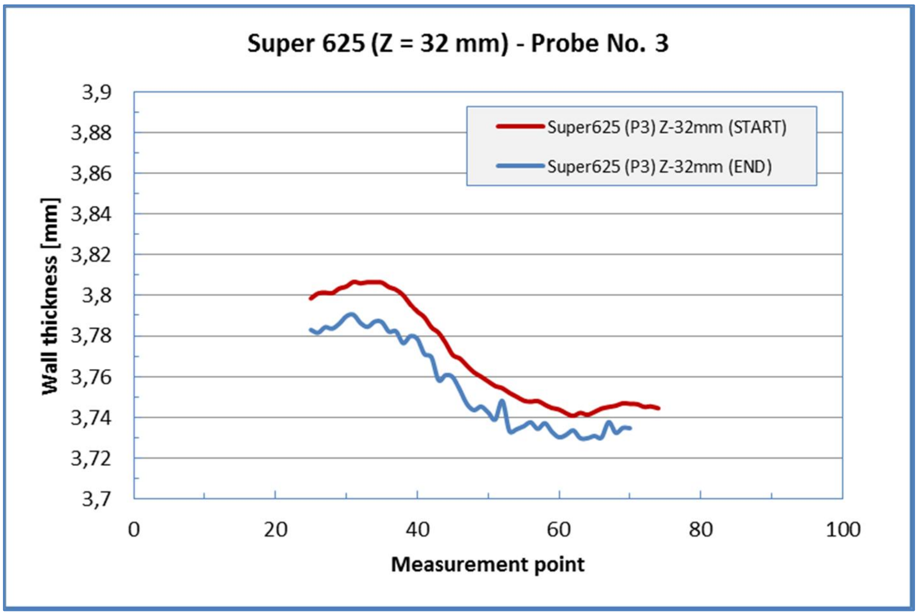


b)

Figure 33. Circumferential wall thinning curves from Sanicro 38 specimen (Probe No. 3): a) axial location Z = 25 mm and b) axial location Z = 32 mm.

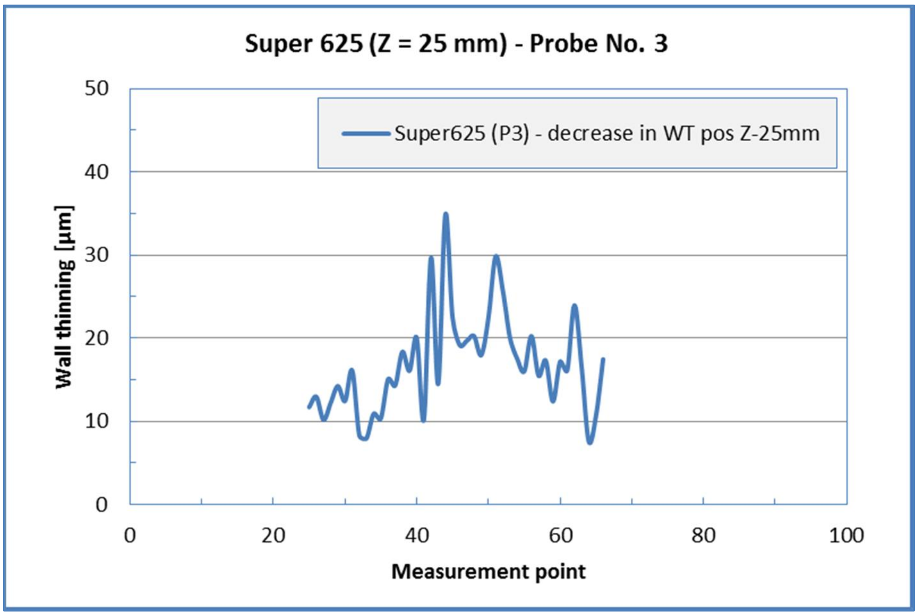


a)

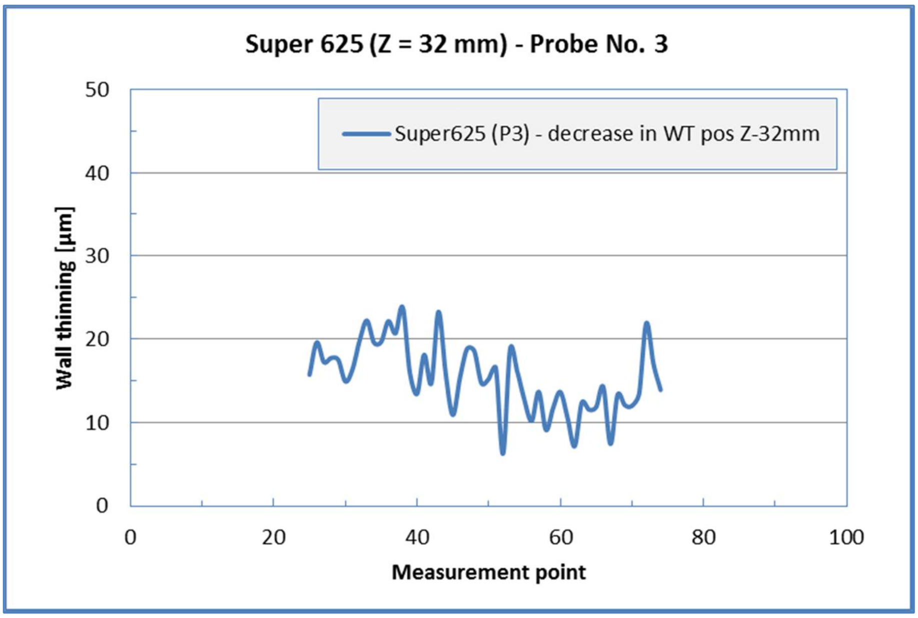


b)

Figure 34. Circumferential wall thickness profiles from Super 625 specimen (Probe No. 3): a) axial location Z = 25 mm and b) axial location Z = 32 mm.

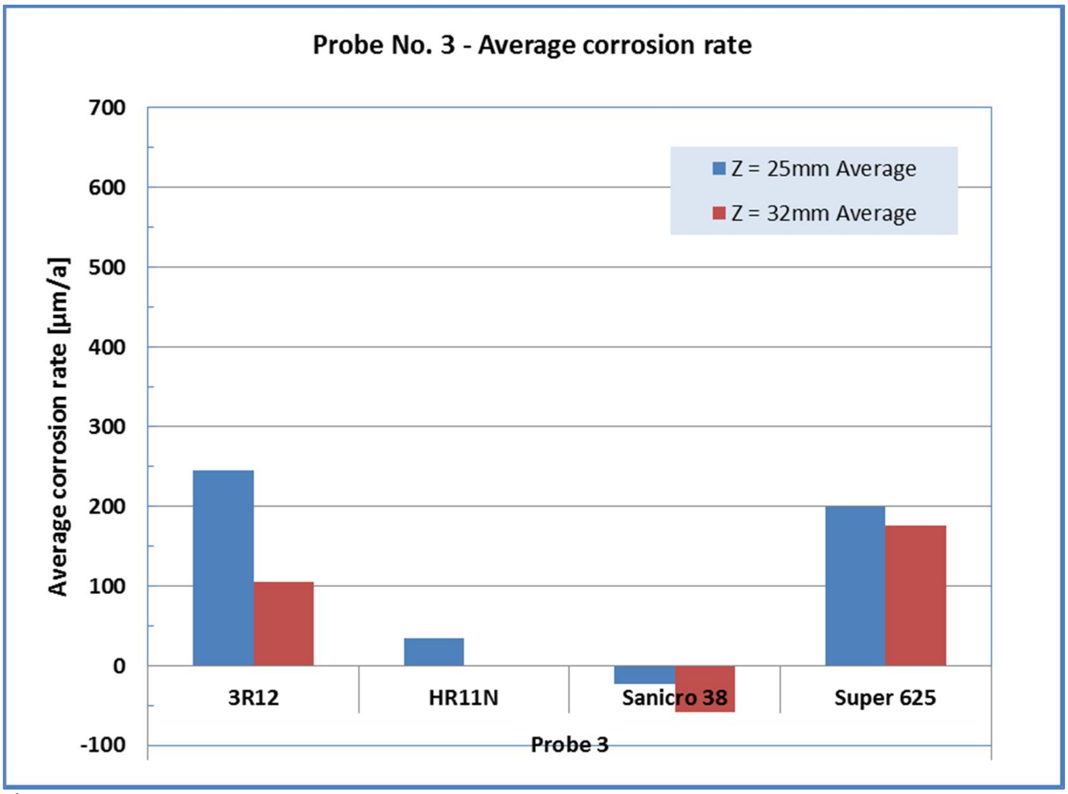


a)

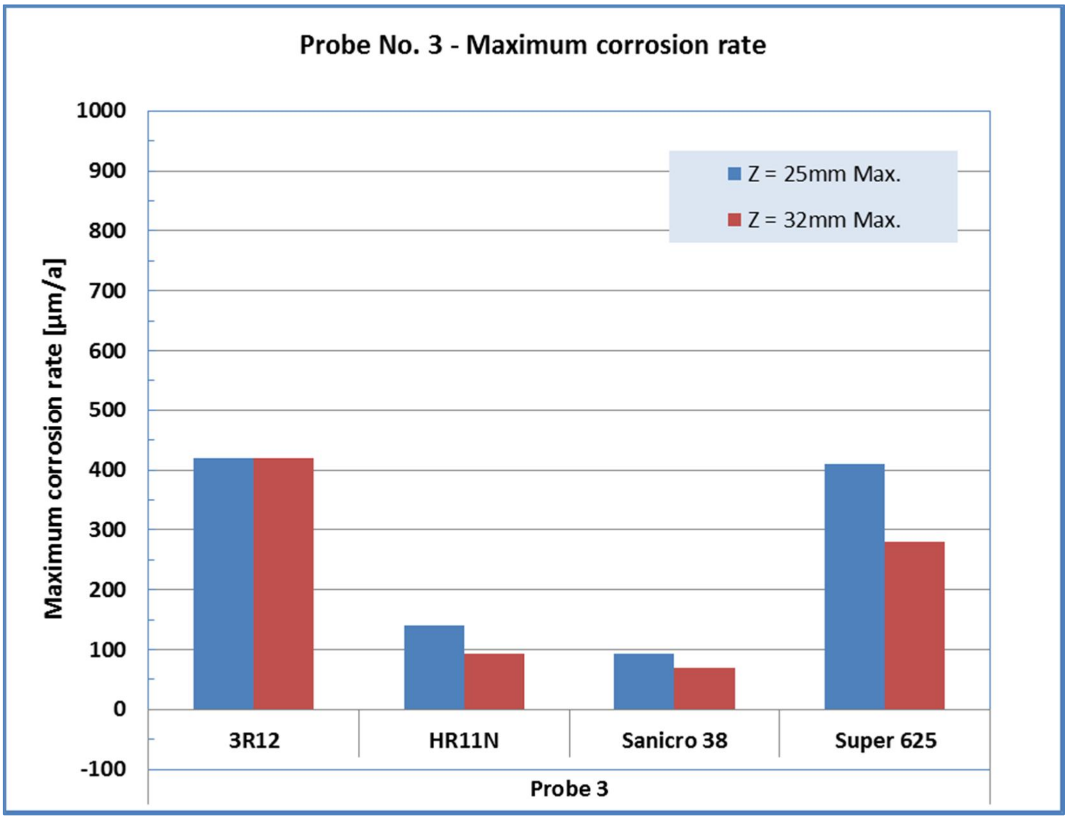


b)

Figure 35. Circumferential wall thinning curves from Super 625 specimen (Probe No. 3): a) axial location Z = 25 mm and b) axial location Z = 32 mm.



a)



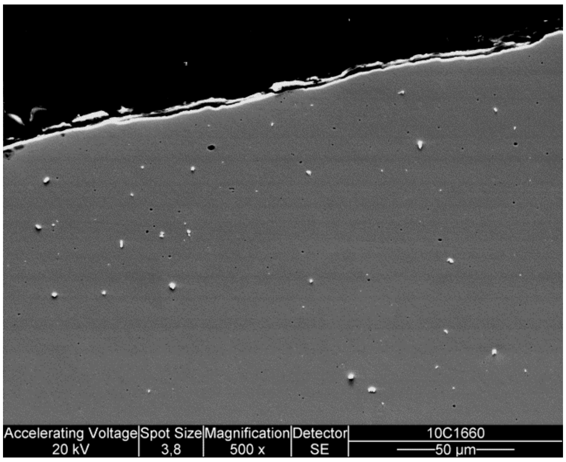
b)

Figure 36. a) Average and b) maximum corrosion rates of the test materials calculated on the basis of the wall thickness measurements after 750 h exposure in lower furnace at 430 °C (Probe test No. 3)

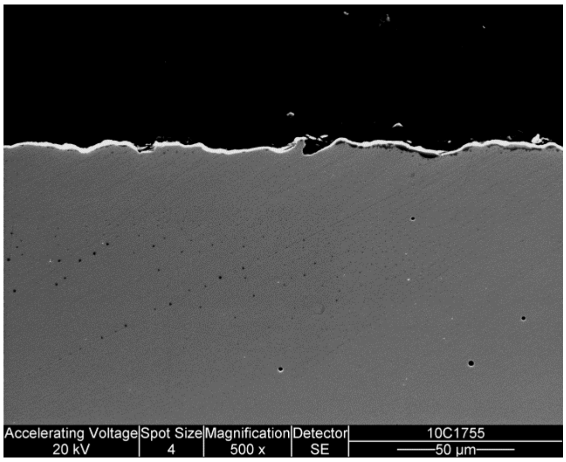
4.3.2 Metallography

After the tests the samples were examined with optical microscope and/or SEM to determine the type of the corrosion attack. All samples had suffered from general thinning. The layers formed on 3R12, HR11N and Sanicro 38 were thin ca.5 µm in thickness. Whereas on the Super 625 ca. 10...20 µm thick peeling like scale was observed.

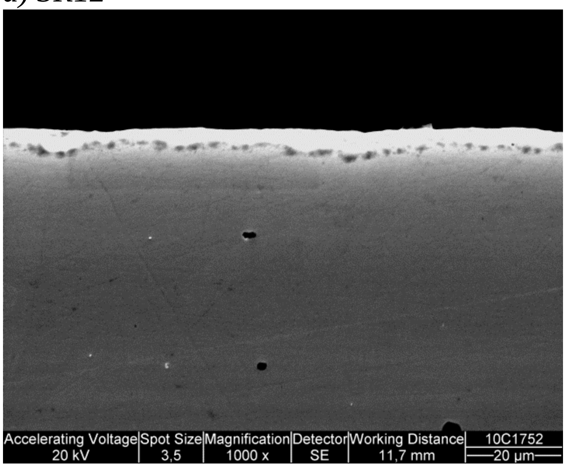
According to the EDS analysis (Figure 38) the layers on 3R12, HR11N and Sanicro 38 were depleted in iron and nickel and enriched in chromium and contained also sulphur. The layers on the Super 625 were depleted in iron, nickel, molybdenum and chromium and contained high amounts of sulphur. Reference analysis made from unexposed reference samples showed that the depleted/enriched layers are formed during exposure and do not originate from the specimen manufacturing process.



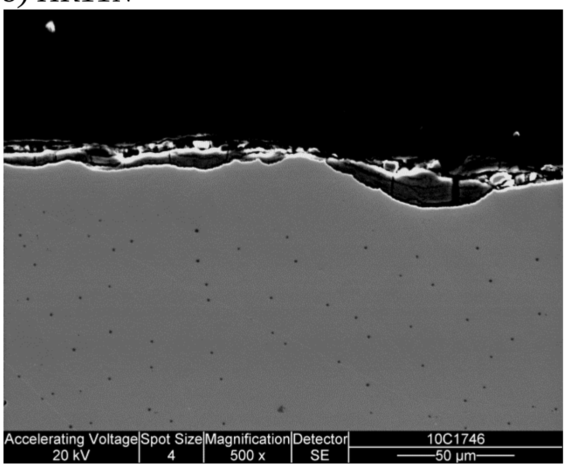
a) 3R12



b) HR11N



c) Sanicro 38



d) Super 625

Figure 37. Cross sections from a) 3R12, b) HR11N, c) Sanicro 38 and d) Super 625 after 750 h exposure in lower furnace at 430 °C (Probe test No. 3)

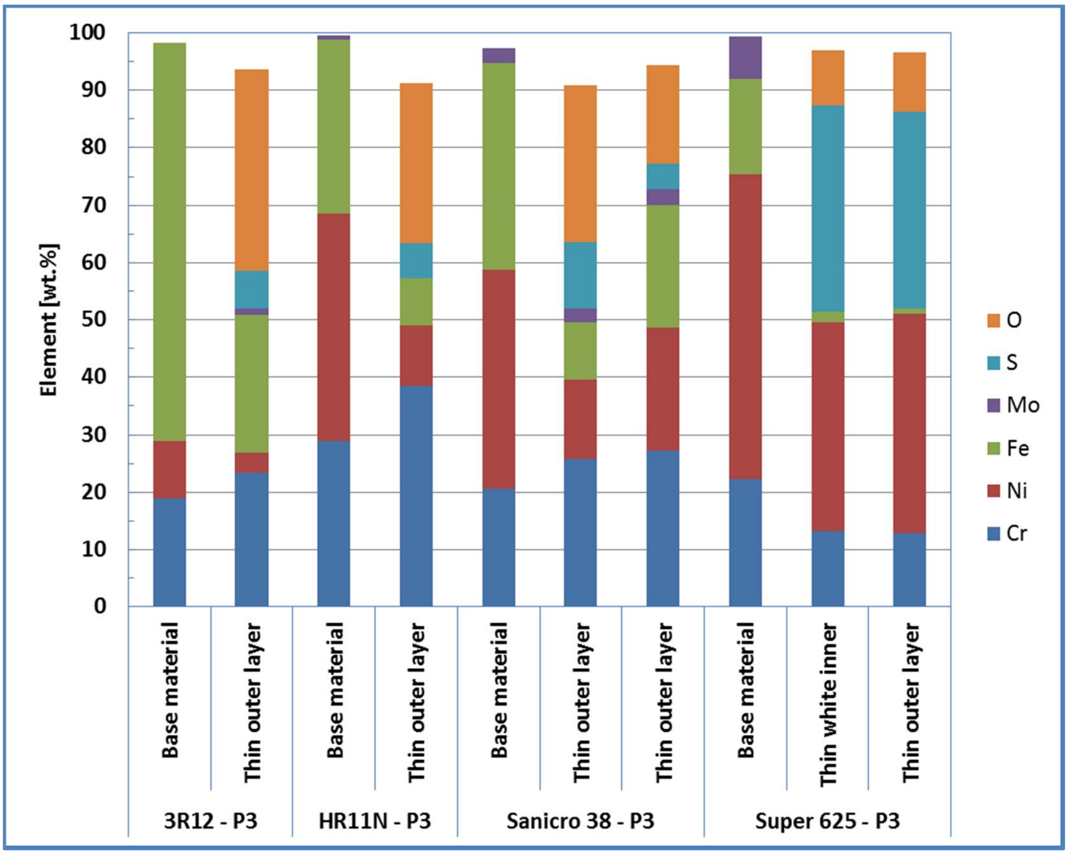
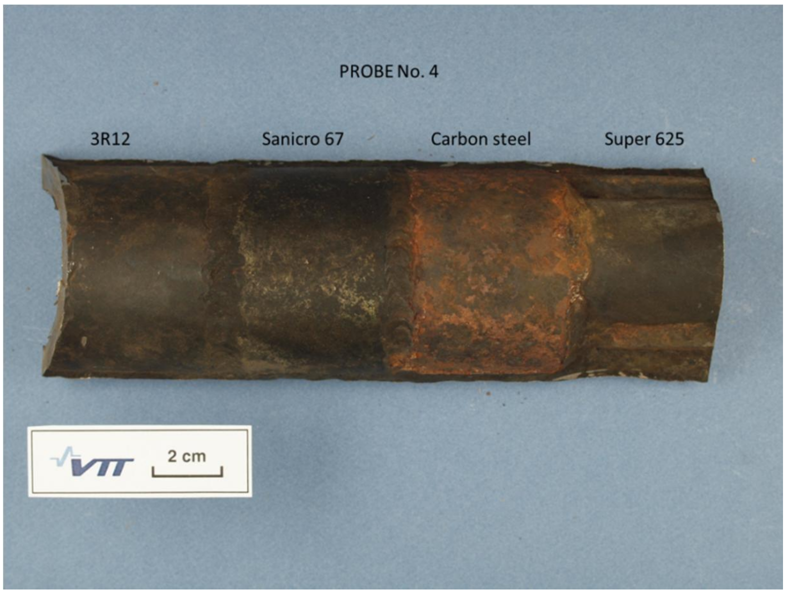


Figure 38. Results from the EDS analysis performed for the 3R12, HR11N, Sanicro 38 and Super 625 specimens after 750 h exposure in lower furnace at 430 °C (Probe test No. 3). Note: Quantitative results from cross sections, carbon excluded. Data from layers are from point analysis, whereas area analysis was used for base materials.

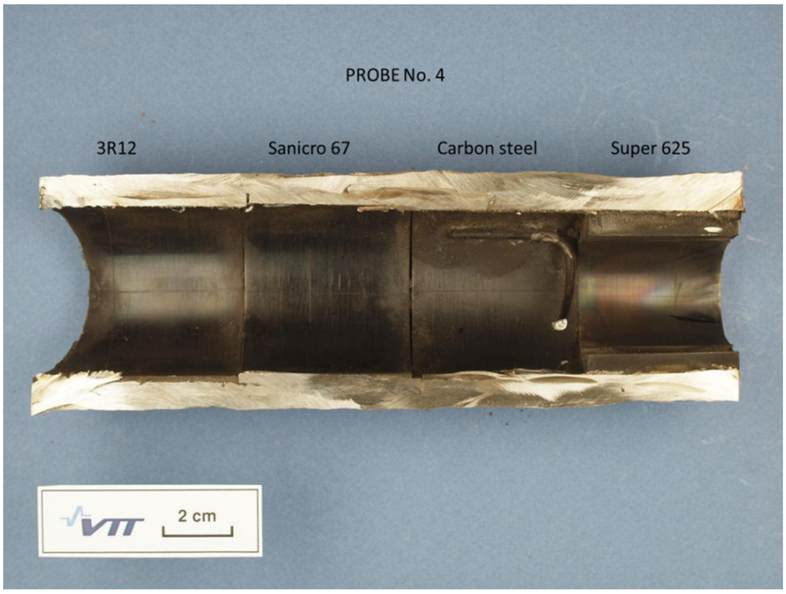
4.4 Probe test No. 4

Total test duration of the test No. 4 was 2700 hours from which 2154 hours at the target temperature of 440 °C. The test materials in this exposure 3R12, carbon steel, Sanicro 67 and Super 625, Figure 39.

According to visual inspection the inner surfaces of the specimens were in good condition after testing. The outer surfaces of the 3R12, Sanicro 67 and Super 625 specimens were covered with thin dark deposits but appeared to be in good condition. The carbon steel specimen was heavily corroded.



a)



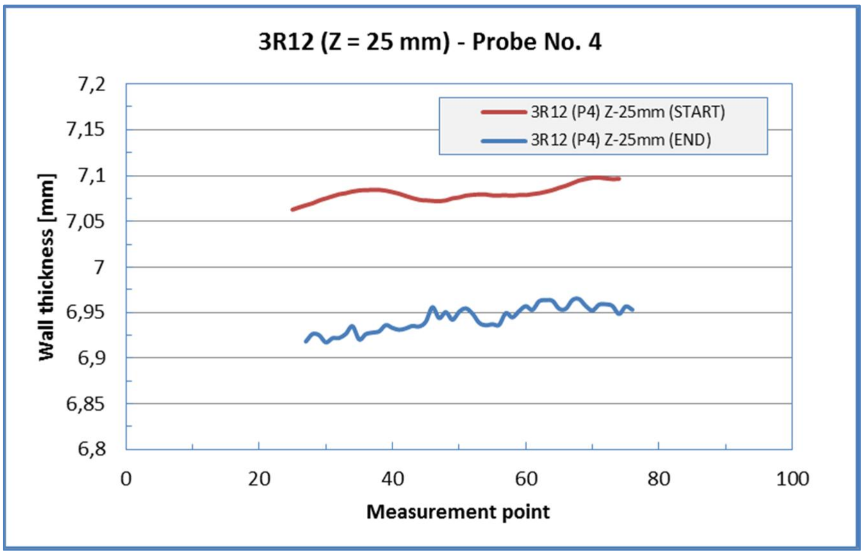
b)

Figure 39. Macrographs taken from the probe No. 4 head after exposure: a) outer surface exposed to the furnace side and b) inner surface exposed to the cooling liquid. A thermocouple soldered on the side surface of carbon steel specimen is clearly visible on inner surface.

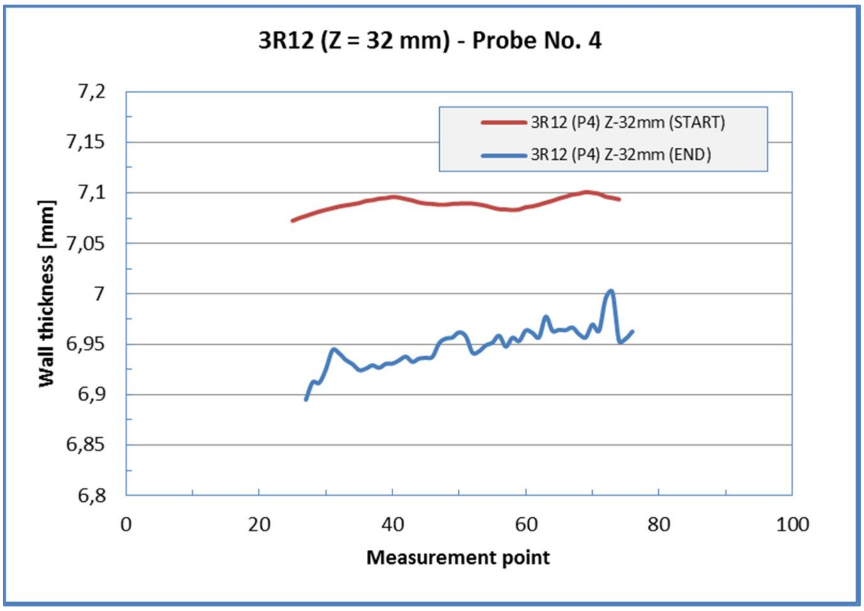
4.4.1 Corrosion rates

The results of the wall thickness profile measurements and the wall thinning curves derived from them are presented in Figures 40...47. The results showed that intense wall thinning had taken place on carbon steel specimen. Marked wall thinning was also observed on the 3R12 specimen and lesser degree also on the Super 625 specimen. The data of the Sanicro 67 specimen was more scattered showing that wall thinning and deposit formation (increase in wall thickness) had taken place locally. The results showed also that surface polishing prior testing together with longer exposure time reduced data scatter and thus improved accuracy.

The average and maximum corrosion rates calculated on the basis of the wall thickness measurements are presented in Figure 48. Highest corrosion rates, ca. 4 mm/a, were measured for the carbon steel as expected. The 3R12 had the second highest corrosion rates, order of 0.6 mm/a. Maximum corrosion rate of the Super 625 was in the order 0.1 mm/a in this test, i.e. significantly lower than in the test No.3, where a maximum corrosion rate of 0.2...0.3 mm/a was observed. The best material in this test was Sanicro 67, its maximum corrosion rate was only about 0.02 mm/a.

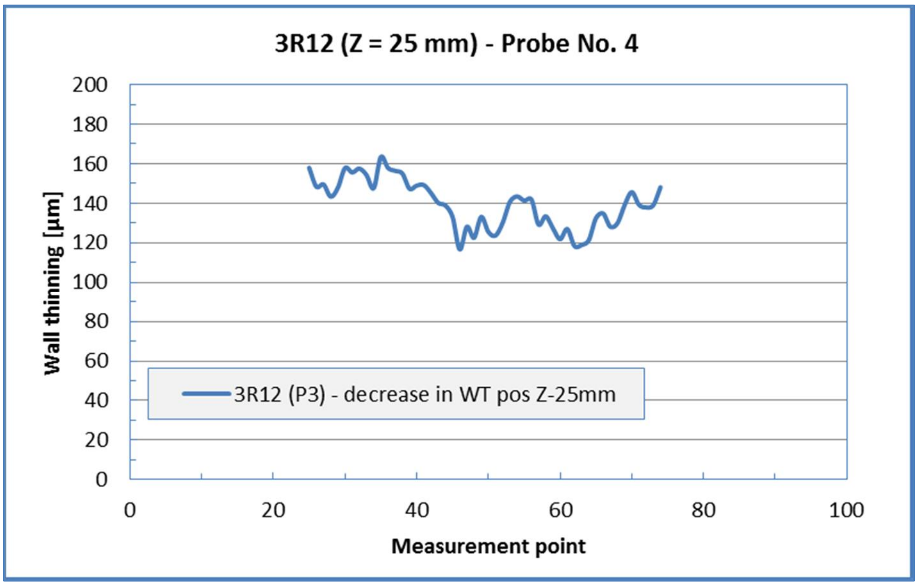


a)

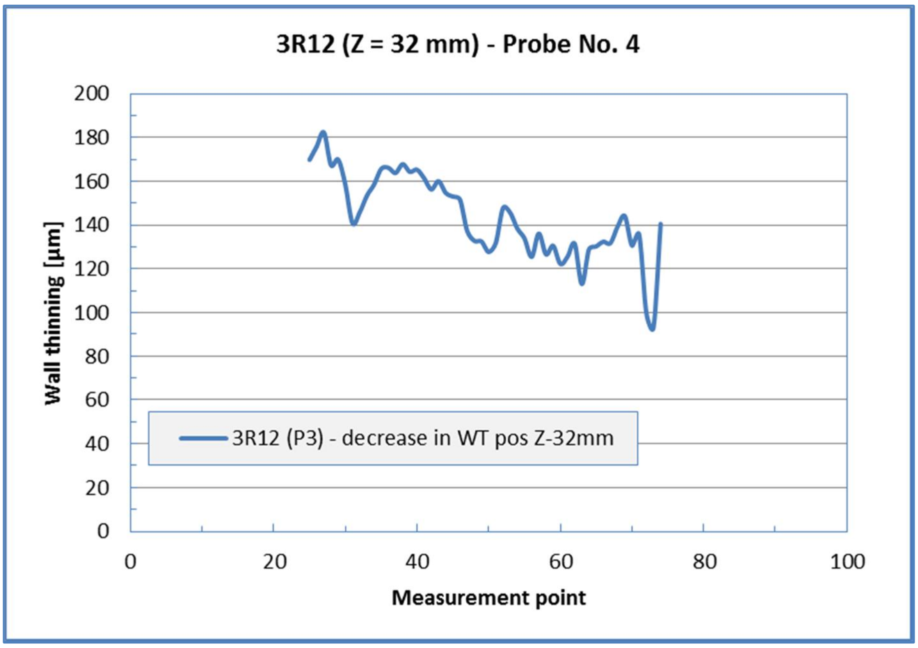


b)

Figure 40. Circumferential wall thickness profiles from 3R12 specimen (Probe No. 4): a) axial location Z = 25 mm and b) axial location Z = 32 mm.

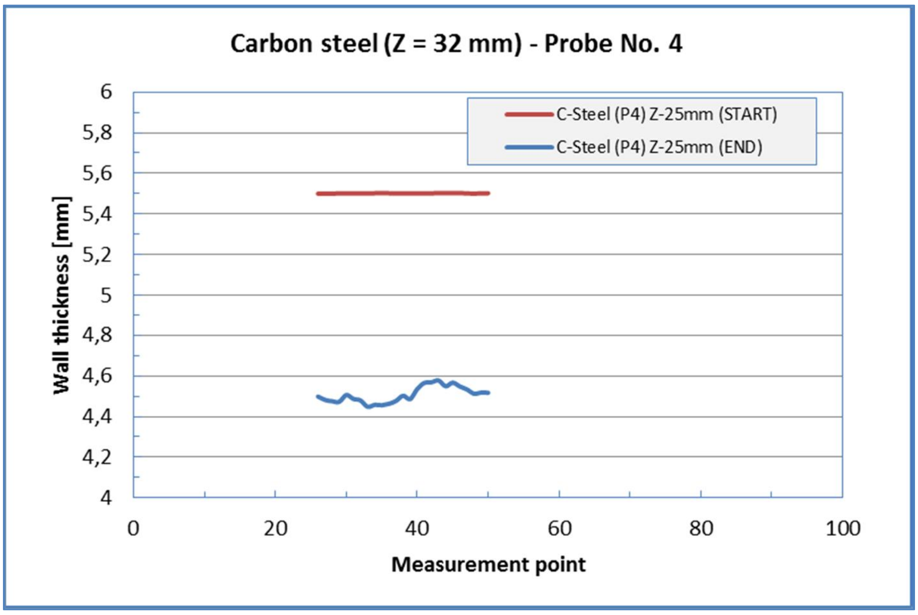


a)

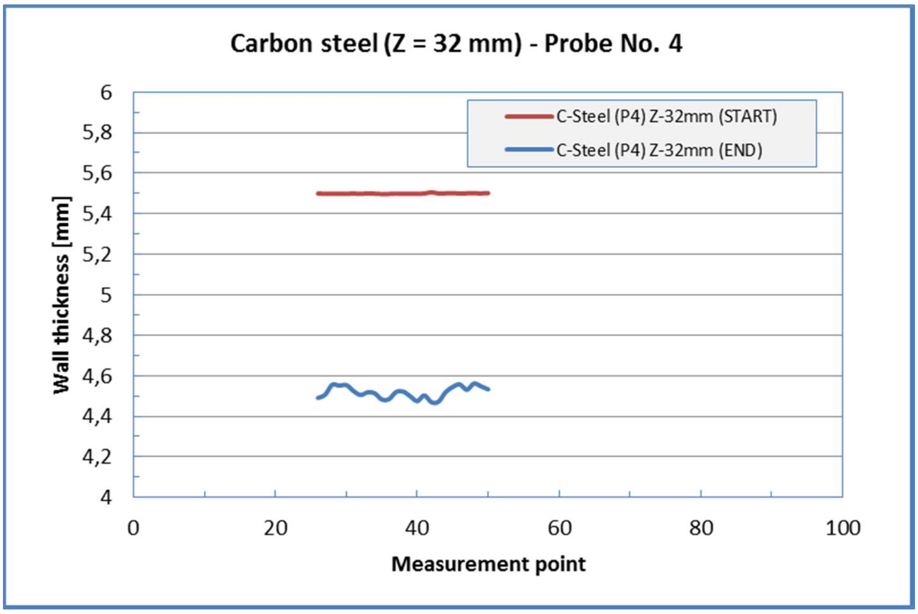


b)

Figure 41. Circumferential wall thinning curves from 3R12 specimen (Probe No. 4): a) axial location Z = 25 mm and b) axial location Z = 32 mm.

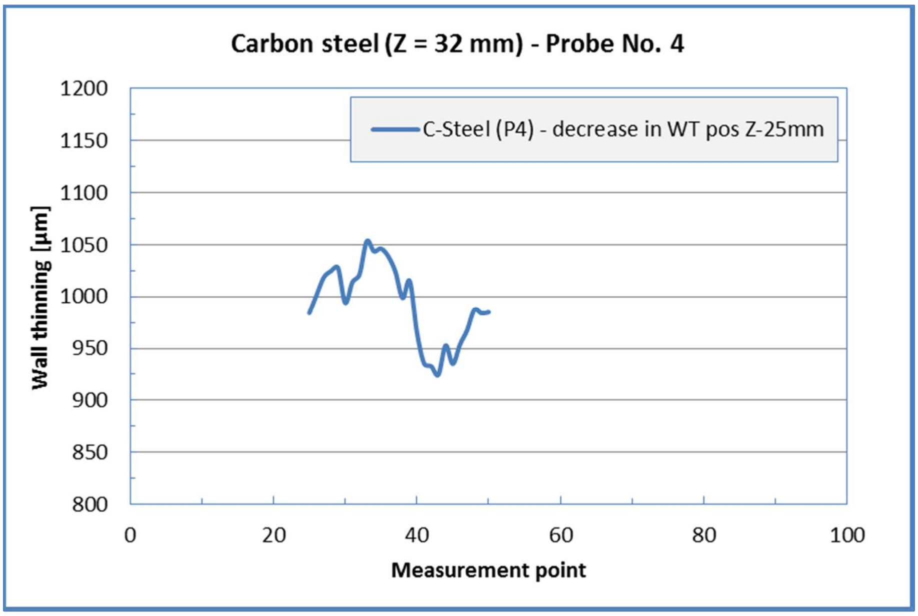


a)

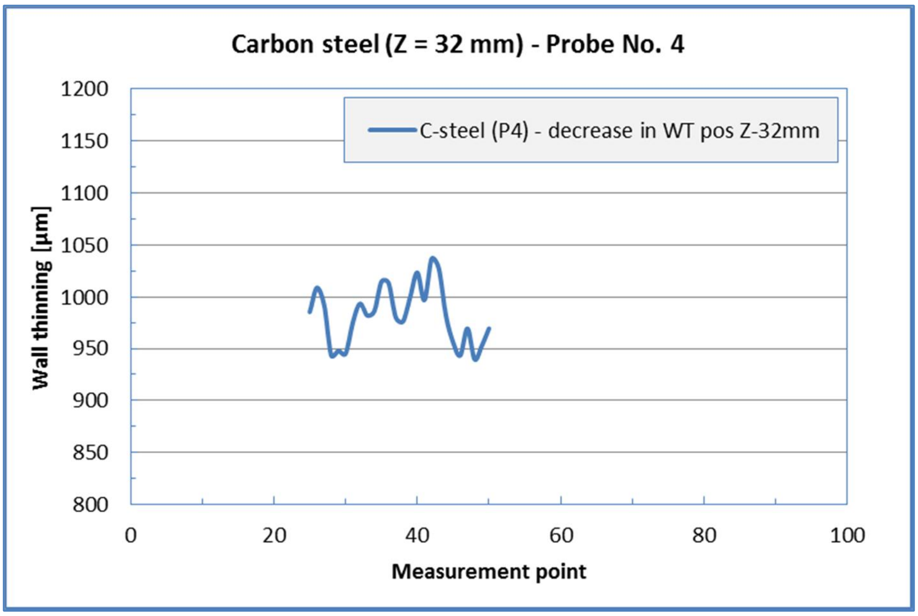


b)

Figure 42. Circumferential wall thickness profiles from carbon steel specimen (Probe No. 4): a) axial location Z = 25 mm and b) axial location Z = 32 mm.

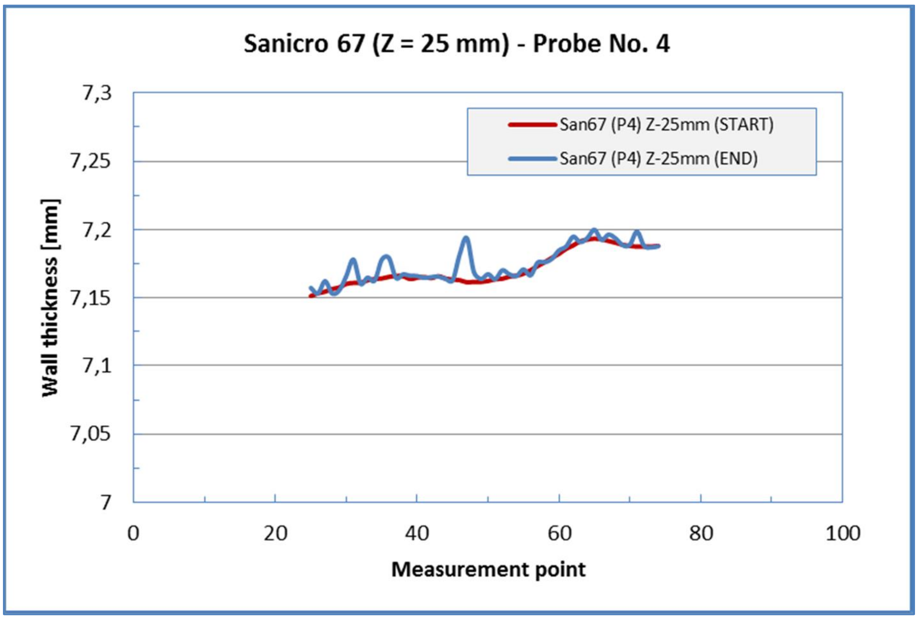


a)

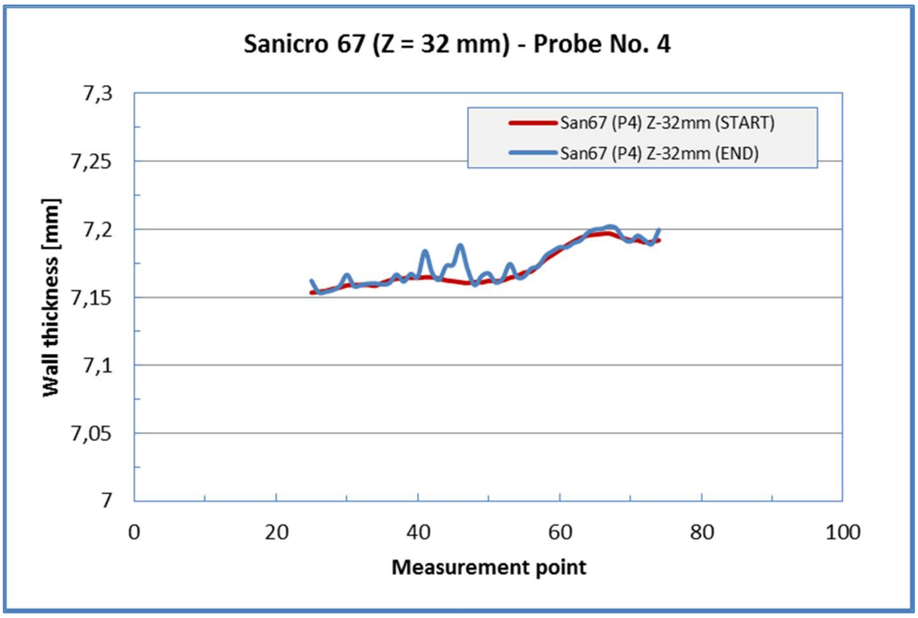


b)

Figure 43. Circumferential wall thinning curves from carbon steel specimen (Probe No. 4): a) axial location Z = 25 mm and b) axial location Z = 32 mm.

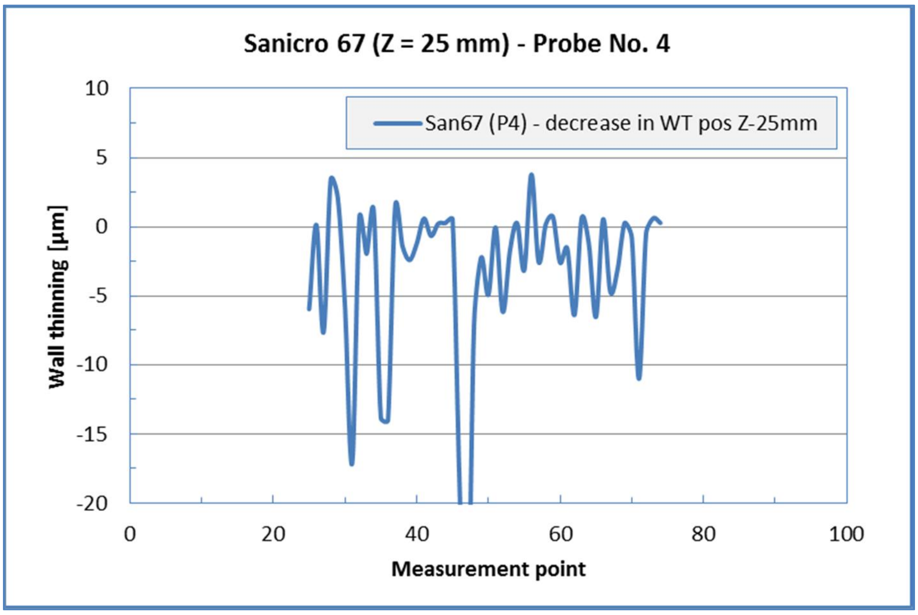


a)

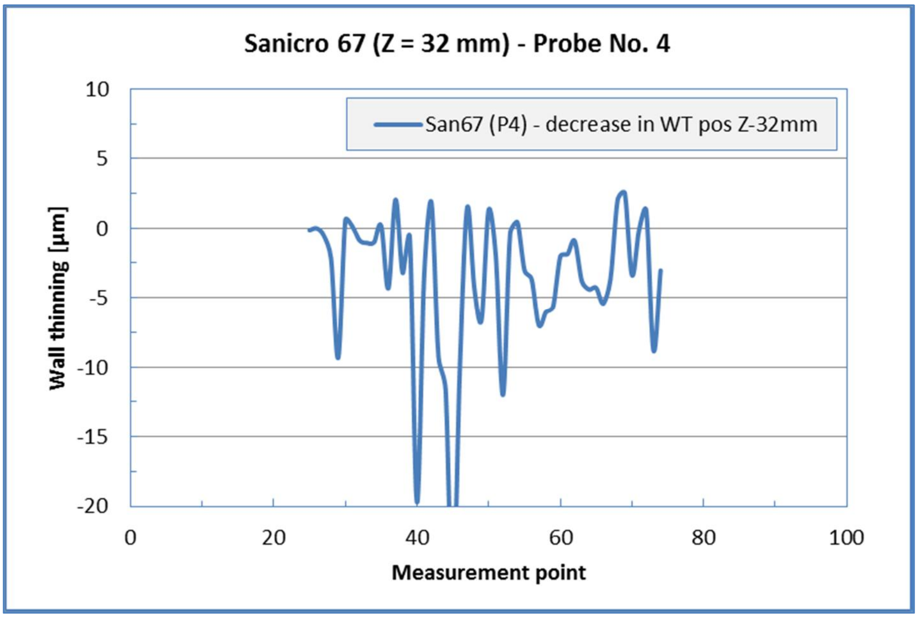


b)

Figure 44. Circumferential wall thickness profiles from Sanicro 67 specimen (Probe No. 4): a) axial location Z = 25 mm and b) axial location Z = 32 mm.

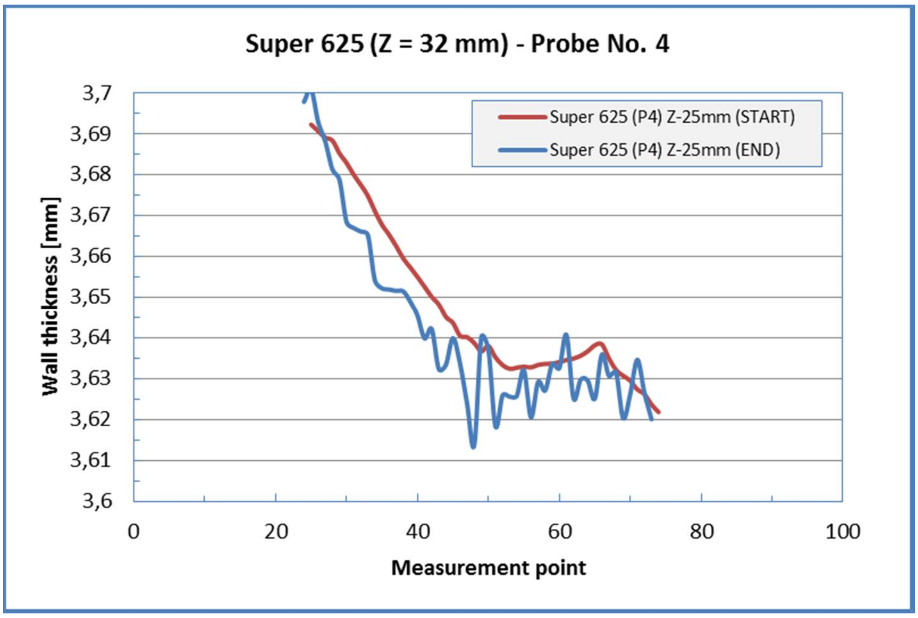


a)

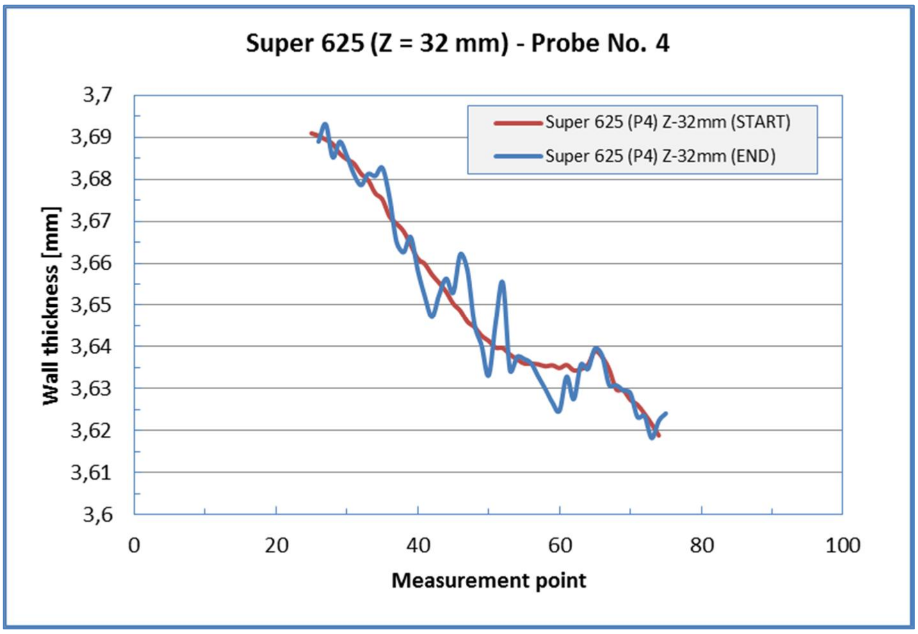


b)

Figure 45. Circumferential wall thinning curves from Sanicro 67 specimen (Probe No. 4): a) axial location Z = 25 mm and b) axial location Z = 32 mm.

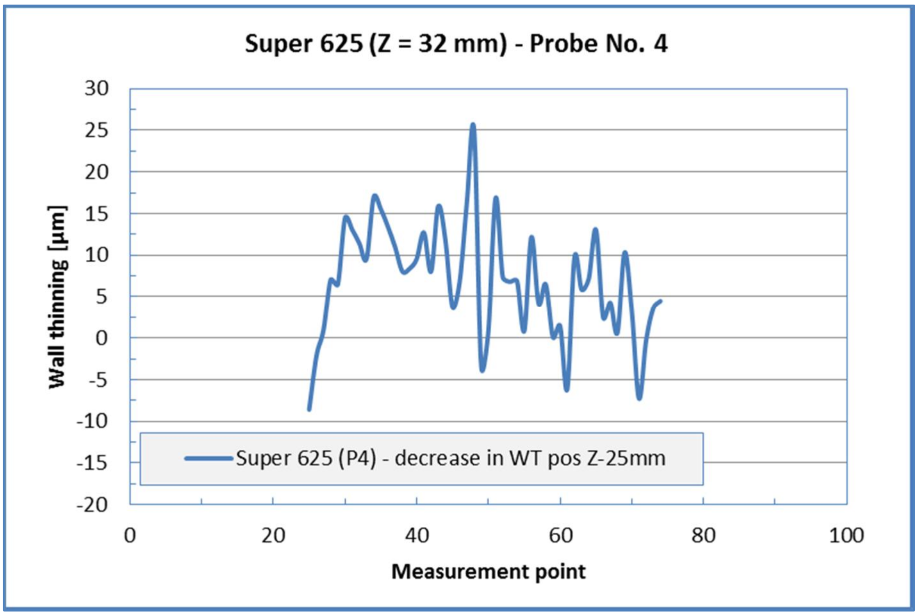


a)

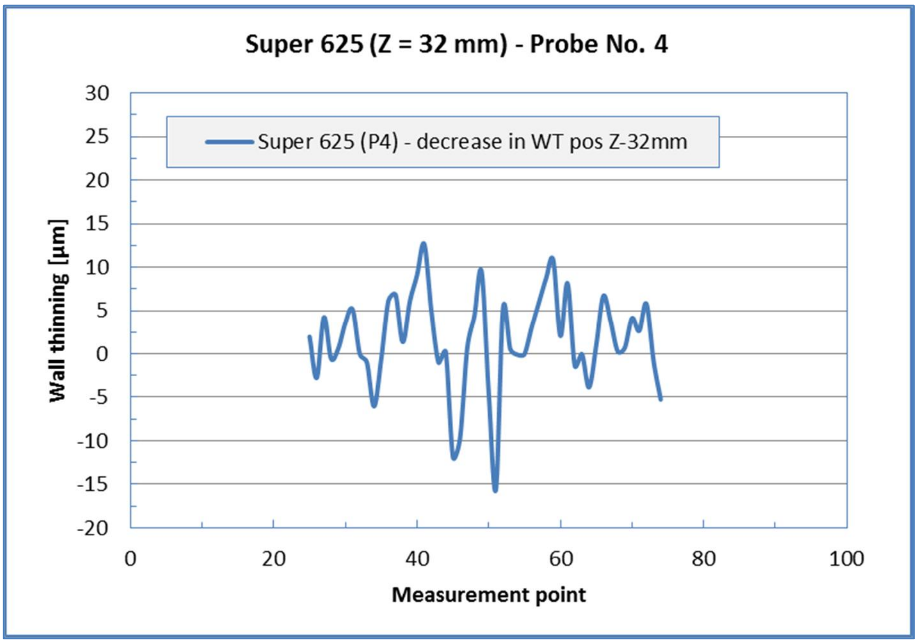


b)

Figure 46. Circumferential wall thickness profiles from Super 625 specimen (Probe No. 4): a) axial location Z = 25 mm and b) axial location Z = 32 mm.

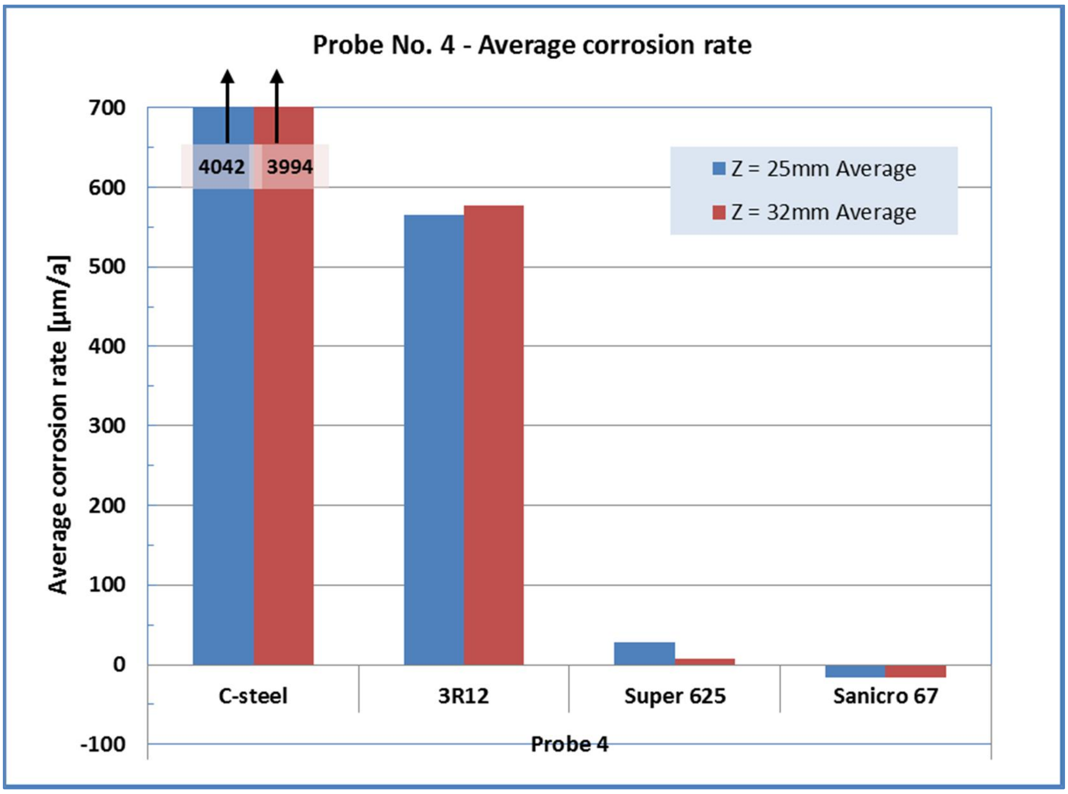


a)

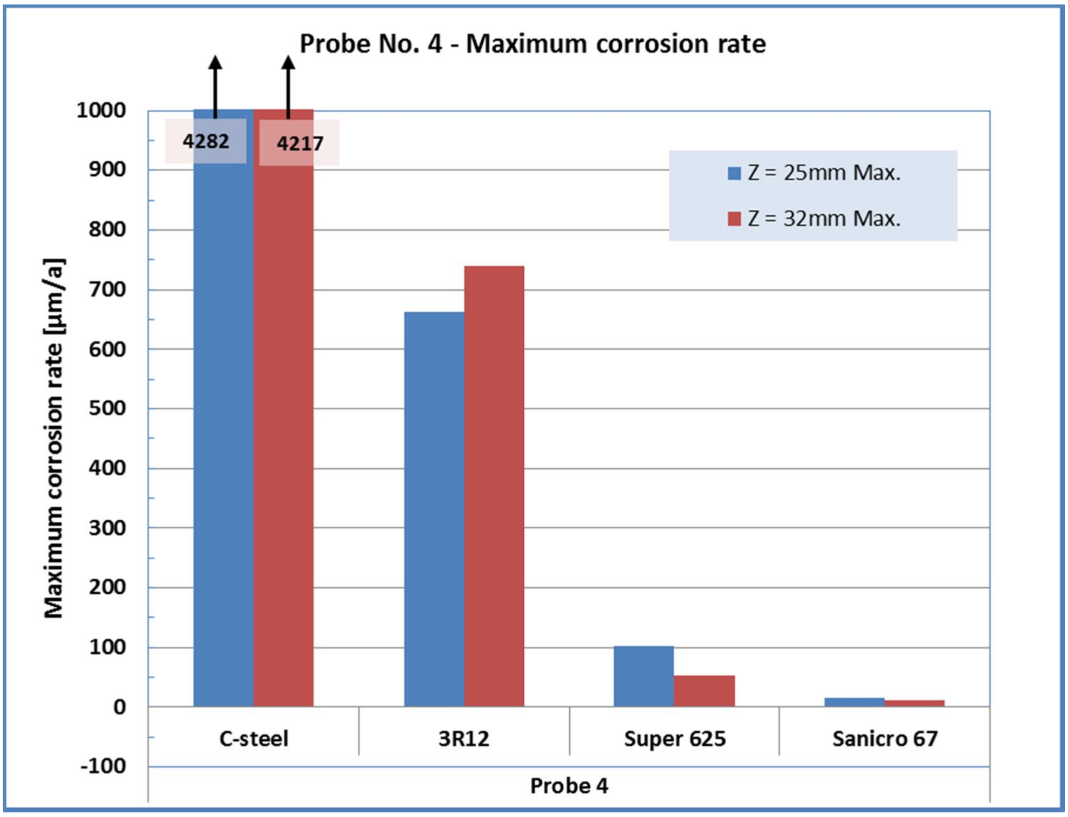


b)

Figure 47. Circumferential wall thinning curves from Super 625 specimen (Probe No. 4): a) axial location Z = 25 mm and b) axial location Z = 32 mm.



a)



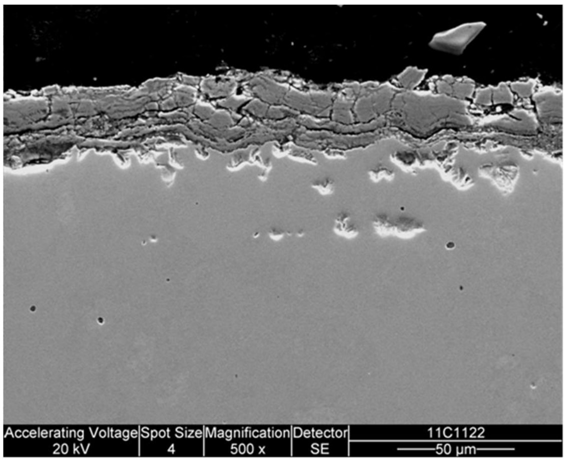
b)

Figure 48. a) Average and b) maximum corrosion rates of the test materials calculated on the basis of the wall thickness measurements after 2154 h exposure in lower furnace at 440 °C (Probe test No. 4).

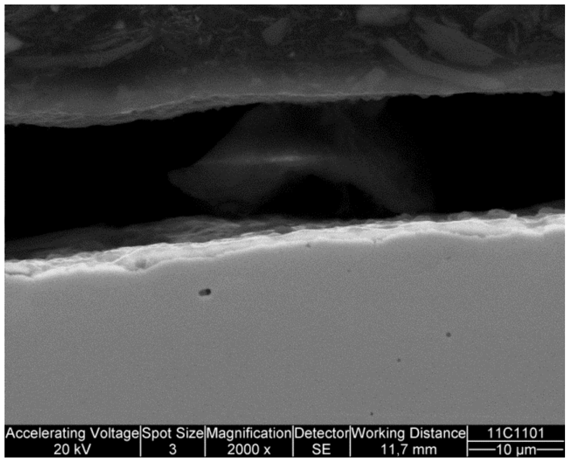
4.4.2 Metallography

After the tests the samples were examined with optical microscope and/or SEM to determine the type of the corrosion attack. All samples had suffered from general thinning, Figure 49. The carbon steel showed scale thickness of about 25 µm after 2700 h exposure. The layers formed on 3R12 and Sanicro 67 were thin ca.5 µm in thickness. Whereas on the Super 625 ca. 10...20 µm thick peeling like scale was observed.

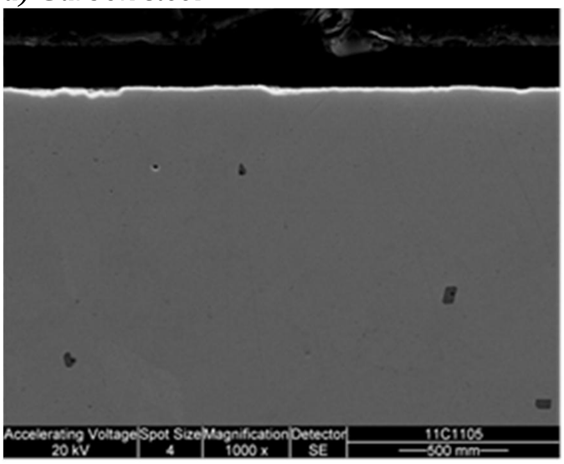
According to the EDS analysis (Figure 50) the layer on 3R12 was depleted in iron and nickel and enriched in chromium and contained also sulphur. The layer on Sanicro 67 contained sulphur and was depleted in iron and nickel, but the chromium content was at the same level than in the base material. The outermost layers on the Super 625 were depleted in iron, nickel, molybdenum and chromium and contained high amounts of sulphur.



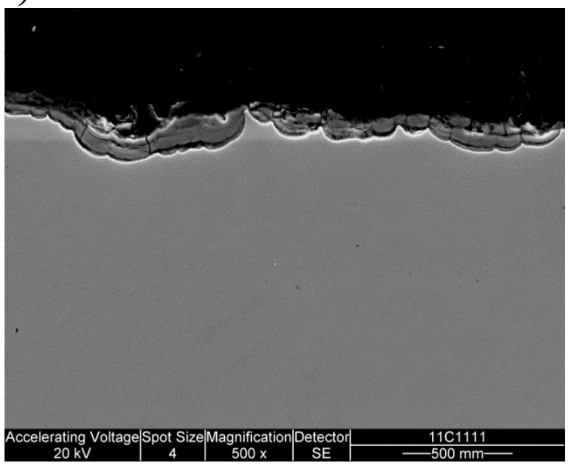
a) Carbon steel



b) 3R12



c) Sanicro 67



d) Super 625

Figure 49. Cross sections from a) carbon steel b) 3R12, c) Sanicro 67 and d) Super 625 after 2154 h exposure in lower furnace at 440 °C (Probe test No. 4).

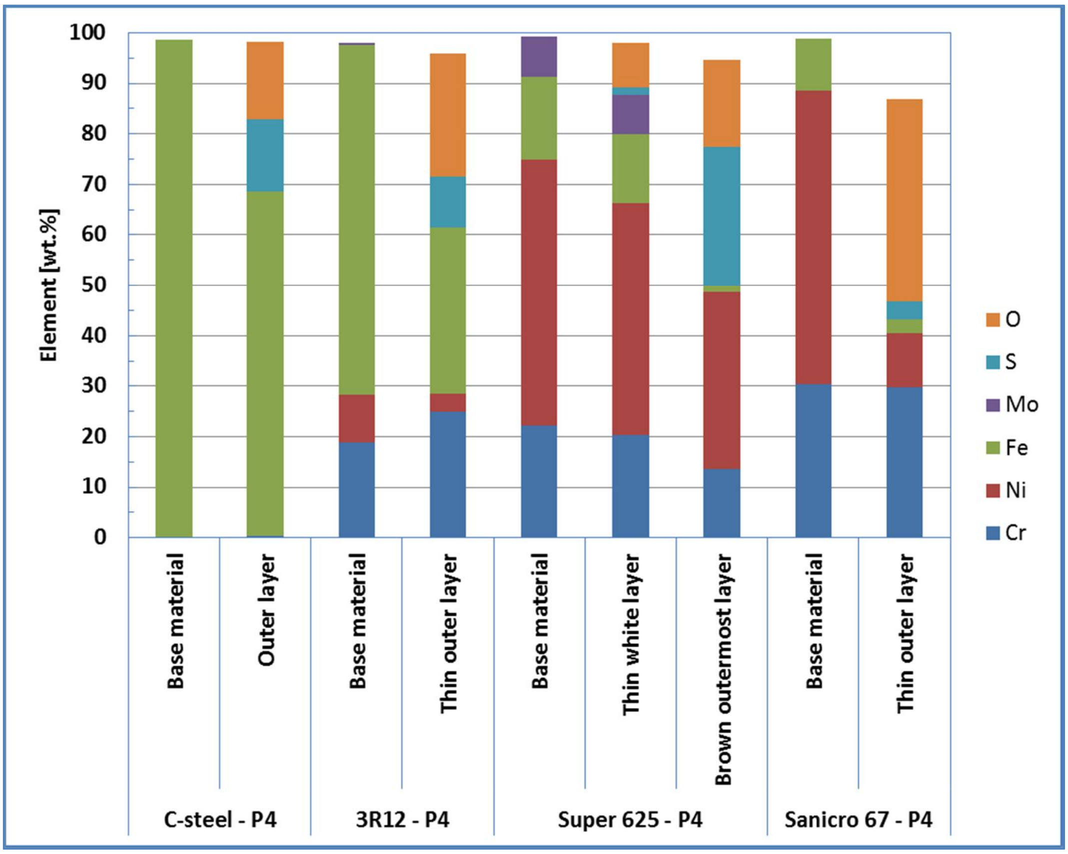


Figure 50. Results from the EDS analysis performed for the carbon steel, 3R12, Sanicro 67 and Super 625 after 2154 h exposure in lower furnace at 440 °C (Probe test No. 4). Note: Quantitative results from cross sections, carbon excluded. Data from layers are from point analysis, whereas area analysis was used for base materials.

4.5 Probe test No. 5

Total test duration of the test No. 5 was 2630 hours from which 2157 hours at the target temperature of 440 °C. The test materials in this exposure were 3R12, Sanicro 28, HR11N and Sanicro 38, Figure 51. According to visual inspection all samples were in good condition after testing i.e. neither marked general or localised corrosion nor deposits or oxide scales were observed either on outer or inner surfaces.

a)

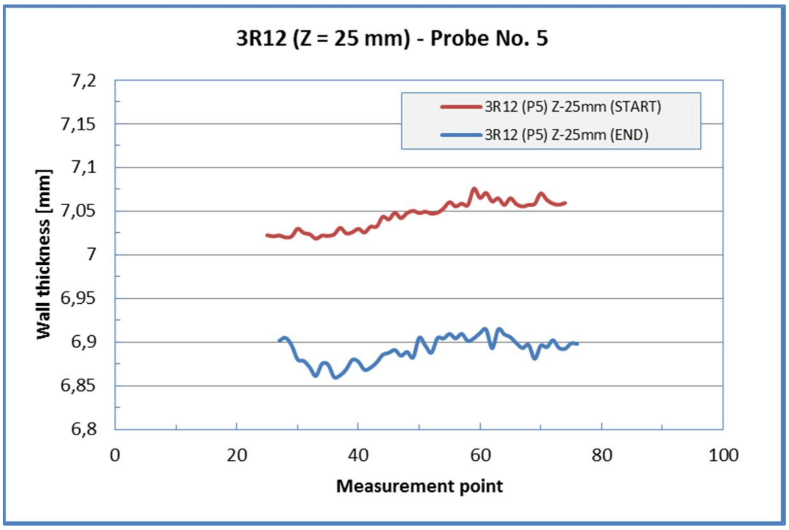
b)

Figure 51. Macrographs taken from the probe No. 5 head after exposure: a) outer surface exposed to the furnace side and b) inner surface exposed to the cooling liquid. A thermocouple soldered on the middle of Sanicro28 specimen, that hindered WT measurements after exposure, is clearly visible on inner surface.

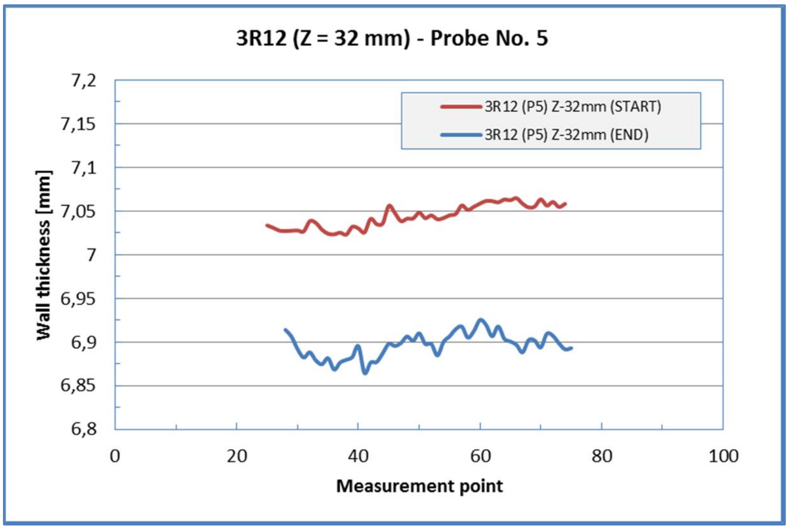
4.5.1 Corrosion rates

The results of the wall thickness profile measurements and the wall thinning curves derived from them for 3R12, HR11N and Sanicro 38 are presented in Figures 52...57. The results showed that marked wall thinning had taken on the 3R12 specimen. Some wall thinning was observed also on the Sanicro 38 specimen and locally also on the HR11N specimen. The WT profile measurements for the Sanicro 28 sample after the test failed due to the thermocouple that was soldered on the inner surface of the specimen (Figure 51b).

The average and maximum corrosion rates calculated on the basis of the wall thickness measurements are presented in Figure 48. In this test the corrosion rate of the 3R12 was in the order 0.8 mm/a. The maximum corrosion rates of HR11N and Sanicro 38 were in the order of 0.15 mm/a, i.e. at the same range than in the previous tests.

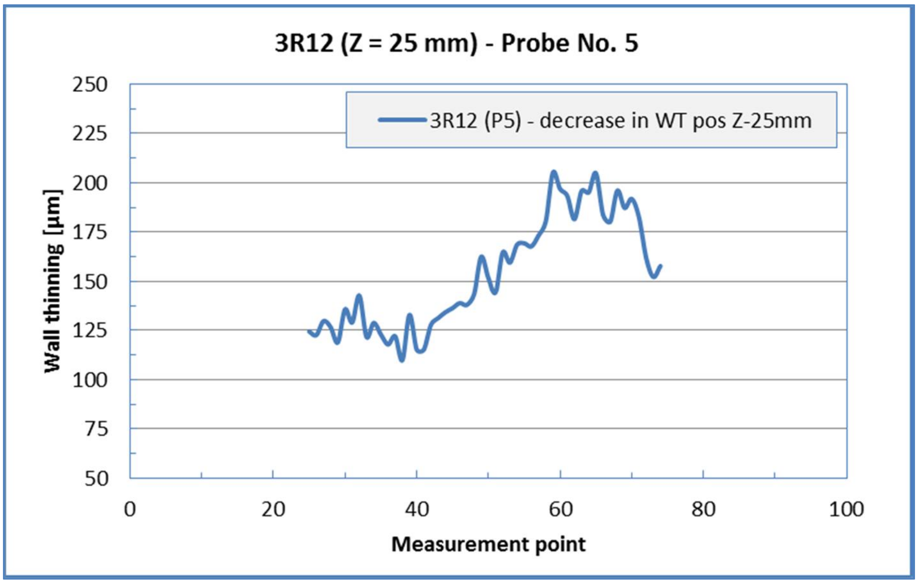


a)

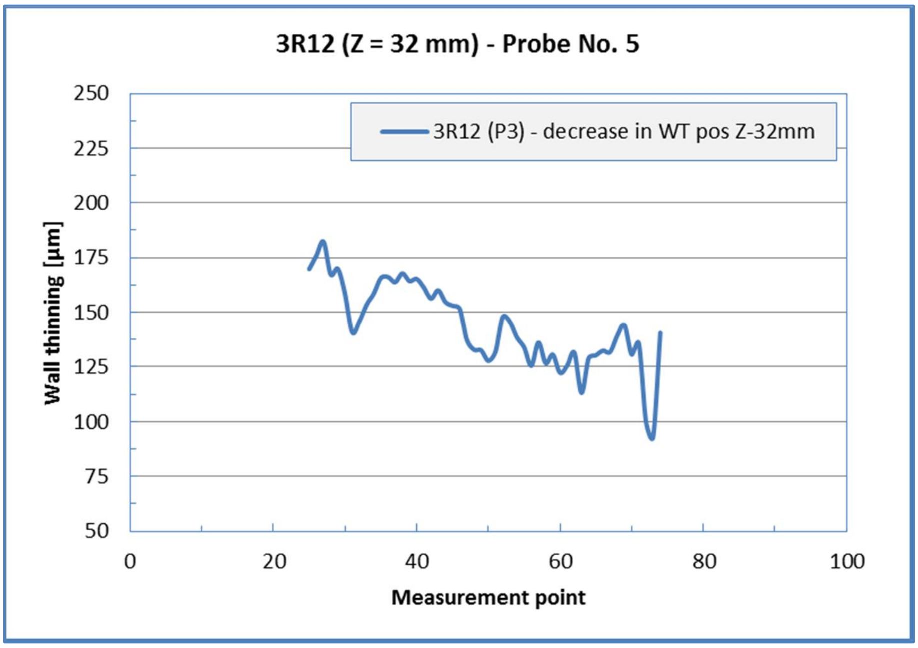


b)

Figure 52. Circumferential wall thickness profiles from 3R12 specimen (Probe No. 5): a) axial location Z = 25 mm and b) axial location Z = 32 mm.

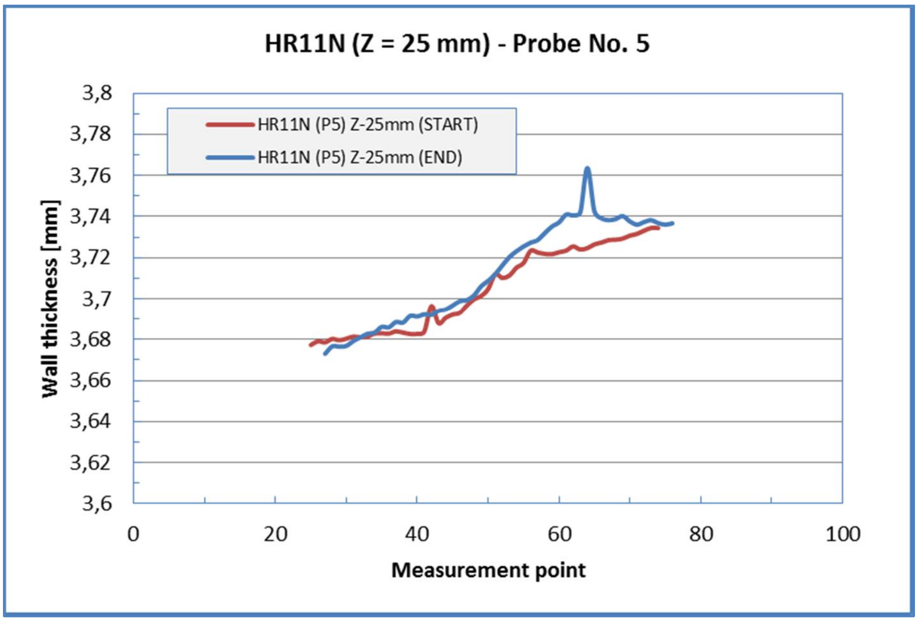


a)

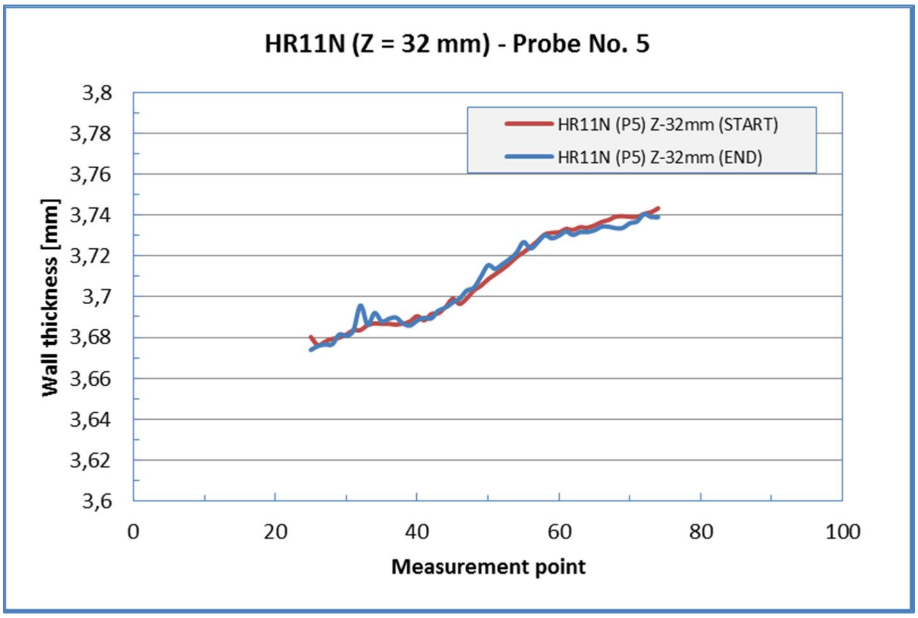


b)

Figure 53. Circumferential wall thinning curves from 3R12 specimen (Probe No. 5): a) axial location Z = 25 mm and b) axial location Z = 32 mm.

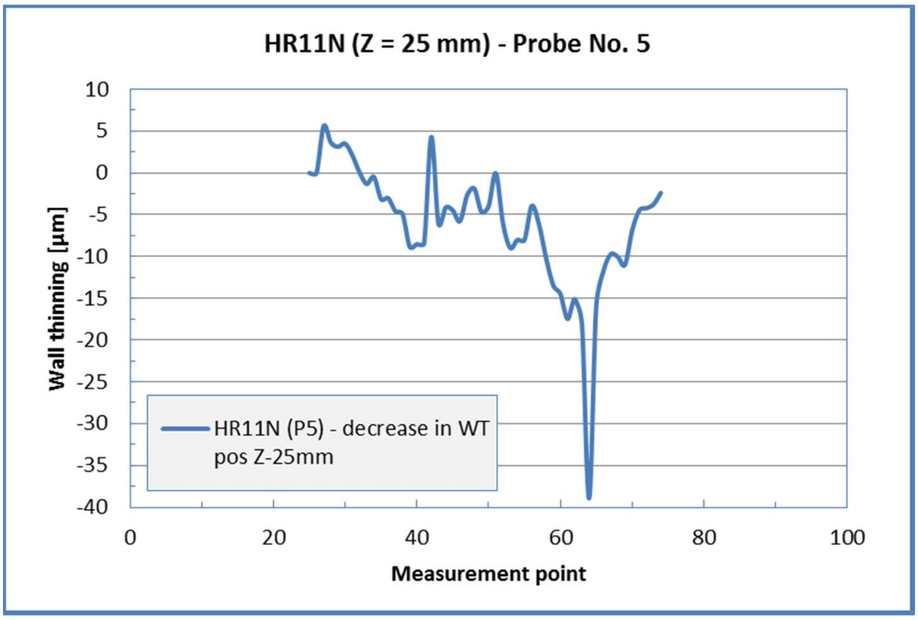


a)

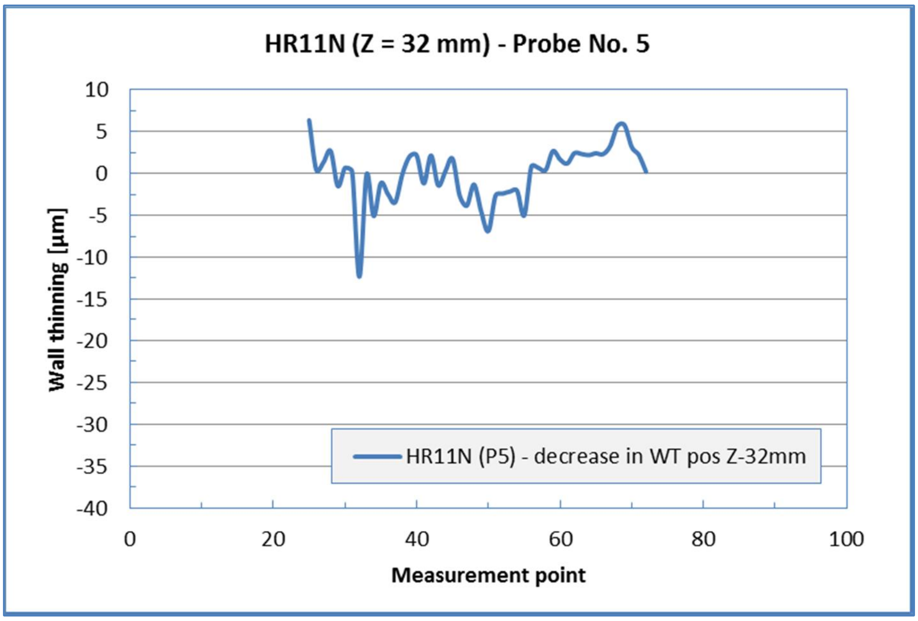


b)

Figure 54. Circumferential wall thickness profiles from HR11N specimen (Probe No. 5): a) axial location Z = 25 mm and b) axial location Z = 32 mm.

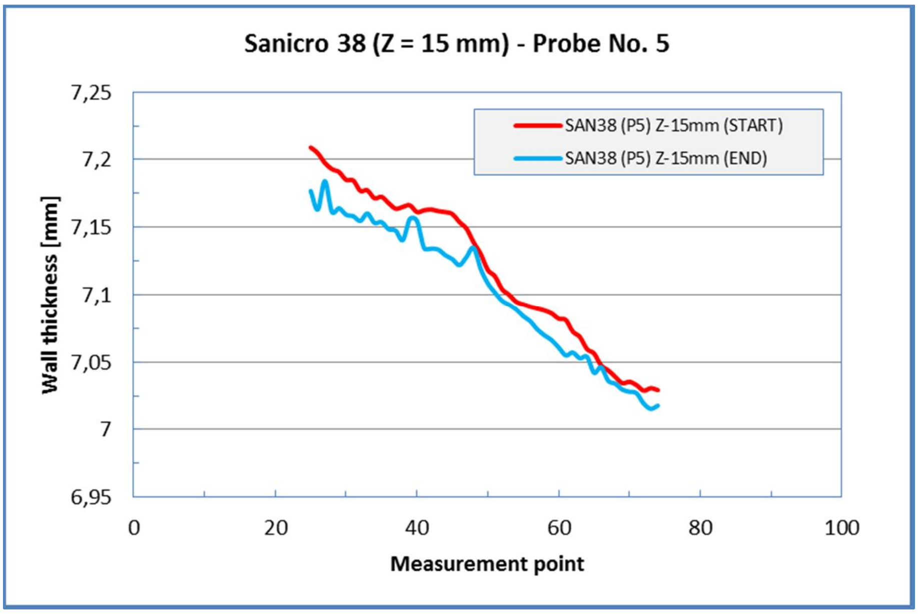


a)

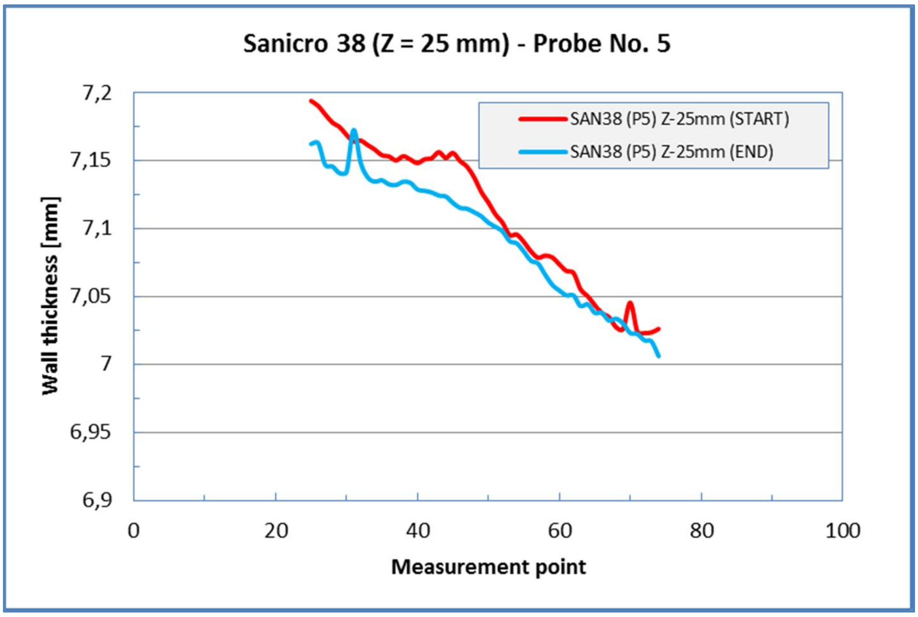


b)

Figure 55. Circumferential wall thinning curves from HR11N specimen (Probe No. 5): a) axial location Z = 25 mm and b) axial location Z = 32 mm.

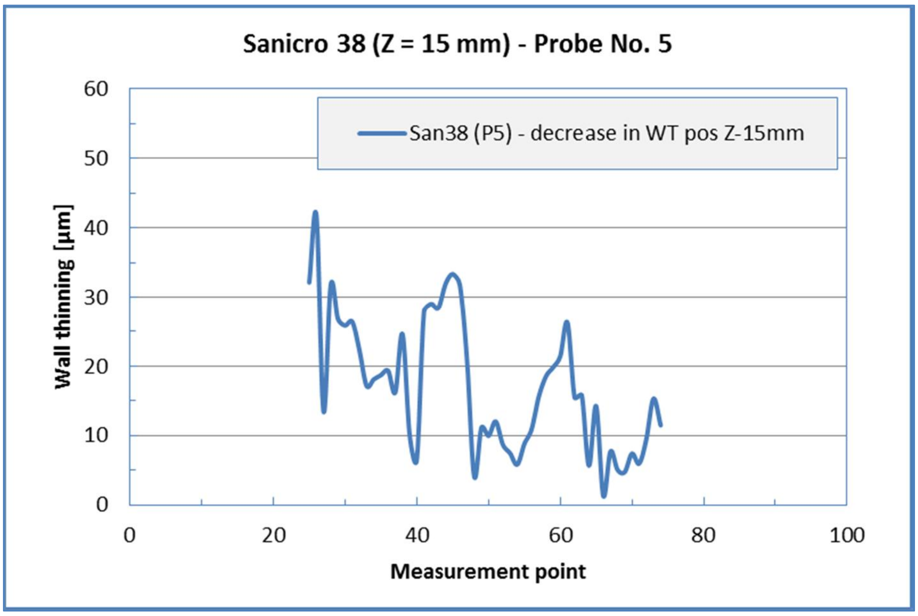


a)

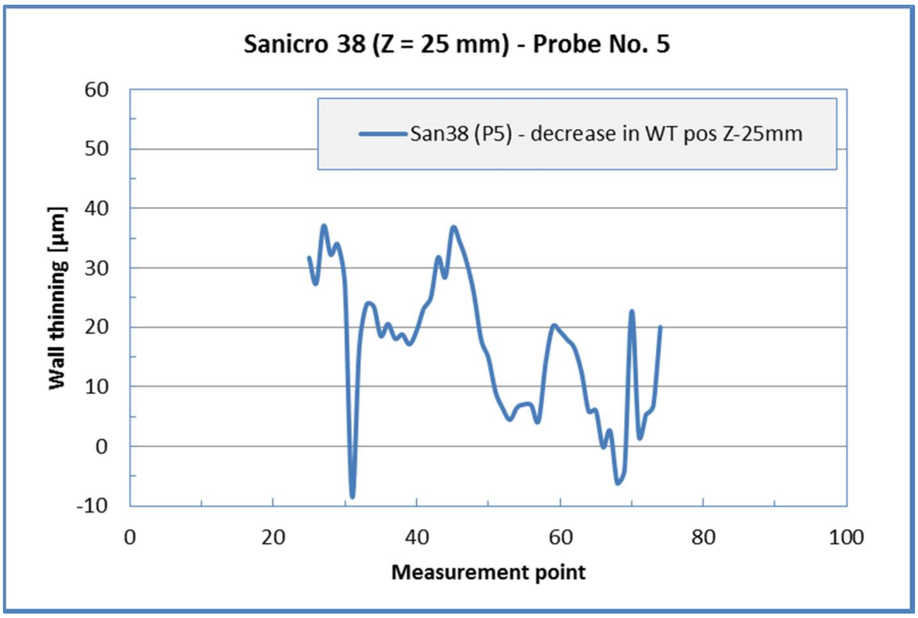


b)

Figure 56. Circumferential wall thickness profiles from Sanicro 38 specimen (Probe No. 5): a) axial location Z = 15 mm and b) axial location Z = 25 mm.

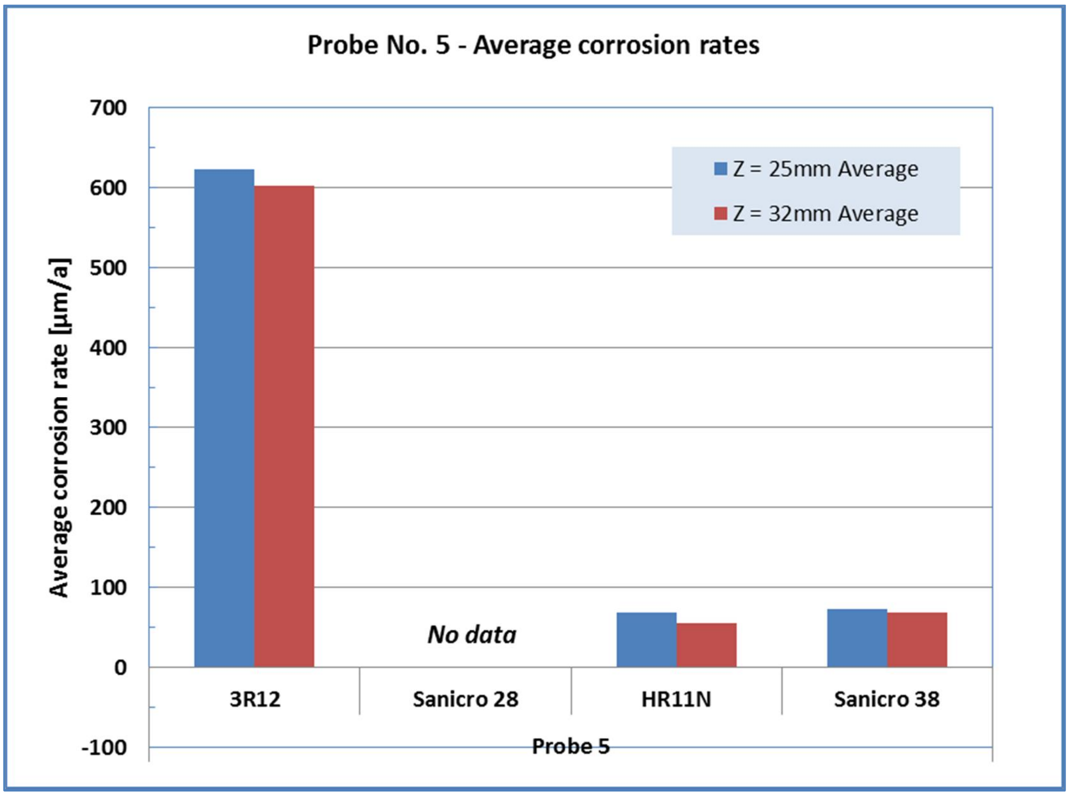


a)

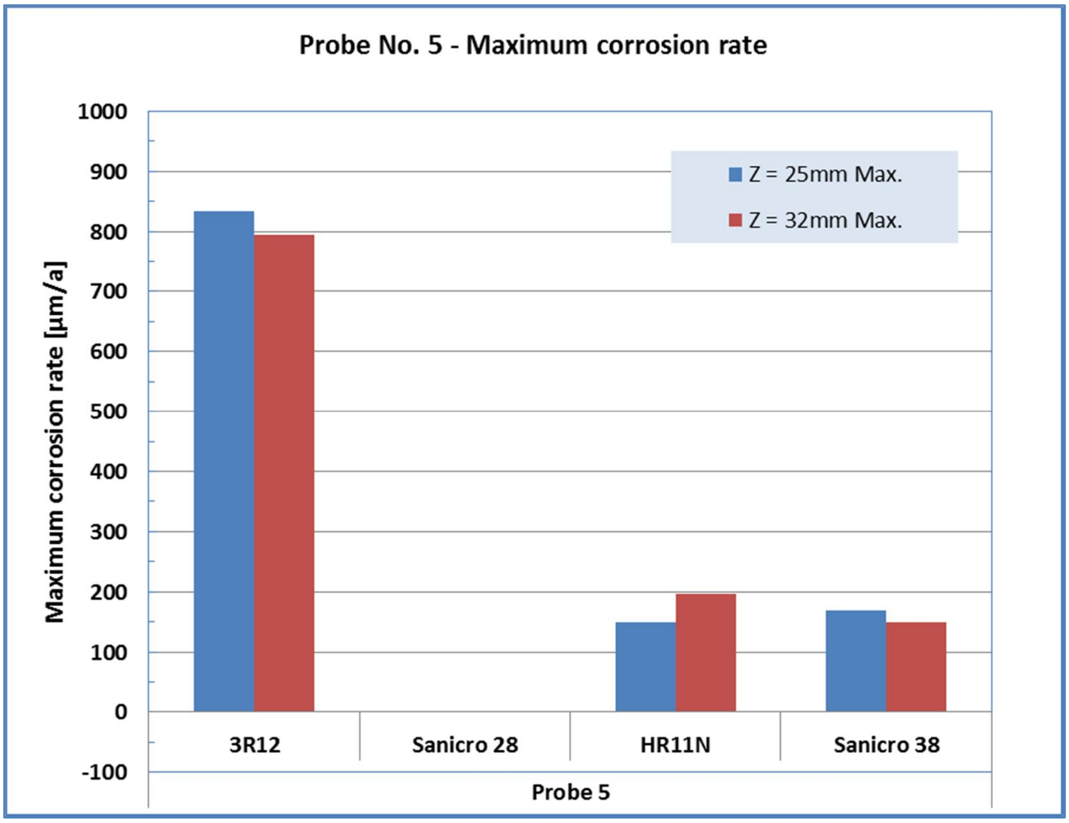


b)

Figure 57. Circumferential wall thinning curves from Sanicro 38 specimen (Probe No. 5): a) axial location Z = 25 mm and b) axial location Z = 32 mm.



a)

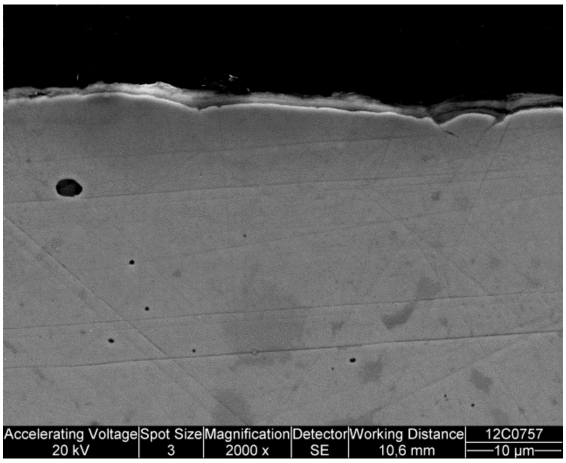


b)

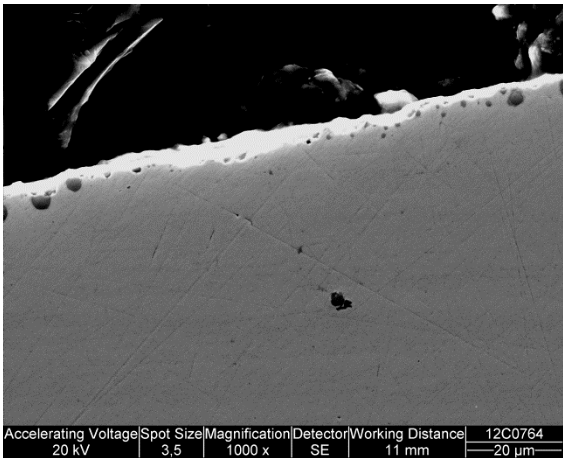
Figure 58. a) Average and b) maximum corrosion rates of the test materials calculated on the basis of the wall thickness measurements after 2157 h exposure in lower furnace at 440 °C (Probe test No. 5).

4.5.2 Metallography

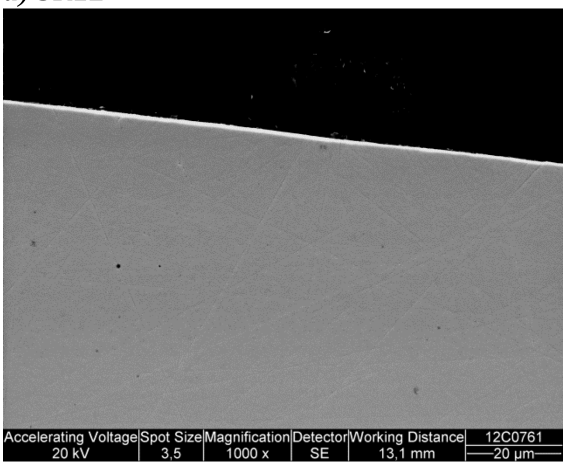
After the tests the samples were examined with optical microscope and/or SEM to determine the type of the corrosion attack. All samples had suffered from general thinning and no marked deposits or oxide/sulphide scales were observed on the surfaces, Figure 49. The layers found on 3R12, Sanicro 28, HR11N and Sanicro 38 were very thin ca. 2 µm in thickness. EDS analysis showed that iron and nickel depletion and chromium enrichment had taken place in some locations in all materials and that in these locations sulphur was also detected (Figure 50).



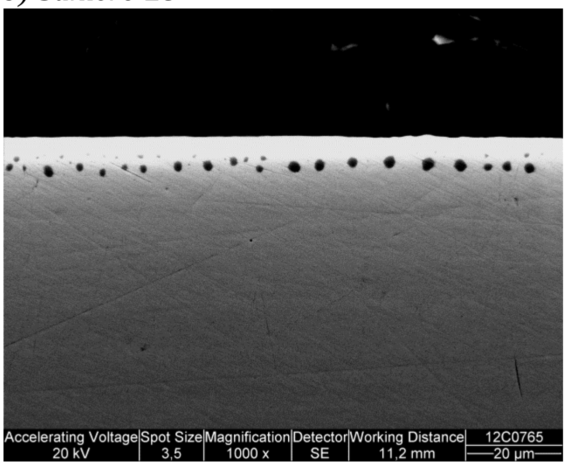
a) 3R12



b) Sanicro 28



c) HR11N



d) Sanicro 38

Figure 59. Cross sections from a) 3R12, b) Sanicro 28, c) HR11N and d) Sanicro 38 after 2157 h exposure in lower furnace at 440 °C (Probe test No. 5).

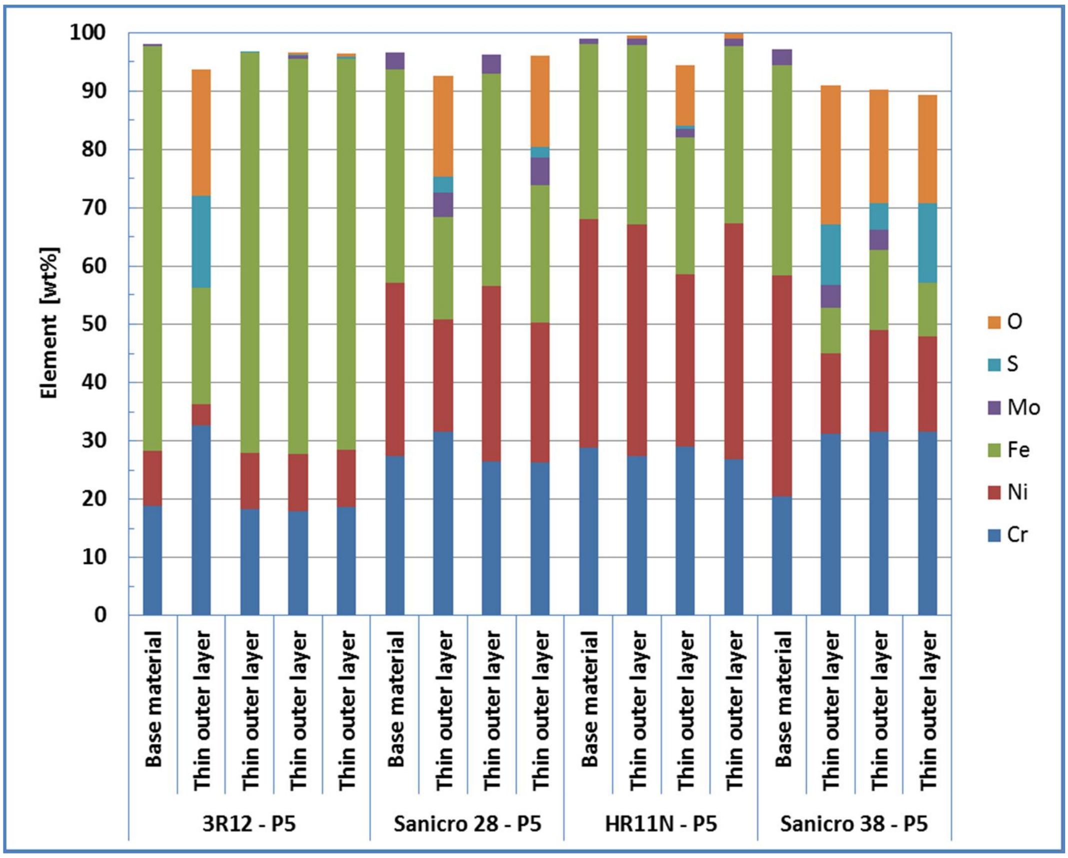


Figure 60. Results from the EDS analysis performed for the 3R12, Sanicro 28, HR11N and Sanicro 38 after 2157 h exposure in lower furnace at 440 °C (Probe test No. 5). Note: Quantitative results from cross sections, carbon excluded. Data from layers are from point analysis, whereas area analysis was used for base materials.

5 Conclusions

The coordinate measurement machine proved its applicability to determine wall thickness profiles from difficult shapes. In current samples the biggest problem was the specimen alignment i.e. it was impossible to measure the thickness profiles exactly from the same location before and after the test. This caused some error to the measurement results; especially to the maximum corrosion rates calculated from the tests No. 1-3, where the materials were tested in as received condition i.e. when the samples had surface scratches and dents. Another factor that affected to the accuracy was the surface deposits that were not completely removed during washing. Their adverse effect was clearly seen as negative average corrosion rate values in most resistant alloys.

Tests showed that polishing together with longer exposure time improves the accuracy, both of which are recommended to be used in future tests and especially when evaluating highly alloyed materials.

In current tests highest corrosion rate, ca. 4 mm/a, was measured for the carbon steel as expected. The traditional composite tube material 3R12 had the second highest corrosion rate, order of 0.6...0.8 mm/a at the temperature of 440 °C and ca. 0.4 mm/a at 430 °C (Figure 61). Based on the results of 3R12 the reproducibility of the probe tests was so good that different probe tests can be used to compare different materials to each other.

In current tests no marked differences were observed between Sanicro 38 and HR11N. Their maximum corrosion rates were in the order of 0.15...0.2 mm/a in the long term (>2000 h) test, i.e. about four times lower than that of the 3R12 (Figure 61).

In short term (<1000 h) tests the corrosion resistance of the 3RE28, 3XRE28 and Sanicro 28 were as good as or even slightly better than that of the Sanicro 38 or HR11N (Figure 62). Because the 3RE28 and 3XRE28 were not included in the long term tests and no results were obtained for the Sanicro 28 from the long term test No. 5, due to the misplaced thermocouple, it is recommended to verify their promising performance with long term tests in the future.

The results for the Super 625 were inconsistent. In short term 750 h test at 430 °C it's corrosion resistance was only slightly better than that of the 3R12, but in the long term 2154 h test at 440 °C it's resistance was even better that of the Sanicro 38 and HR11N (Figure 62). Similar kind of behaviour was observed in Sanicro 67. In short term 744 h test at 440 °C it's corrosion resistance was only slightly better than that of the Sanicro 38 and HR11N, but in the long term 2154 h test at 440 °C it's corrosion rate was only 1/10 of that of the Sanicro 38 and HR11N and 1/5 of the Super 625.

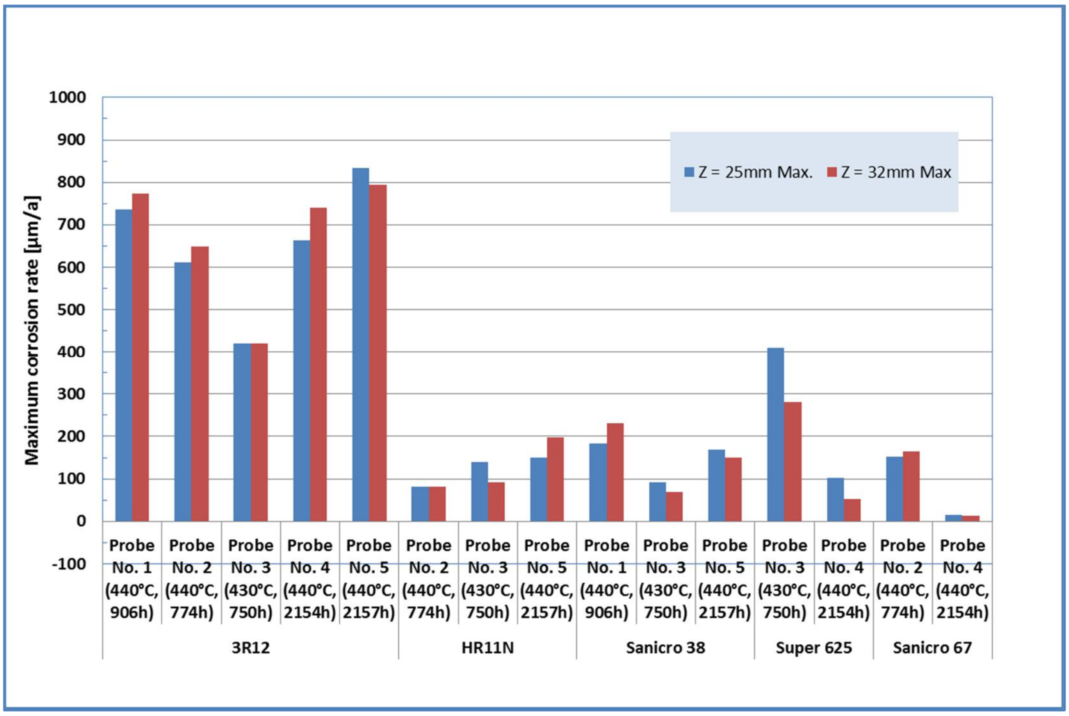


Figure 61. Calculated maximum corrosion rates for the 3R12, HR11N, Sanicro 38, Super 625 and Sanicro 67 materials from the probe test No. 1 - 5.

Figure 62. Calculated maximum corrosion rates for the 3RE28, 3XRE28, HR11N and Sanicro 38 from the probe test No. 1-3 and 5.

6 Summary

The aim of this study was to evaluate different potential cladding materials for compound tubes in actual recovery boiler lower furnace conditions**.** The work was divided so that specimen manufacturing and probe tests were conducted by Boildec Oy, whereas the sample characterisation was performed by VTT. The test materials were carbon steel; austenitic stainless steels 3R12, 3RE28 and 3XRE28; high nickel alloys Sanicro 28, HR11N and Sanicro 38 and two nickel base alloys Super 625 and Sanicro 67. The test temperature was 440°C and test duration varied from 1000 to 2700 hours.

The results show that materials with superior corrosion resistance to AISI 304L exist and hence corrosion in lower furnace can be managed by proper material selection. Corrosion resistance in lower furnace conditions is improved by alloying, especially by chromium. According to the wall thickness measurements the test materials can be put in following order based on increased resistance:

C-steel << 3R12 < HR11N ~ Sanicro 38 (~ Sanicro 28 ~ 3RE28/3XRE28) < Super 625 < Sanicro 67

The carbon steel corroded at extremely high rate (>4 mm/a) at the temperature of 440 °C. Also the 3R12 (AISI 304L) corrodes in such high rate (>0.6 mm/a) at 440 °C that it can't be safely used in the lower furnace in the future high pressure recovery boilers, where material temperatures are expected to rise to level of 400…440 °C. The performance of the Sanicro 38 and HR11N was satisfactory in long term test at 440 °C (CR_{max} ~ 0.1...0.2 mm/a), but it is recommended to verify their performance also at lower temperature (400 °C). The new material group which looks promising is the high chromium alloys 3RE28/3XRE28 and Sanicro 28, but their long term performance should be verified in the future. If the corrosion resistance is the determining factor, the Sanicro 67 seems to be a good material for future boilers, since its corrosion rate was lowest from the studied alloys. Based on the long term test the Super 625 in the second best choice for the future high pressure boiler, but because of its relatively high corrosion rate in short term test more and longer tests are needed to verify its performance.

Liite 3

VTT, Characterisation of probe test samples exposed to BLRB lower furnace environments – presentation 19.12.2012

Business from technology

Characterisation of probe test samples exposed to BLRB lower furnace environments

SKYREC JR 19.12.2012

Pekka Pohjanne, VTT

Test materials

Material	%C	%Mn	%Si	%Cr	%Ni	%Mo	%Fe	%Cu	Other
Carbon steel									
P265GH	≤0.2	0.80 - 1.40	≤0.40	≤0.30	≤0.30	≤0.08	bal.	≤0.30	
Austenitic stainless steels									
3R12 [304L]	≤0.02	1.3	0.4	18.5	10.5	...	bal.	...	
3RE28[A)] [310]	0.023	1.77	0.39	25.6	21.0	0.06	bal.	0.06	
3xRE28 [A)]	0.012	1.63	0.35	25.2	21.3	0.25	bal.	0.14	
High nickel alloys									
Sanicro 28 [UNS N08028]	≤0.02	≤2.0	≤0.6	27	31	3.5	bal.	1.0	
Sanicro 38 [mod. 825]	≤0.03	0.8	≤0.5	20	38.5	2.6	bal.	1.7	Ti: 0.8
HR11N	0.03	2.0	0.6	27.0	38	0.5 - 1.5	bal.		N: 0.1
Nickel base alloys									
Sanicro 67 [Alloy 690]	0.02	≤0.5	≤0.5	30	60	...	bal.	...	Co: <0,05
Super 625	0.1	≤0.5	≤0.5	20 -23	bal.	...	≤5.0	...	W: 3.15-4.15 Al: 0.4 Co ≤ 1.0

A) Tube samples analysed by VTT

Corrosion resistance evaluation – Procedures

A. Wall thickness measurements before and after testing (corrosion rate)

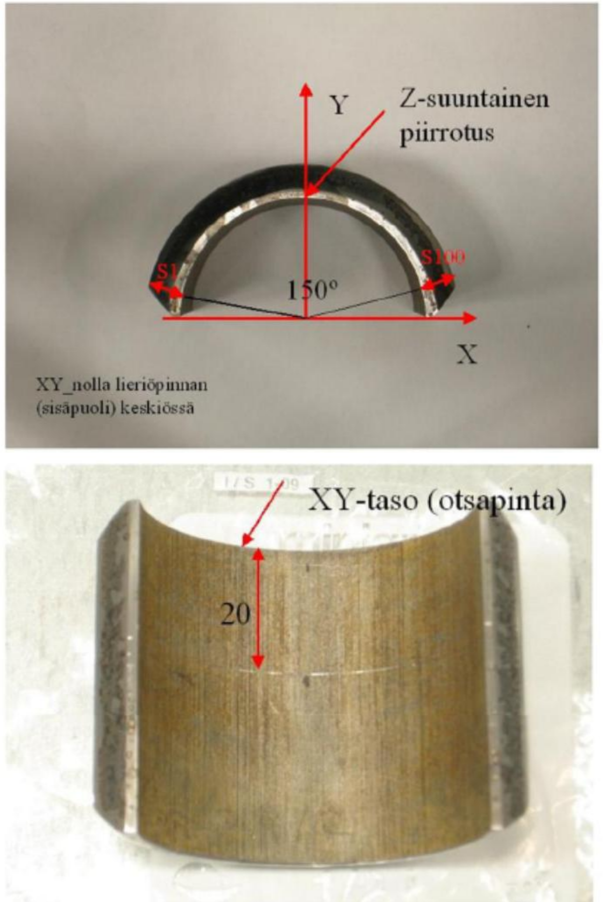
- Thickness profiles at a function of circumference from three locations (axial direction)
  → average & maximum WT losses

B. Characterisation and corrosion mechanism

- SEM/EDS from metallographic cross sections after/before the profile measurements
- Few analysis also from unexposed reference samples

✓ Tests No.1…3 - Materials tested in as received condition

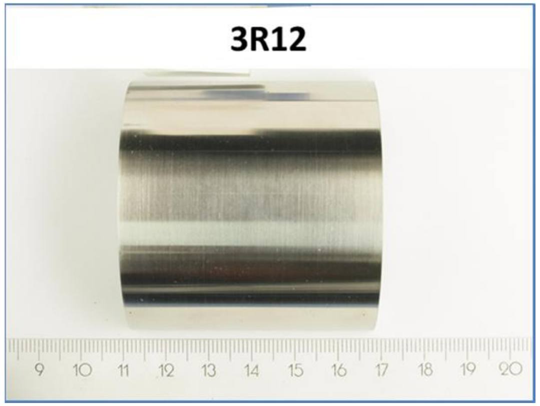
✓ Tests No.4 and 5 - The outer and inner surfaces machined and hand grinded/polished

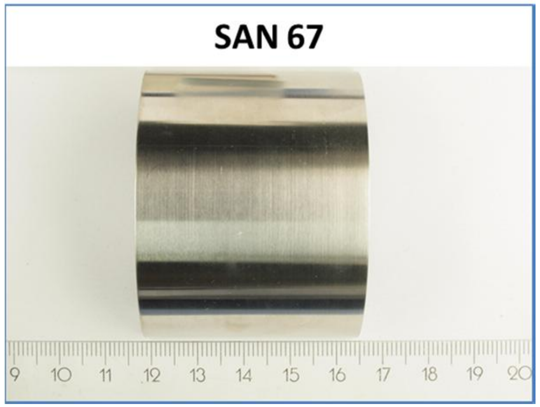


Measurements with coordinate measurement machine

Corrosion resistance evaluation – Procedures

Probe No. 2 – Specimens tested in as received condition





Probe No. 4 - Surfaces machined and hand grinded/polished

Test matrix

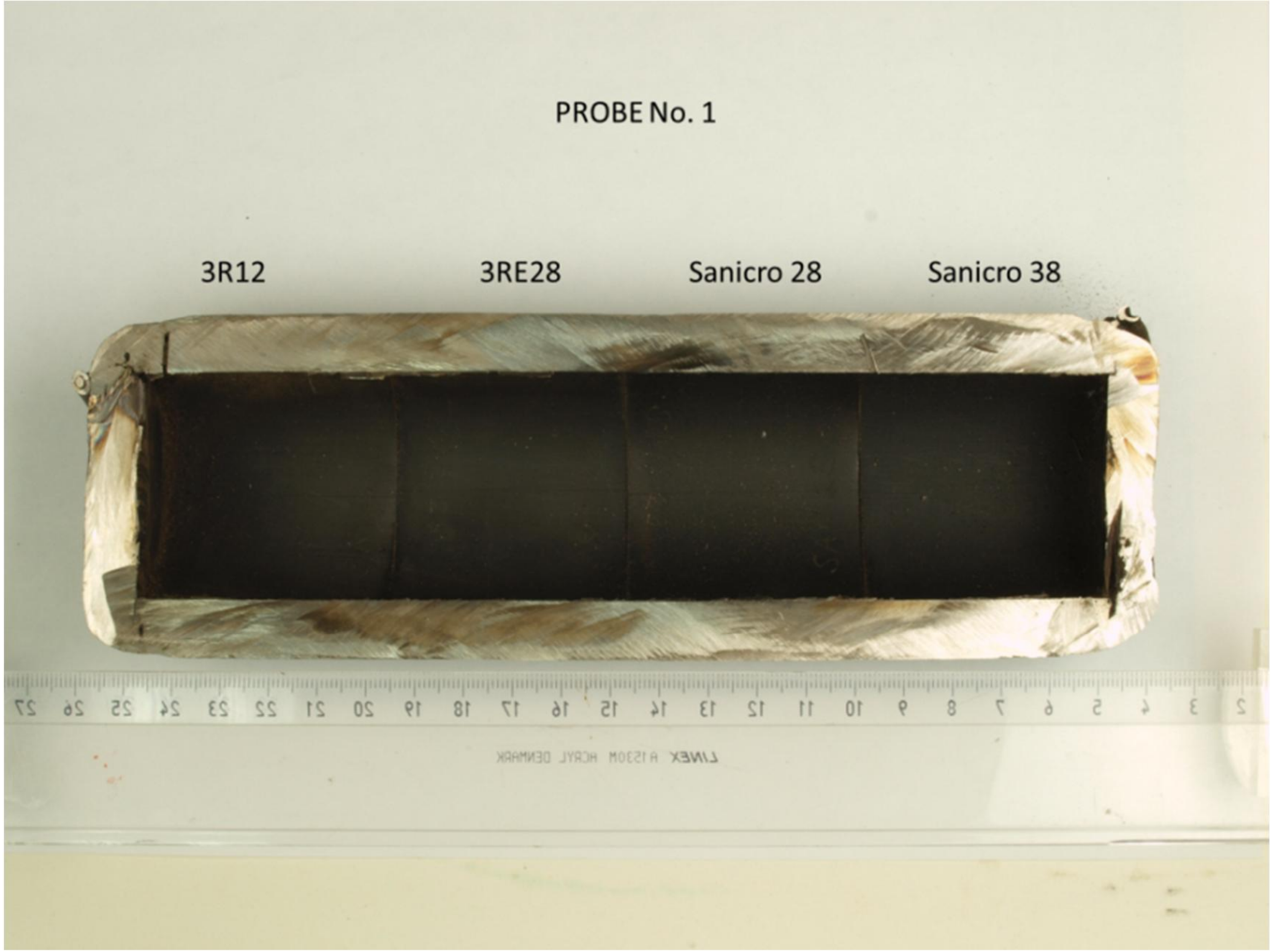
Test No.	Test materials	Test duration, hours		Effective temperature
		Total	Effective[A)]	
1	3R12(AISI 304L), 3RE28(AISI 310S), Sanicro28, Sanicro38	1000	906 (pressure over 9 bar)	ca. 440°C
2	3R12(AISI 304L), 3XRE28, HR11N, Sanicro67,	1000	744 (pressure over 8 bar)	ca. 440°C
3	3R12(AISI 304L), HR11N, Sanicro38, Super625	1000	750 (pressure over 7 bar)	ca. 430°C
4	3R12(AISI 304L), carbon steel (P265GH), Sanicro67, Super625	2700	2154 (pressure over 9 bar)	ca. 440°C
5	3R12(AISI 304L), Sanicro28, HR11N, Sanicro38	2630	2157 (pressure over 9 bar)	ca. 440°C

[A)]Used in corrosion rate calculations

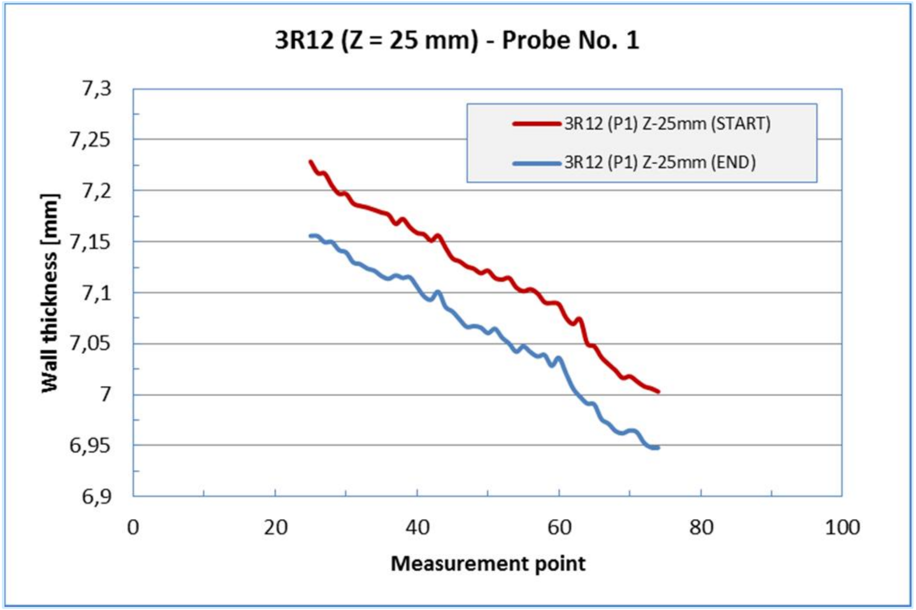
Results – Probe test No. 1

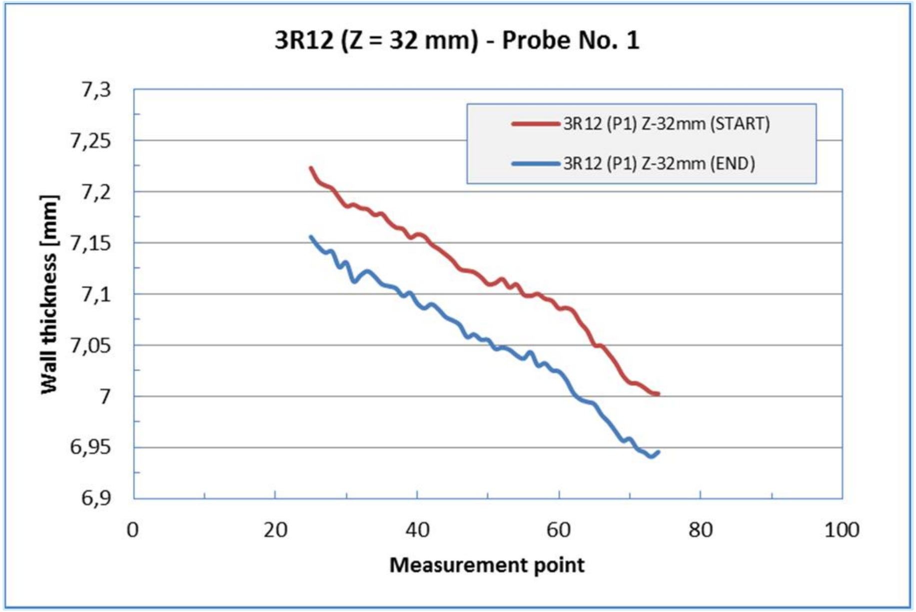
Probe No.1 after the test

Probe No.1 after the test

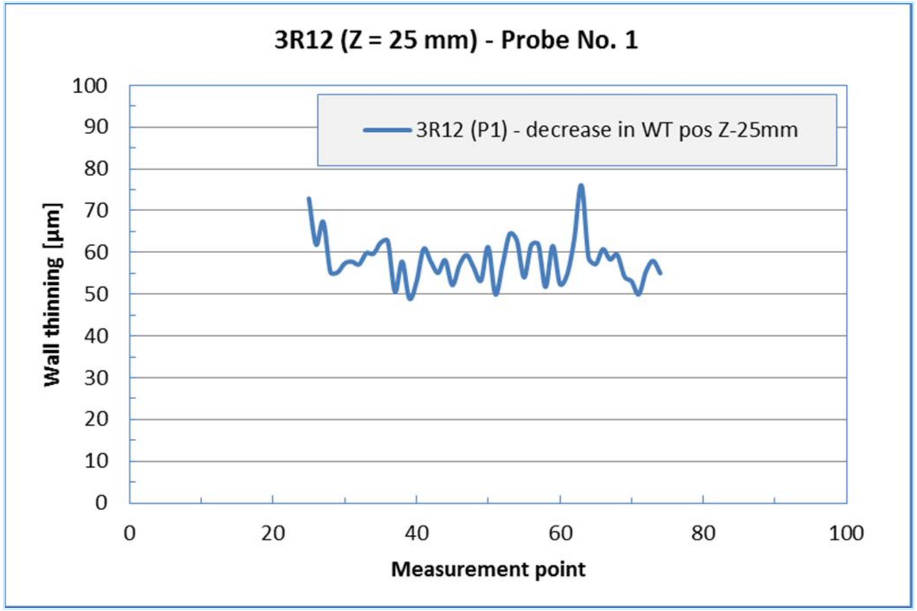


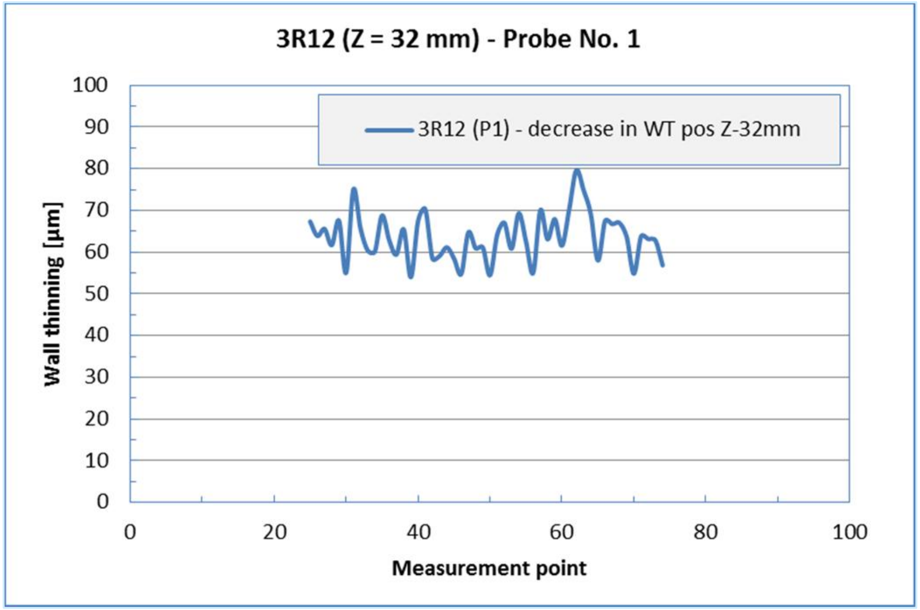
Results – 3R12 (304L)



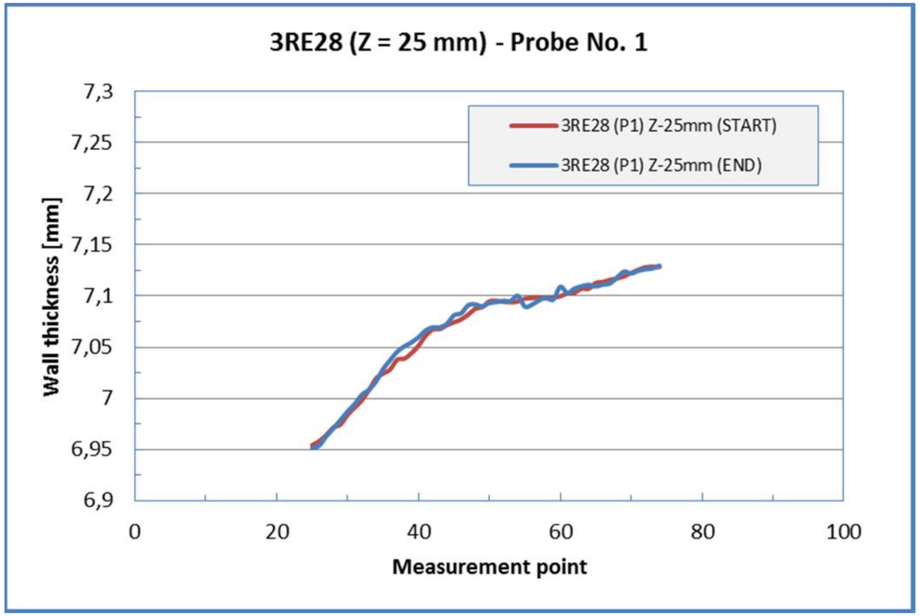


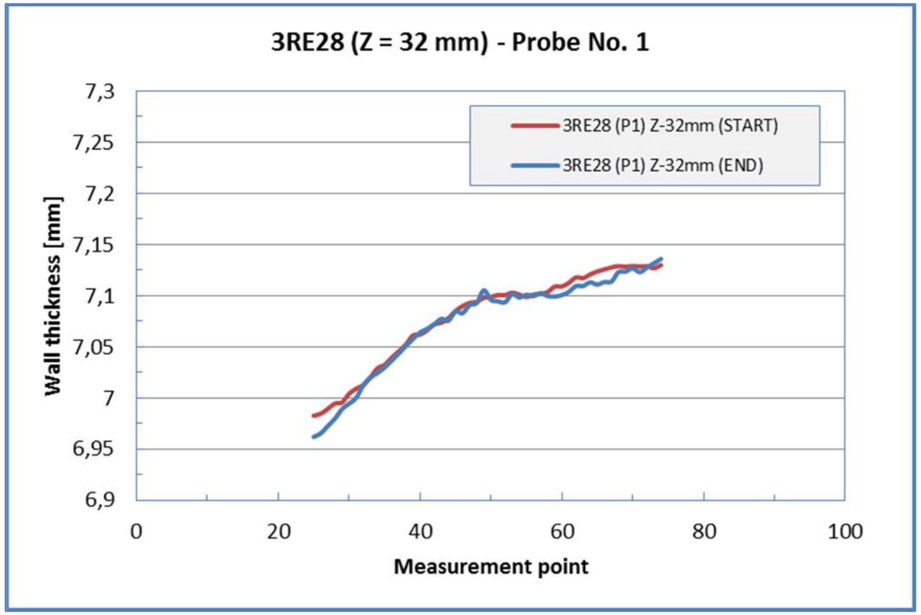
Results – 3R12 (304L)



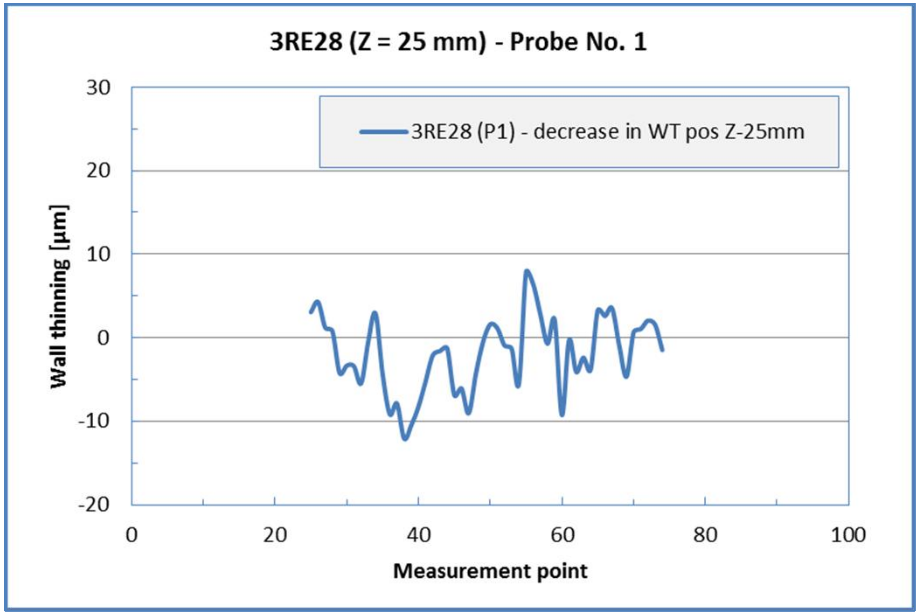


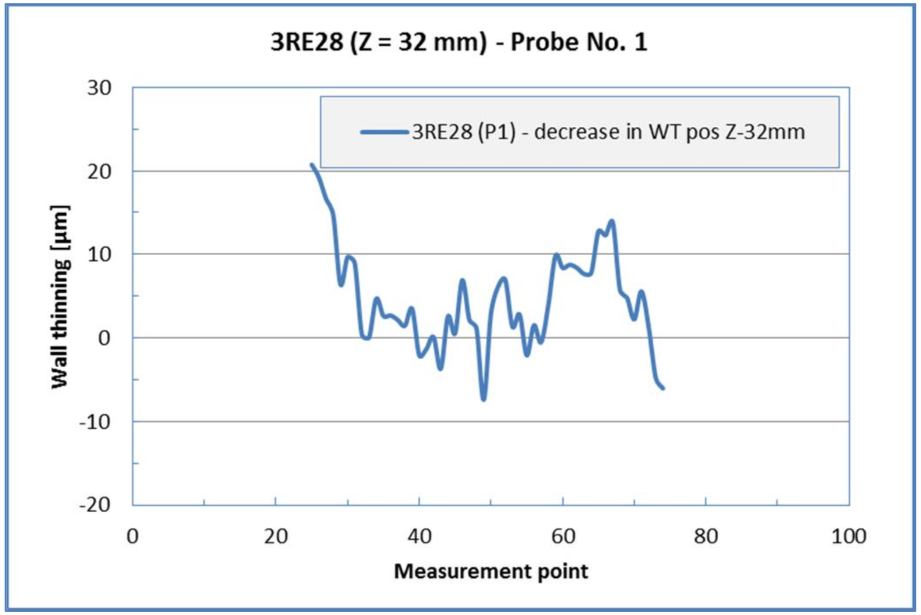
Results – 3RE28



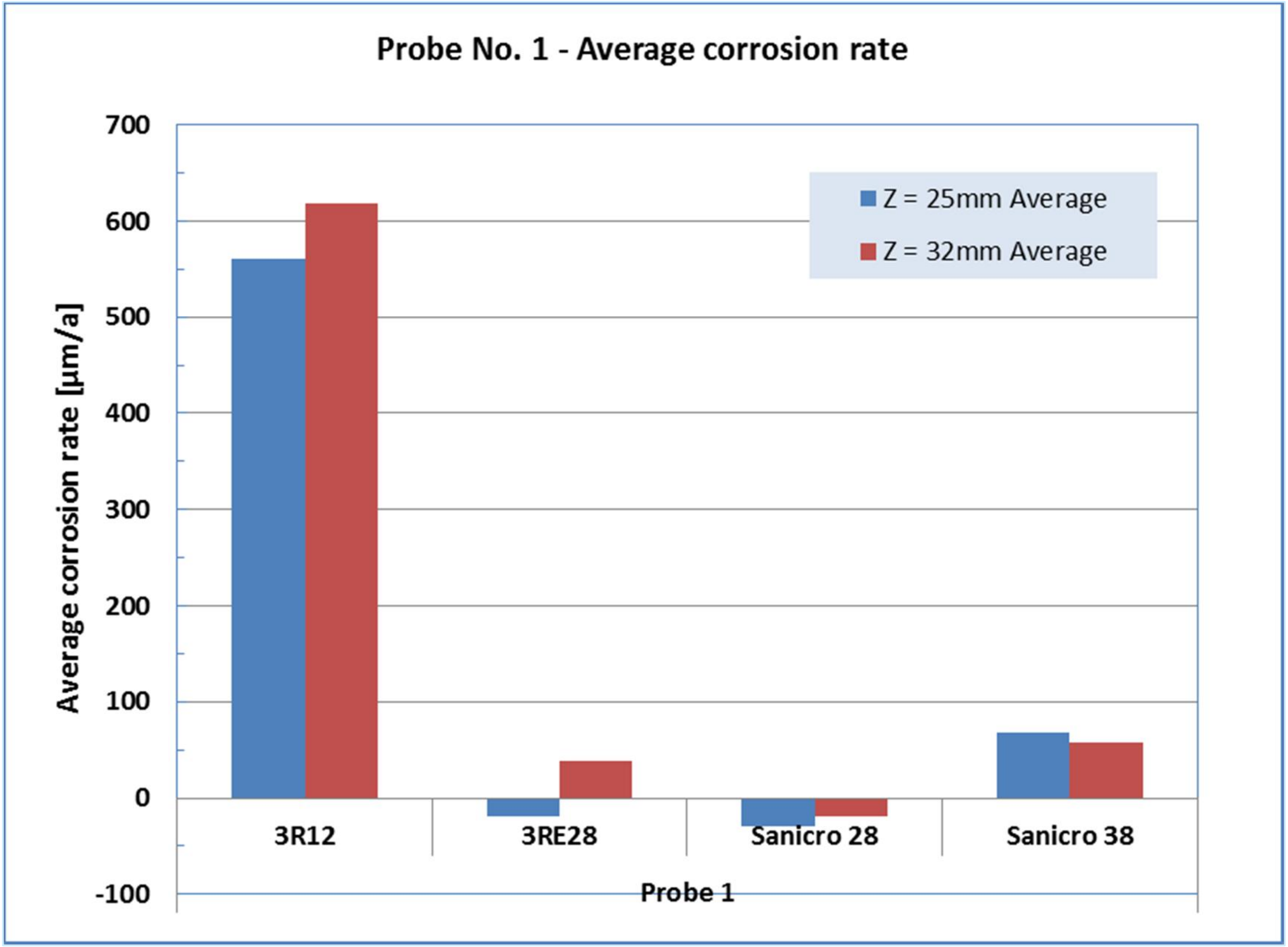


Results – 3RE28

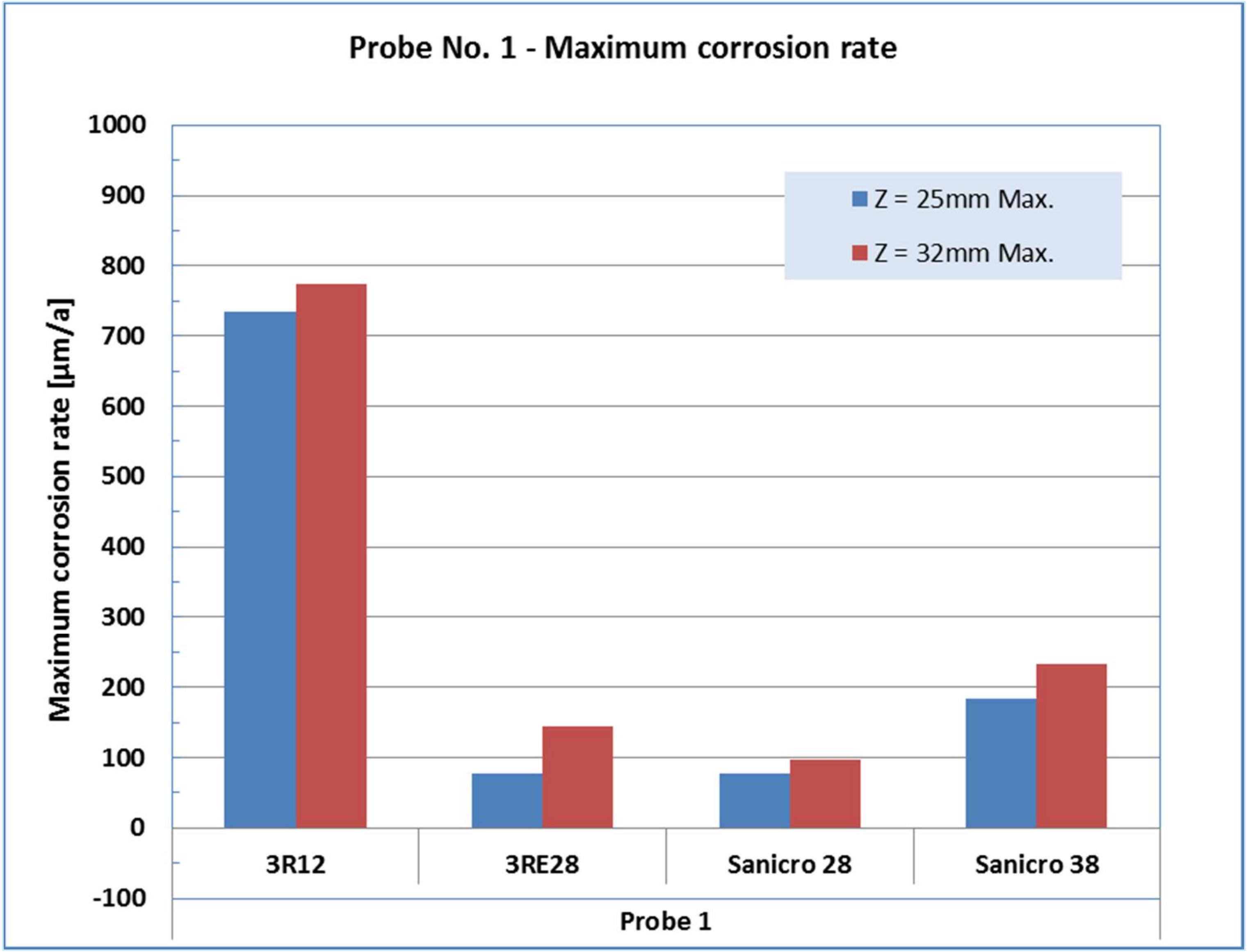




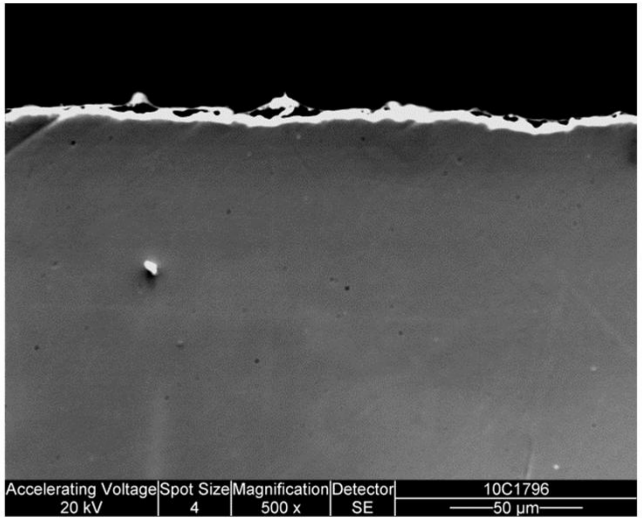
Probe test No. 1 – Average corrosion rates



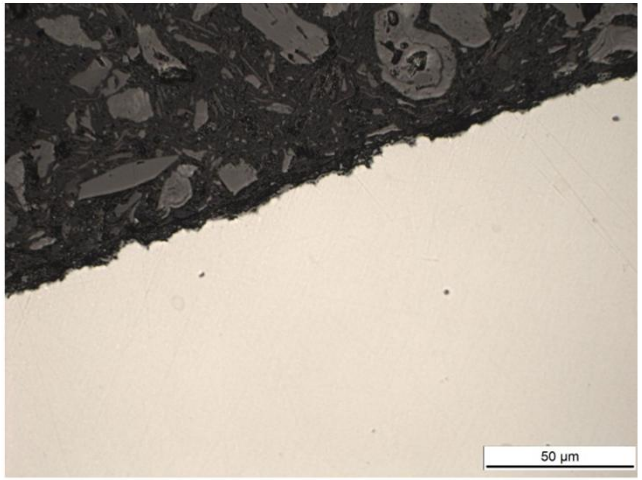
Probe test No. 1 – Maximum corrosion rates



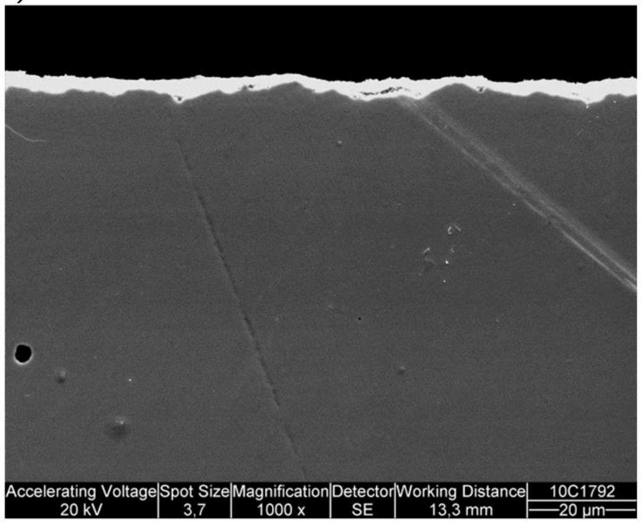
Probe test No. 1 – Metallography



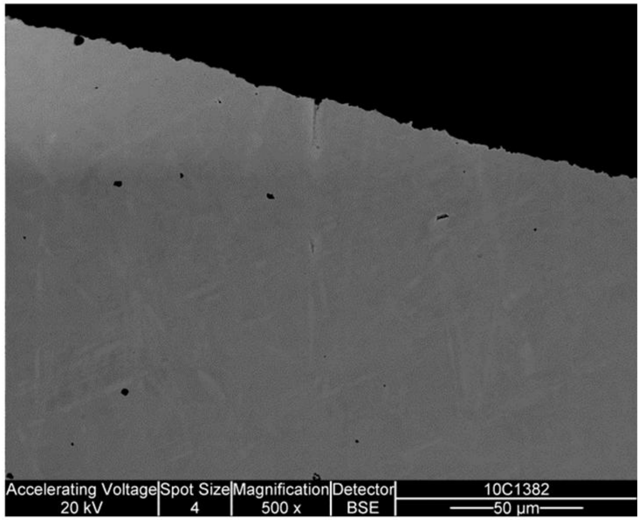
a) 3R12



b) 3RE28

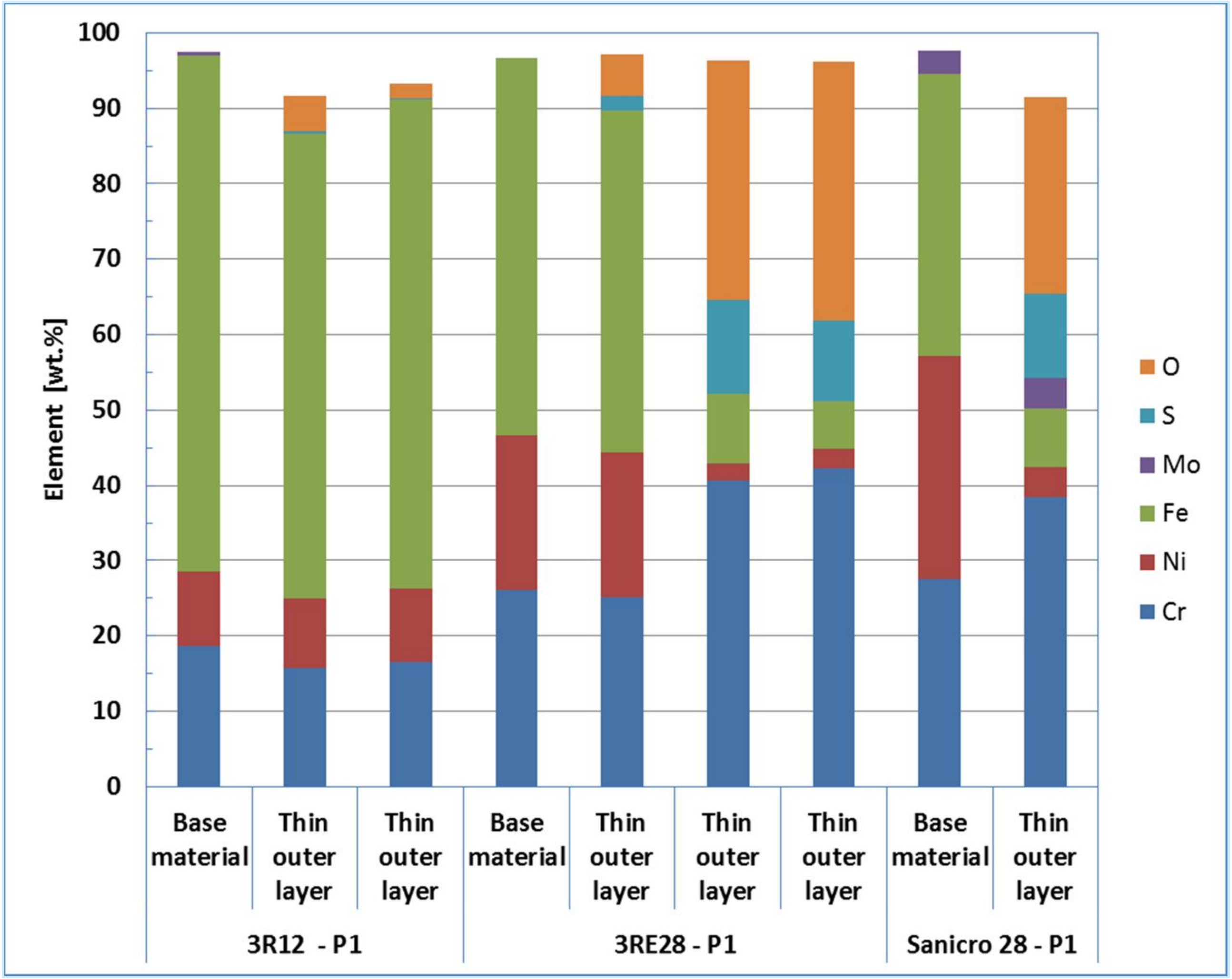


c) Sanicro 28



d) Sanicro 38

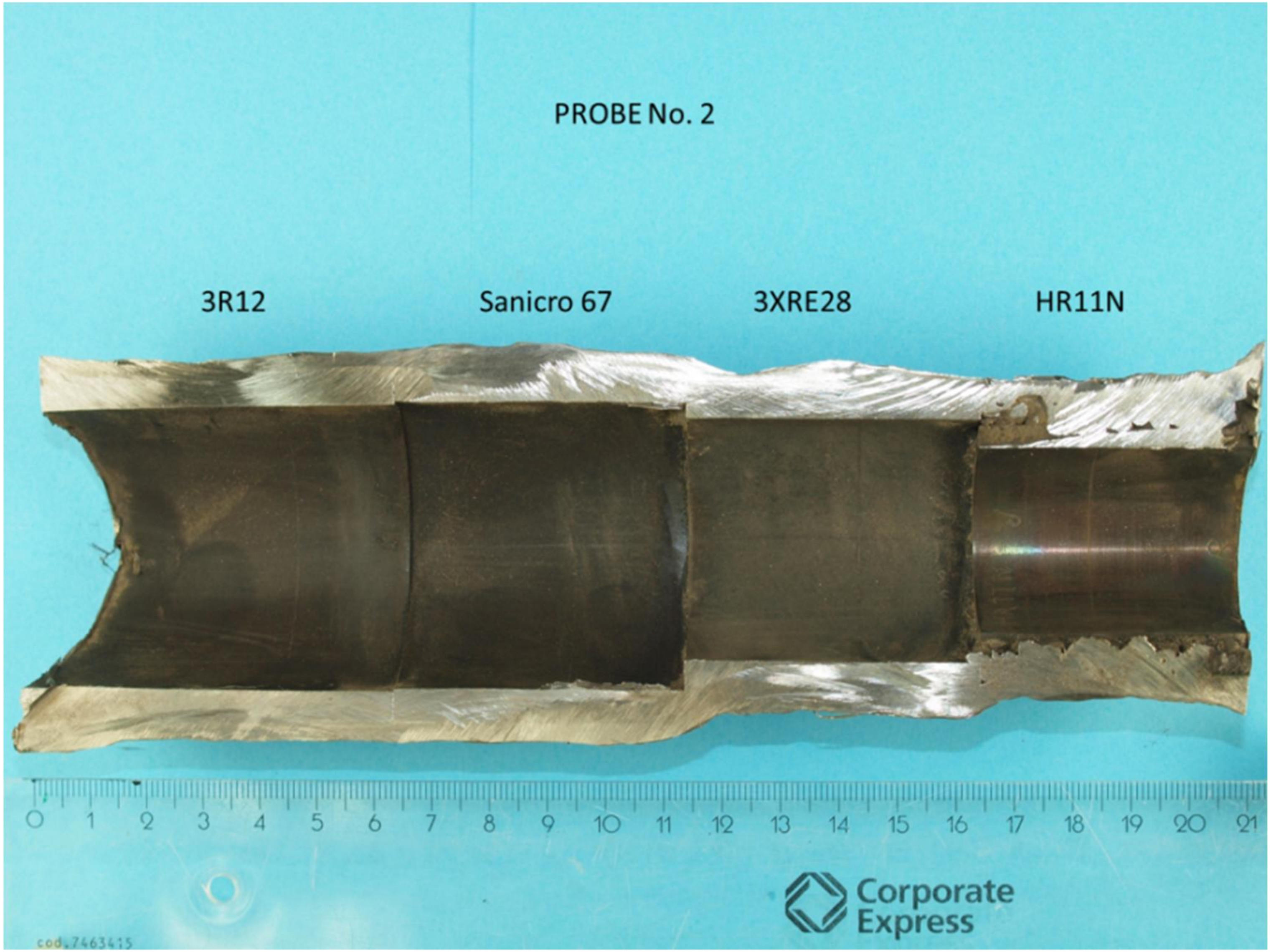
Probe test No. 1 – EDS analysis



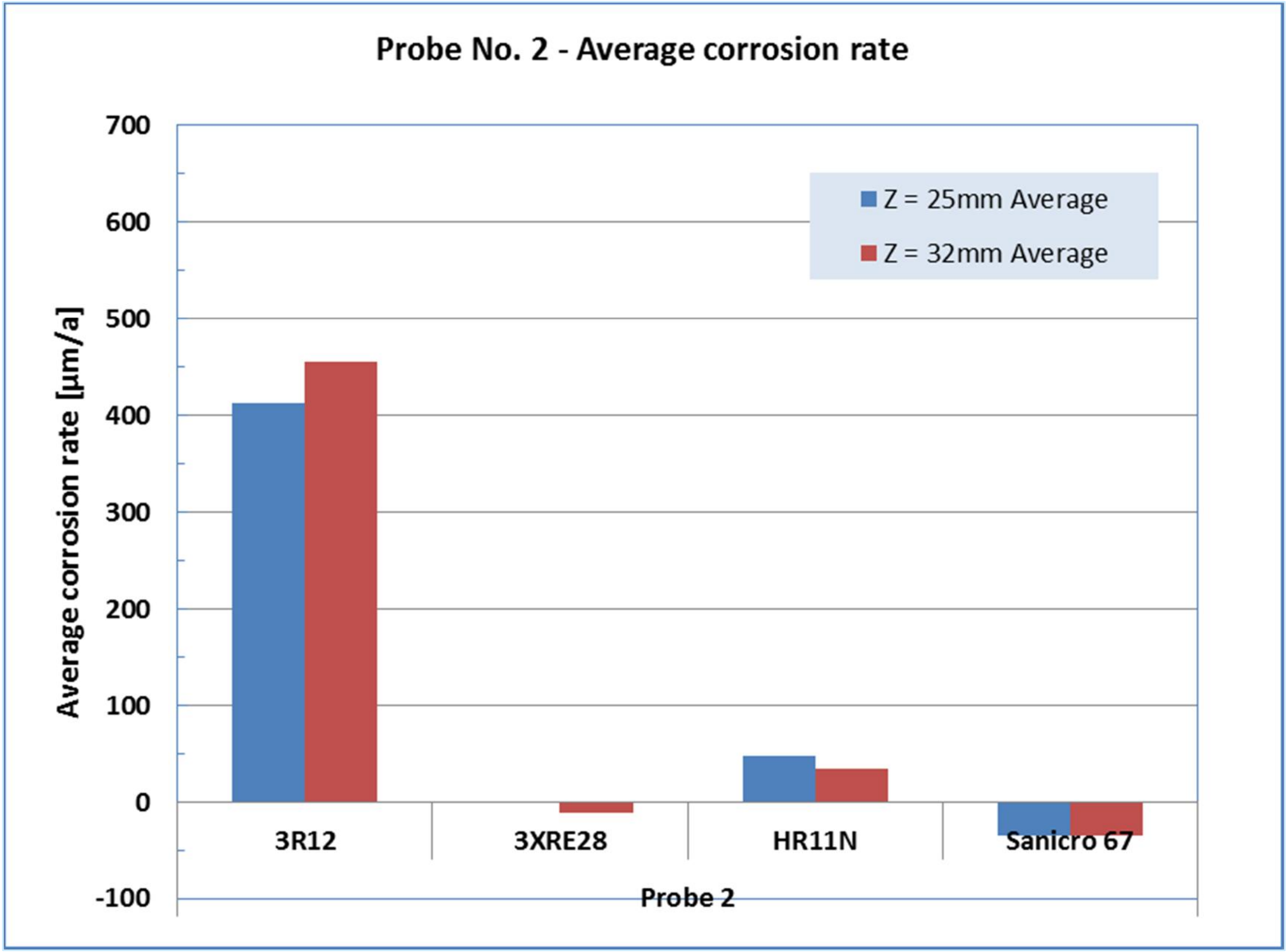
Results – Probe test No. 2

Probe No. 2 after the test

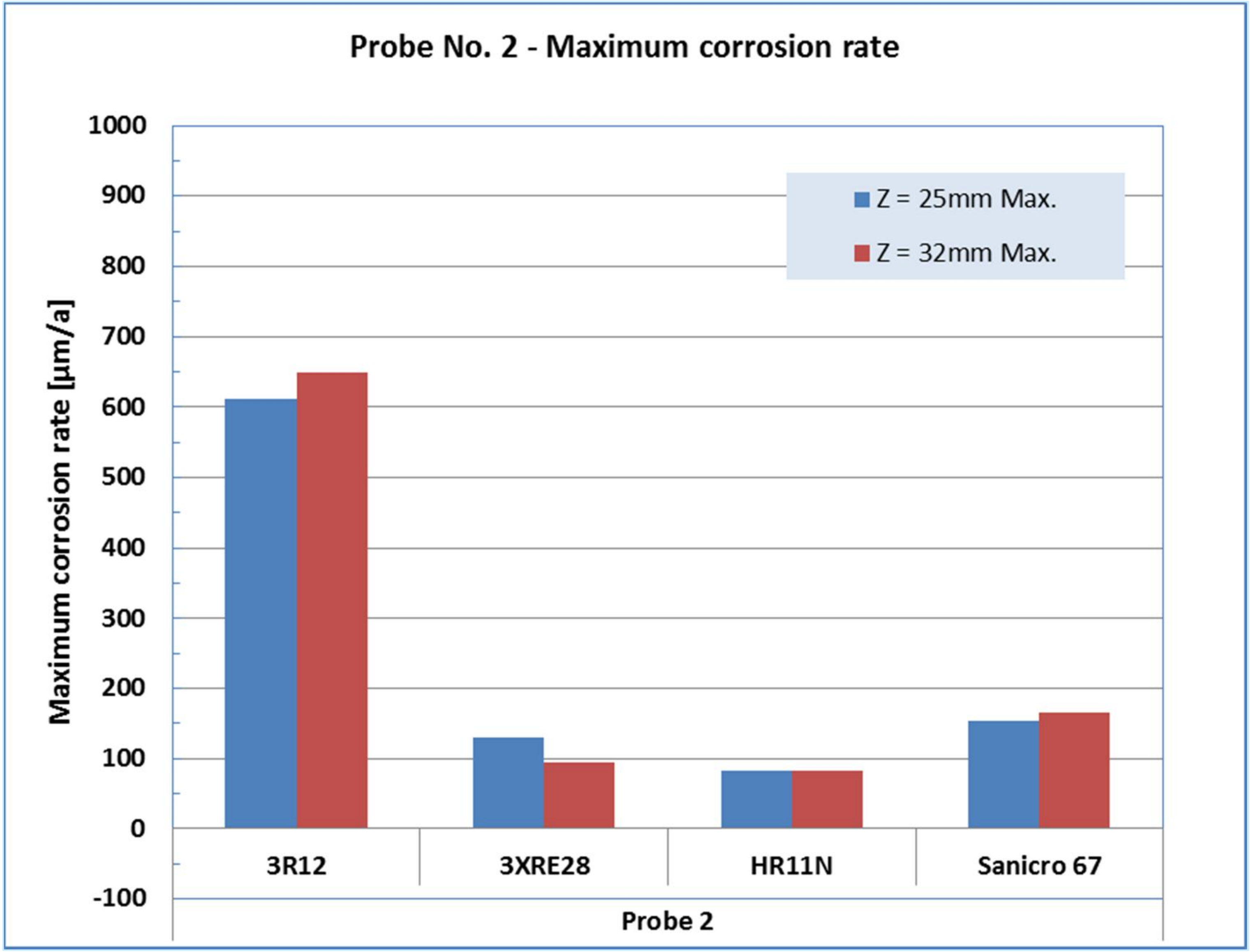
Probe No. 2 after the test



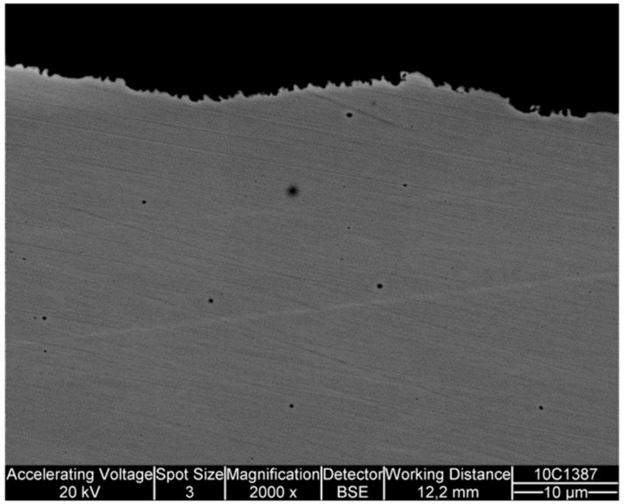
Probe test No. 2 – Average corrosion rates



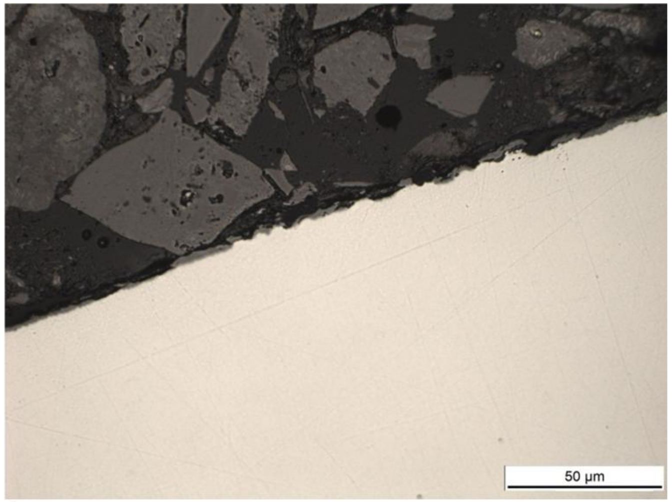
Probe test No. 2 – Maximum corrosion rates



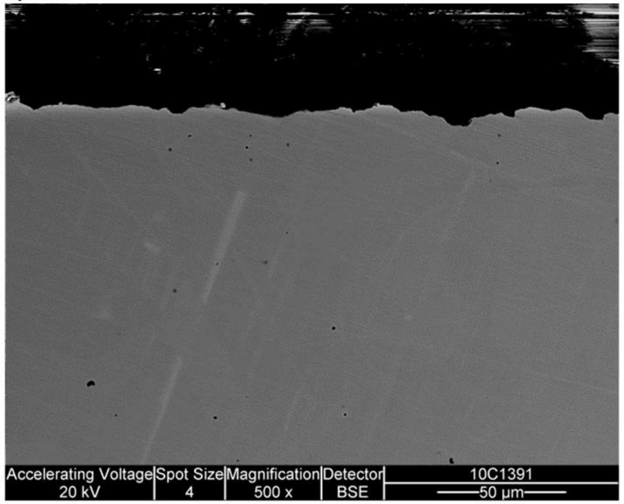
Probe test No. 2 – Metallography



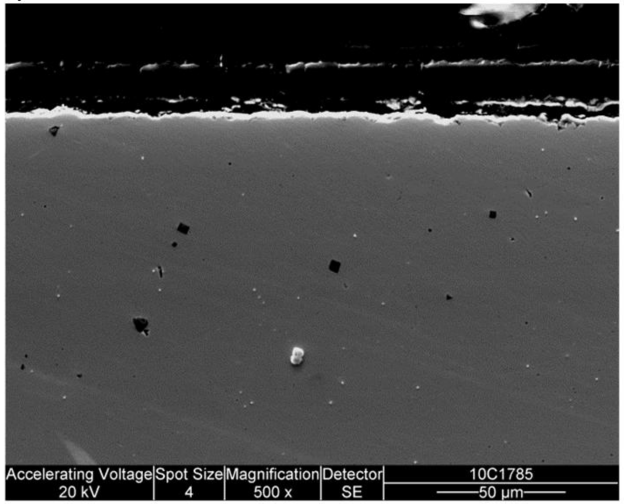
a) 3R12



b) 3XRE28

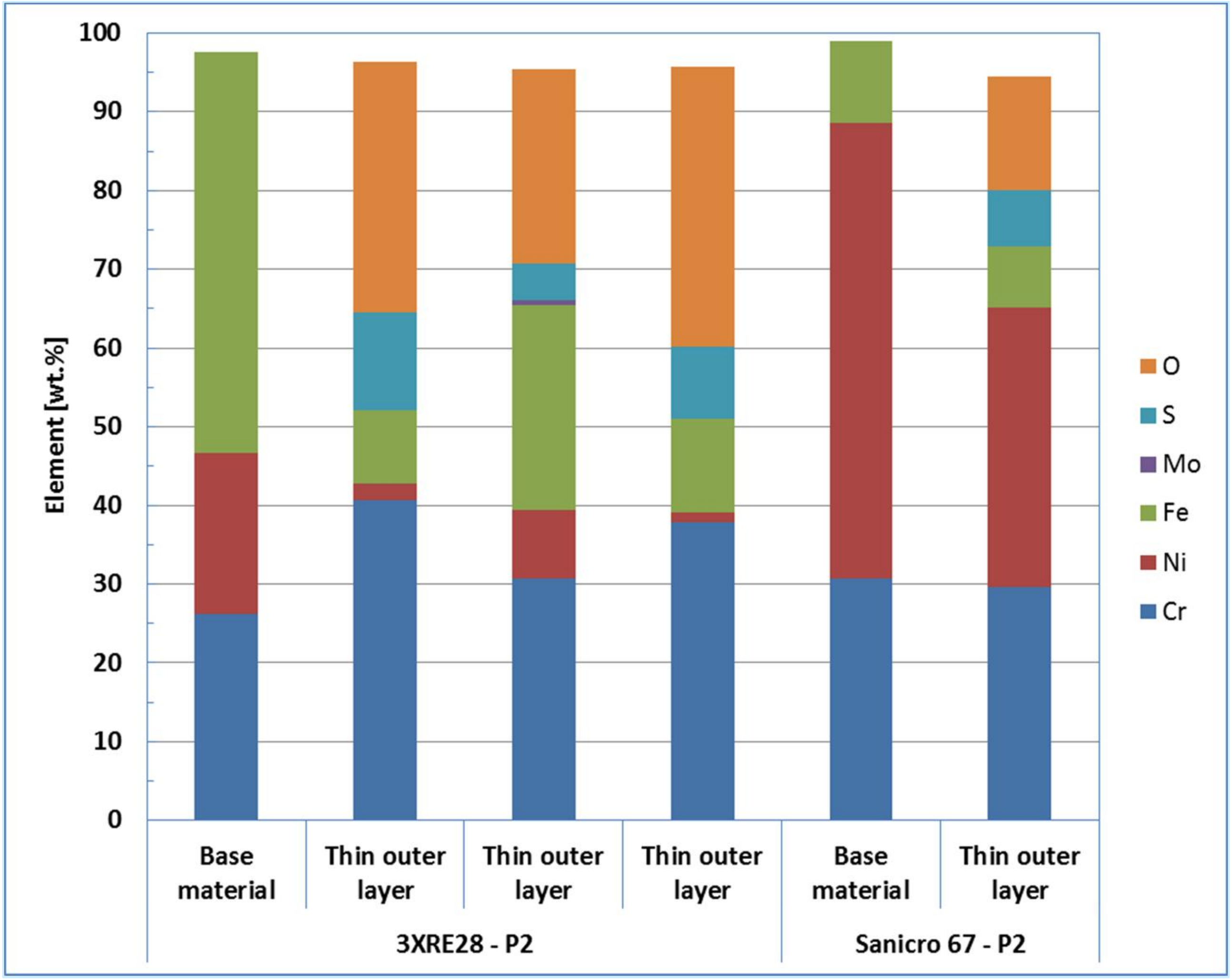


c) HR11N



d) Sanicro 67

Probe test No. 2 – EDS analysis

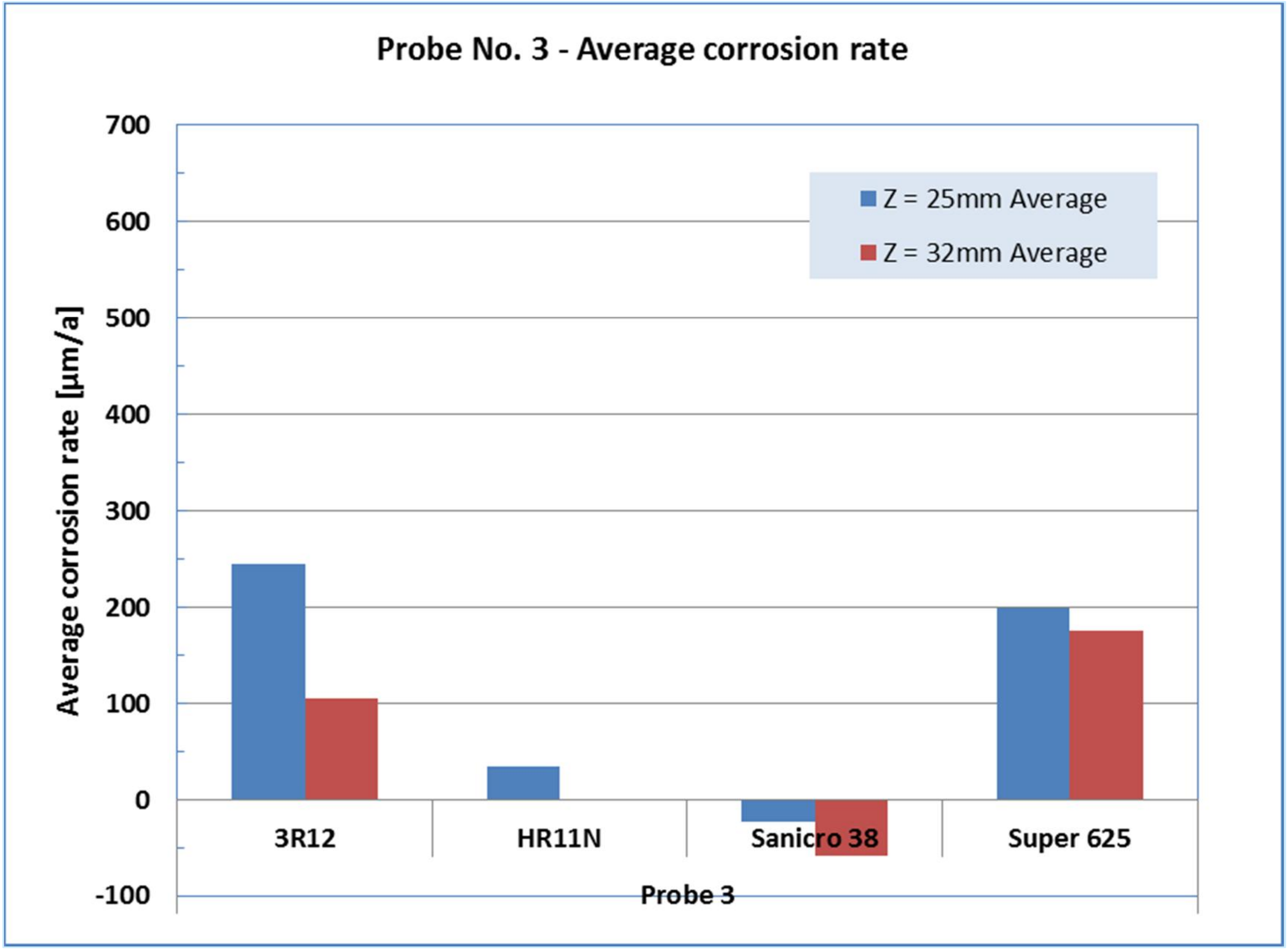


Results – Probe test No. 3

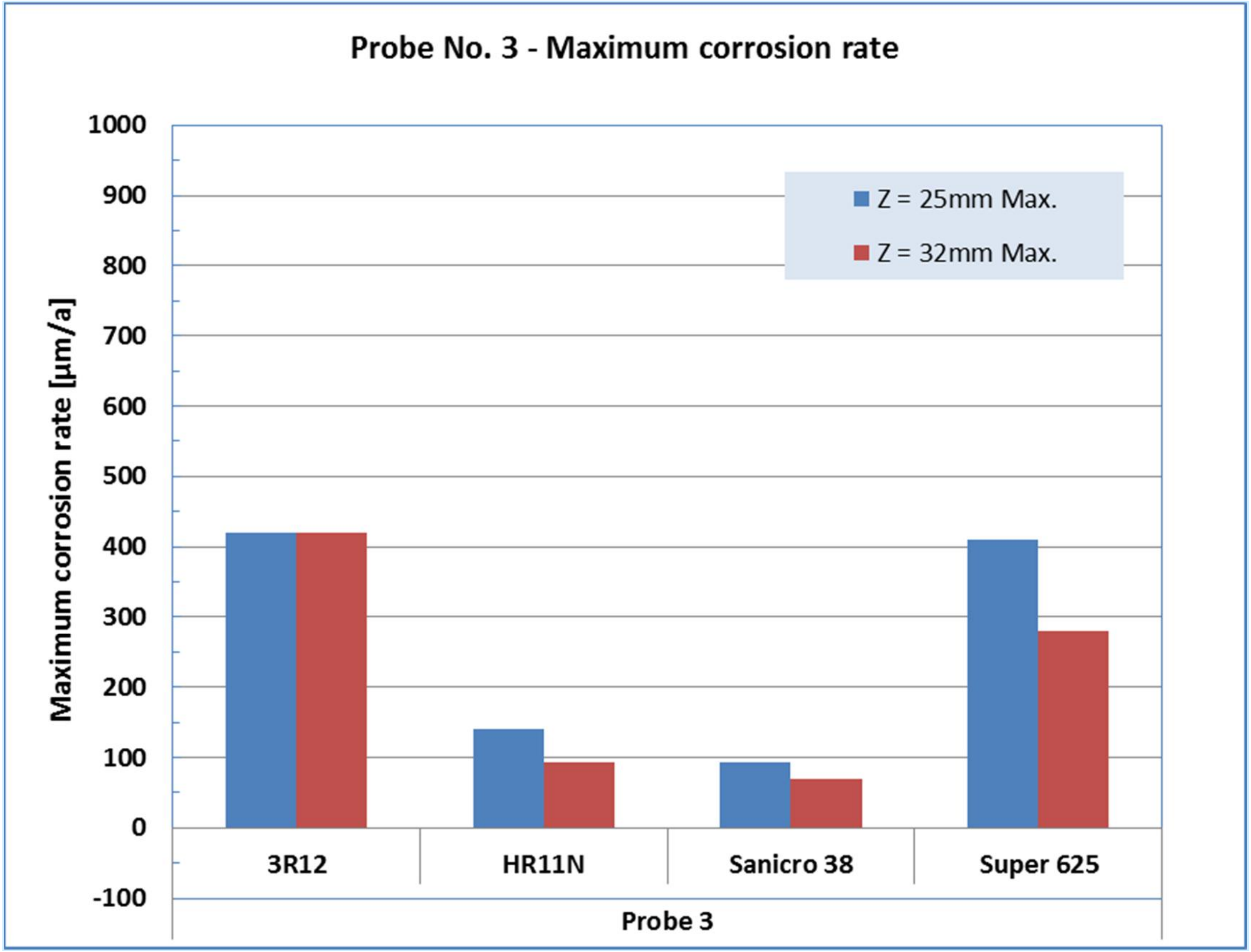
Probe No. 3 after the test

Probe No. 3 after the test

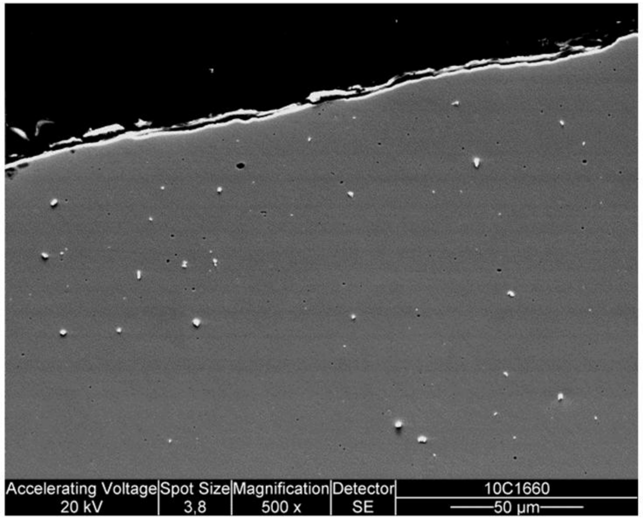
Probe test No. 3 – Average corrosion rates



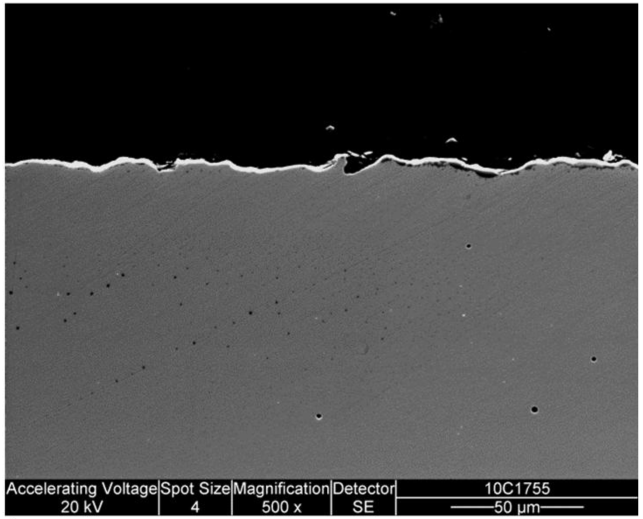
Probe test No. 3 – Maximum corrosion rates



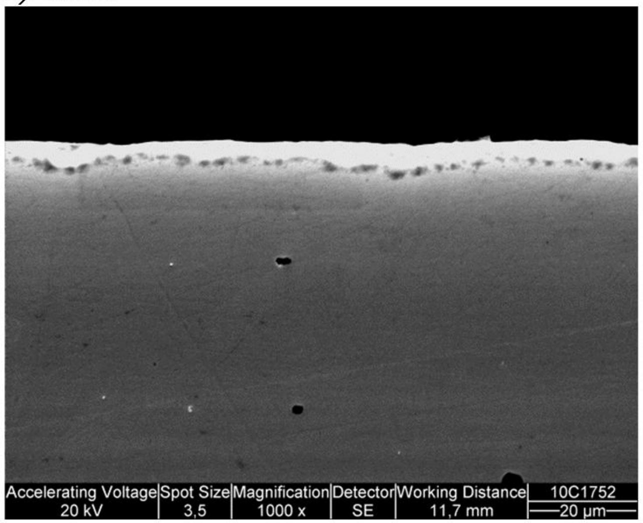
Probe test No. 3 – Metallography



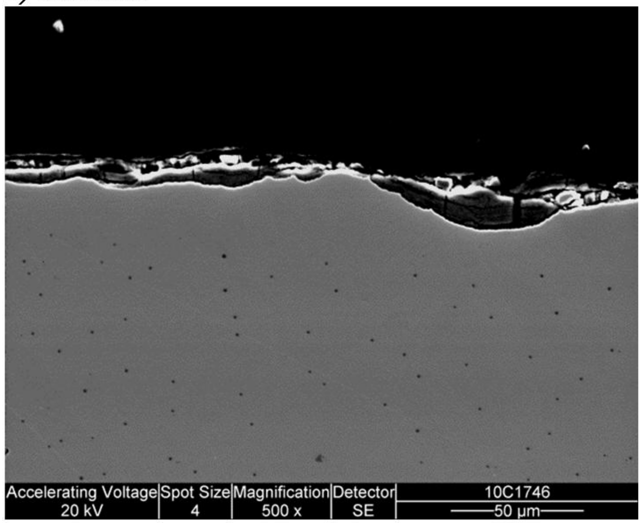
a) 3R12



b) HR11N

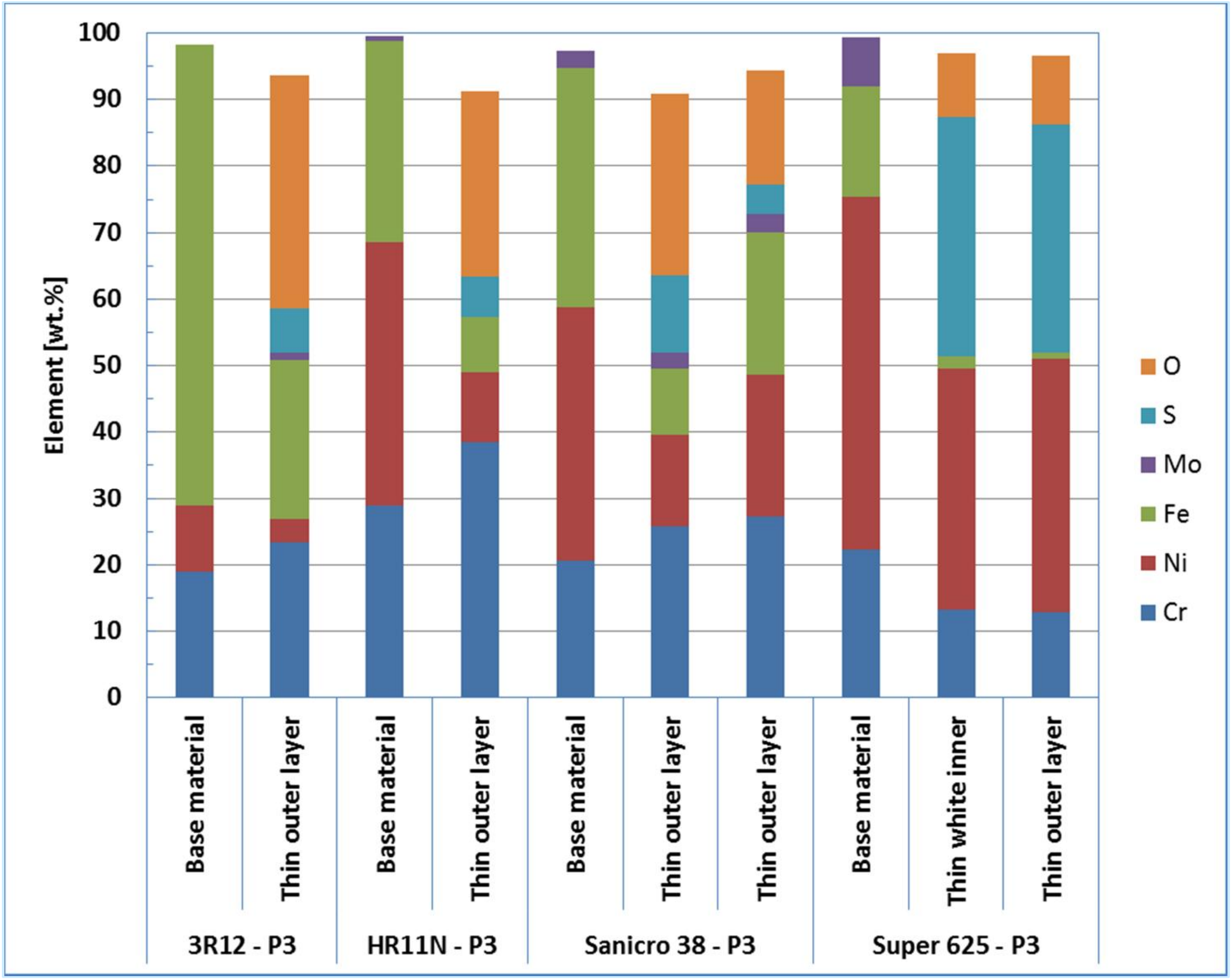


c) Sanicro 38



d) Super 625

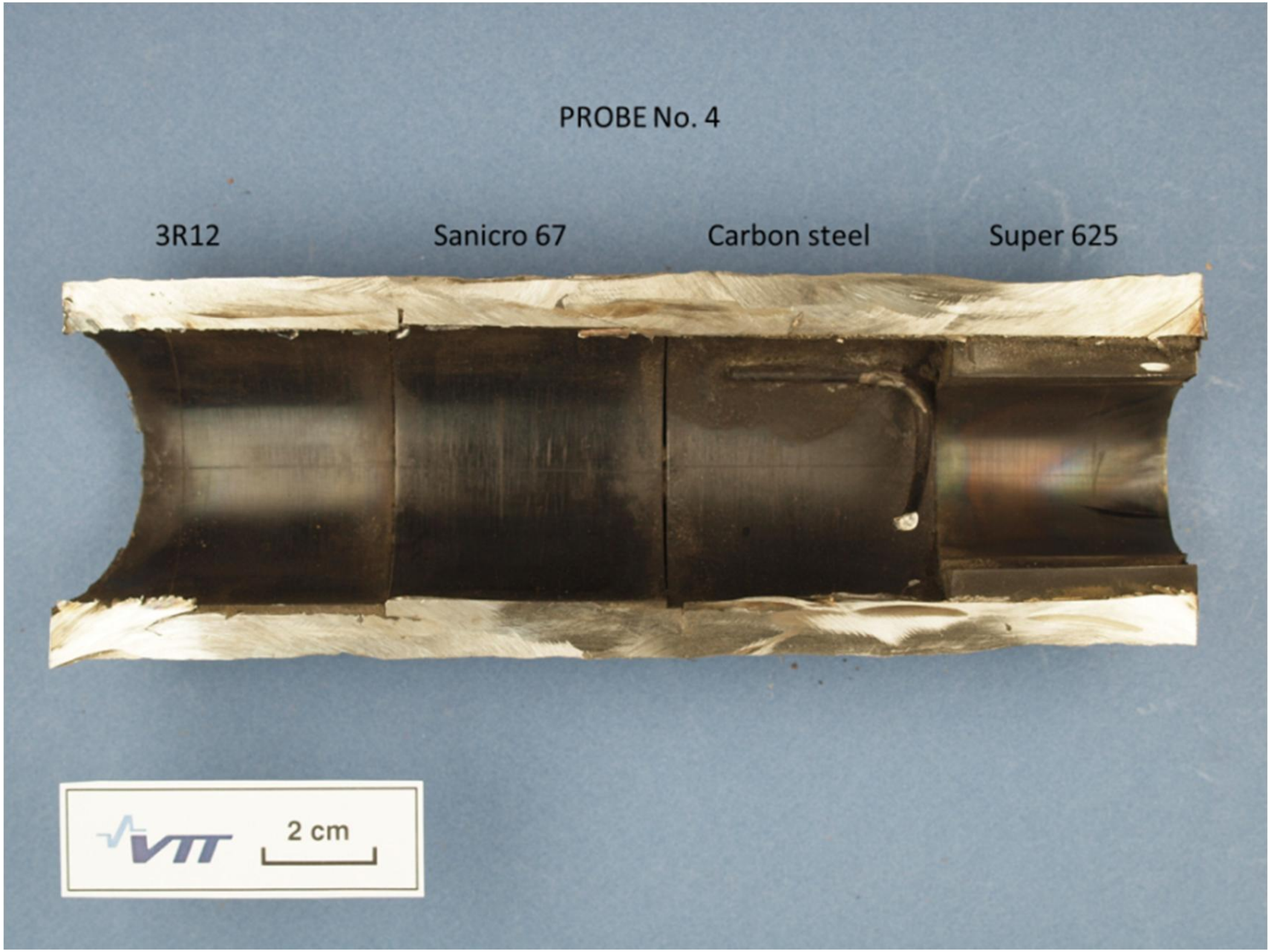
Probe test No. 3 – EDS analysis



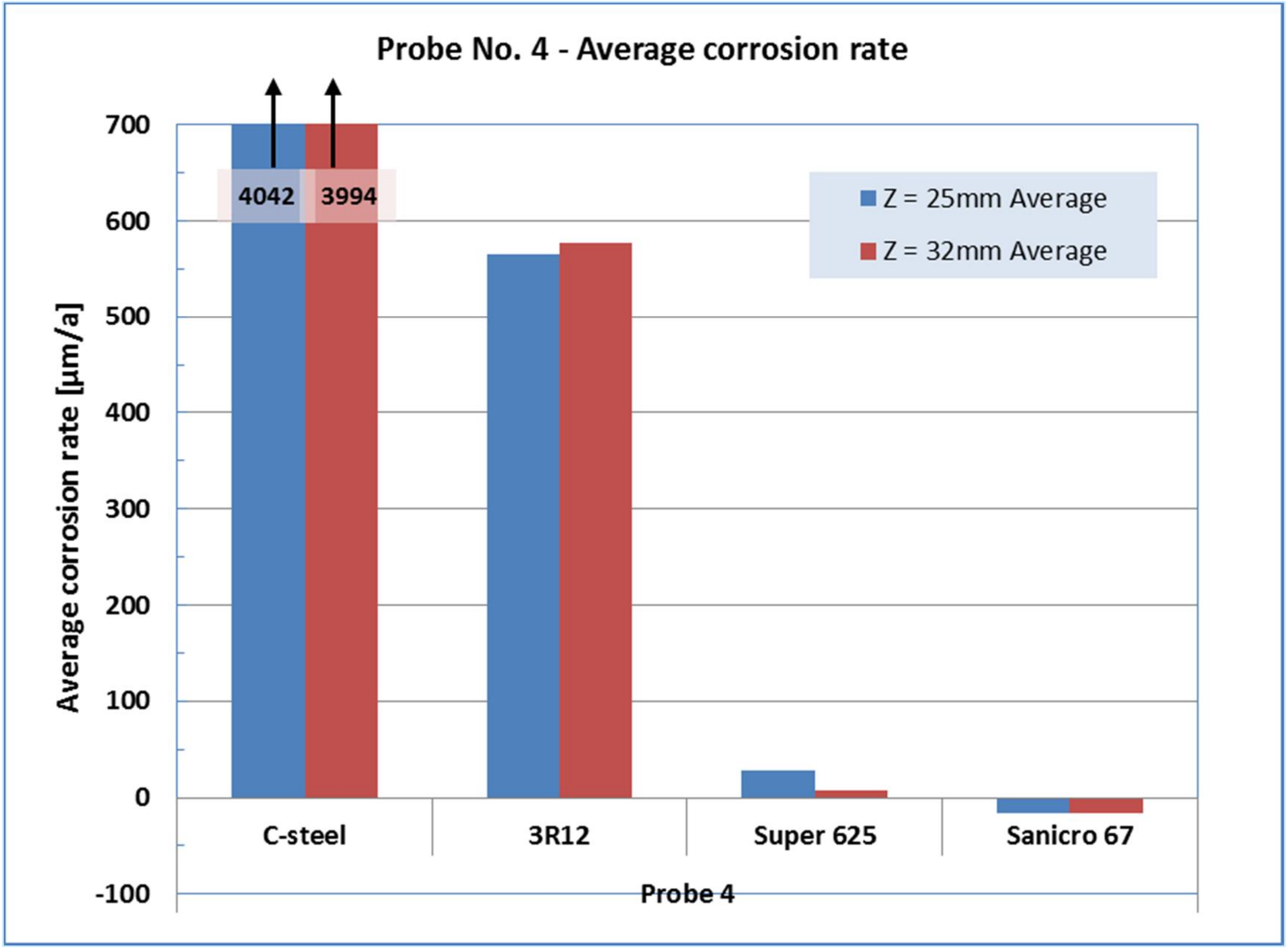
Results – Probe test No. 4

Probe No. 4 after the test

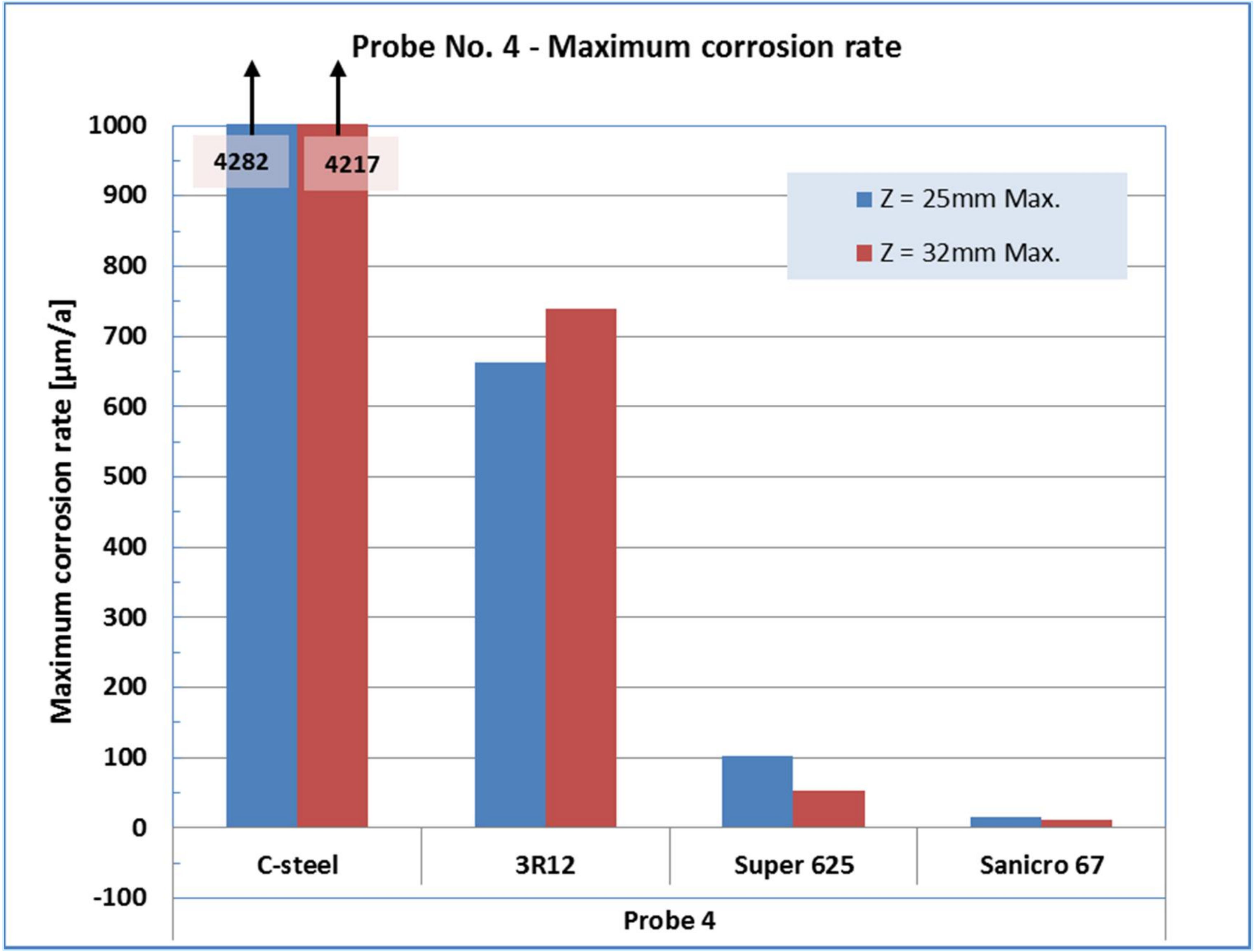
Probe No. 4 after the test



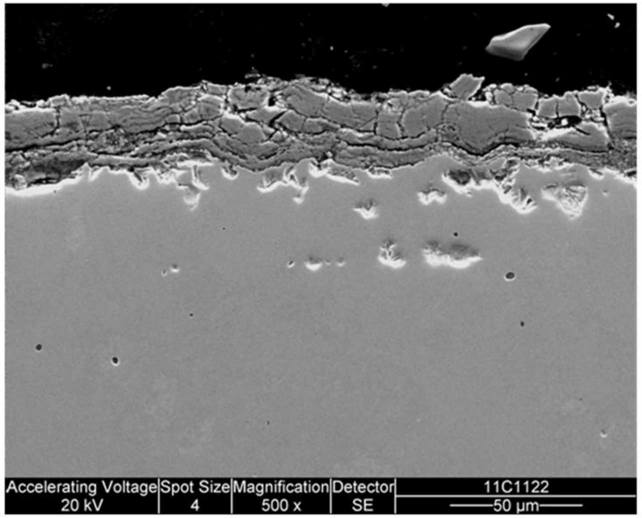
Probe test No. 4 – Average corrosion rates



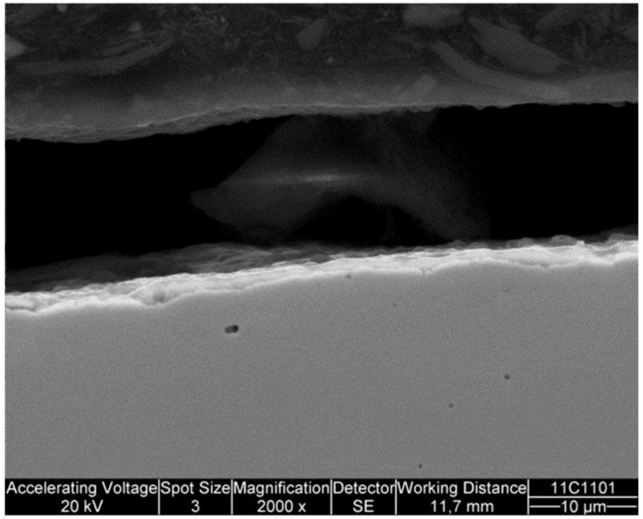
Probe test No. 4 – Maximum corrosion rates



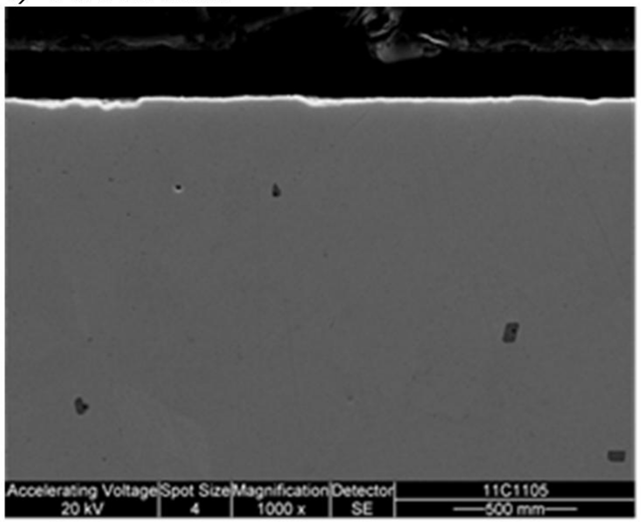
Probe test No. 4 – Metallography



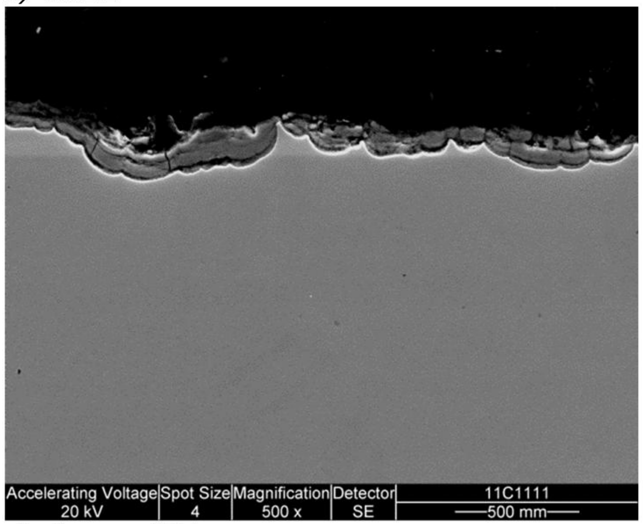
a) Carbon steel



b) 3R12

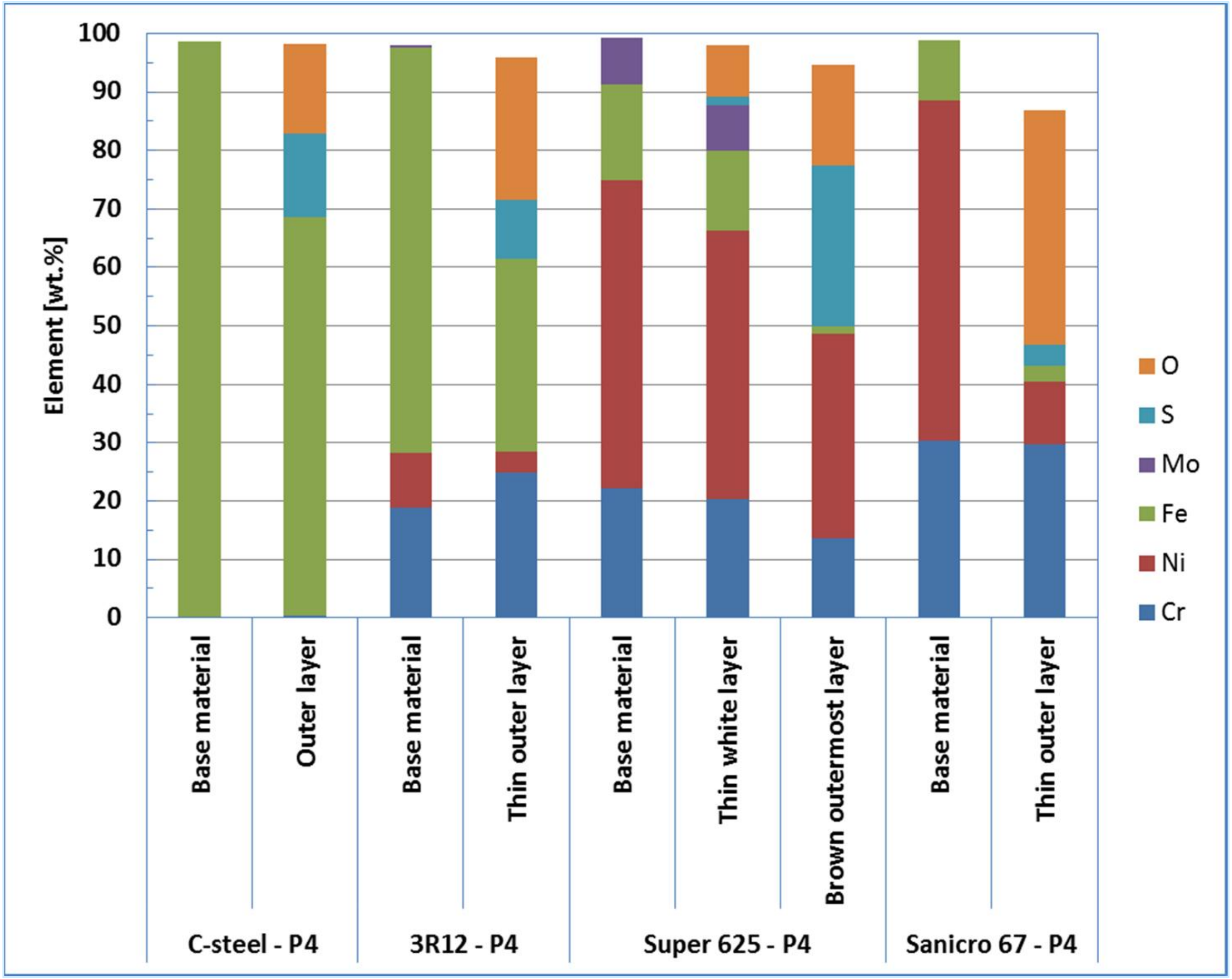


c) Sanicro 67



d) Super 625

Probe test No. 4 – EDS analysis

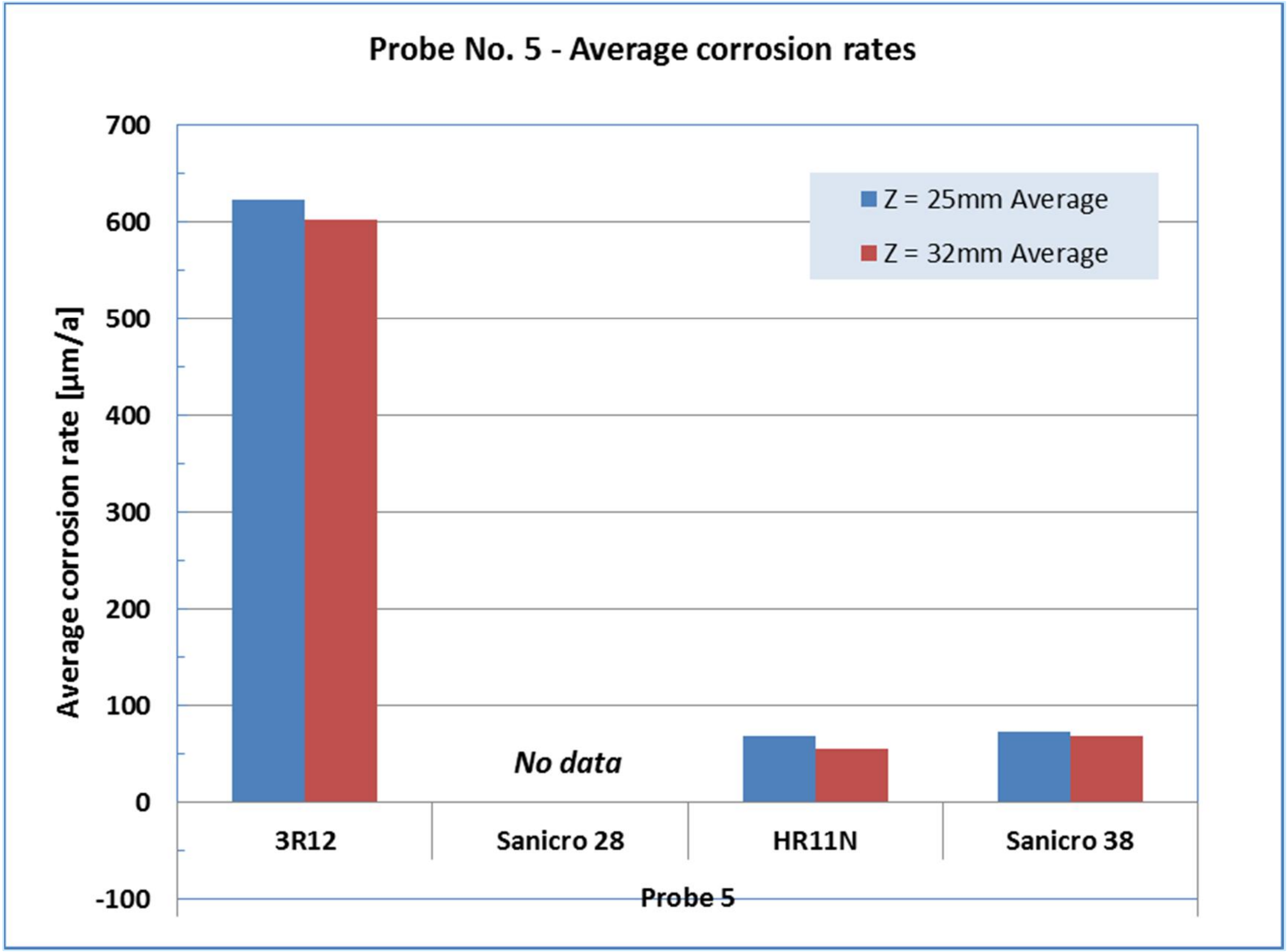


Results – Probe test No. 5

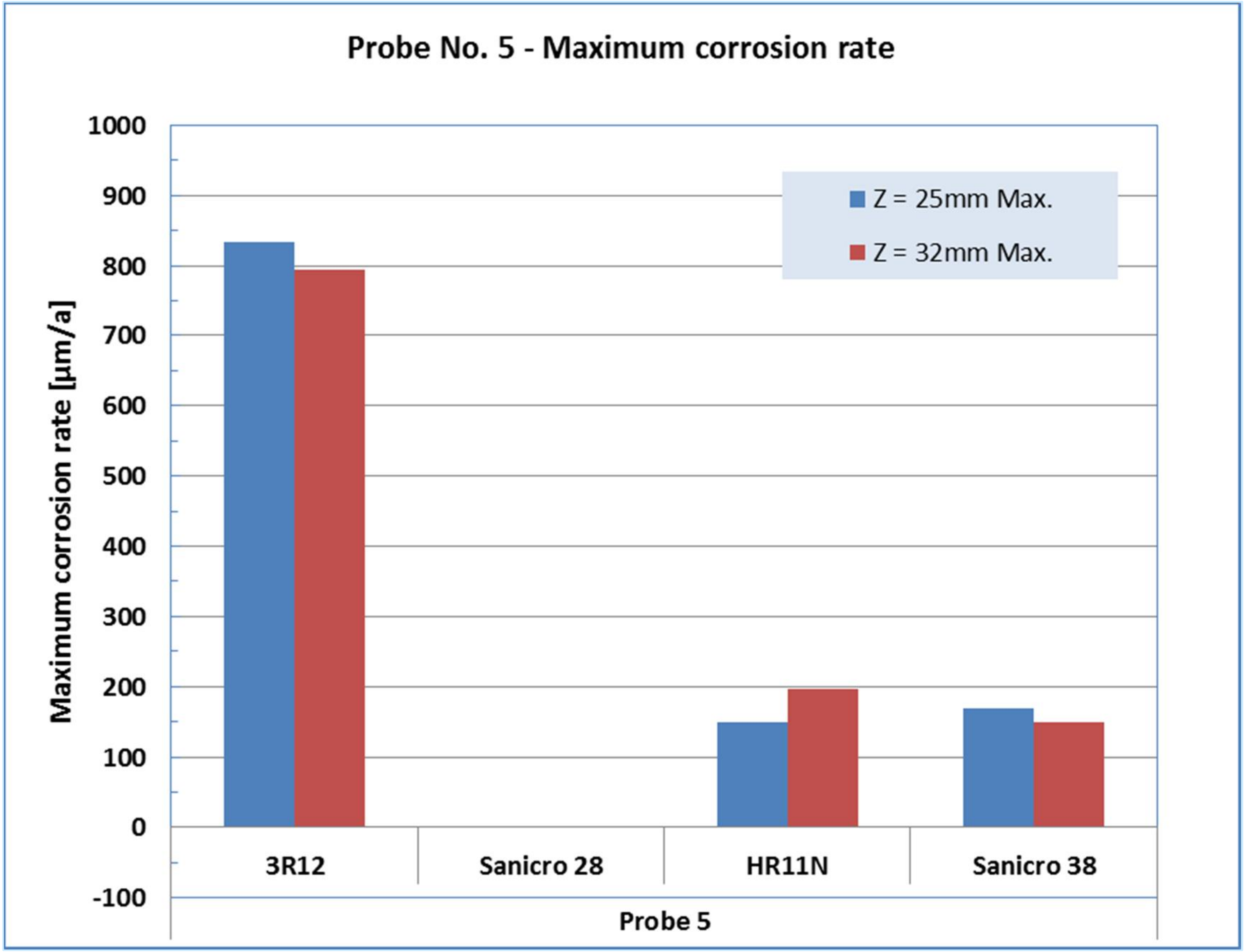
Probe No. 5 after the test

Probe No. 5 after the test

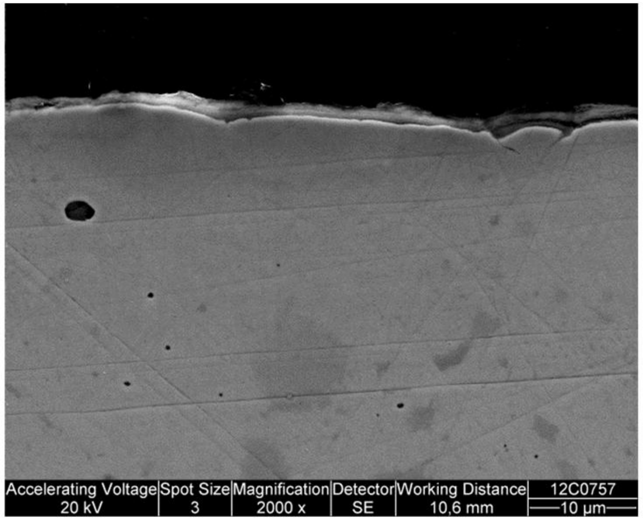
Probe test No. 5 – Average corrosion rates



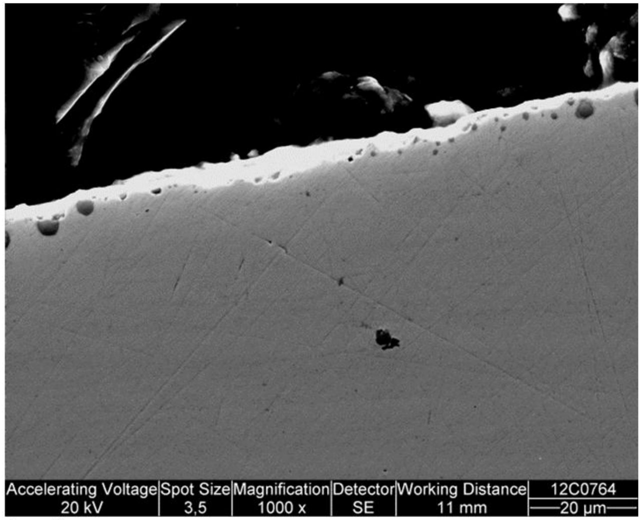
Probe test No. 5 – Maximum corrosion rates



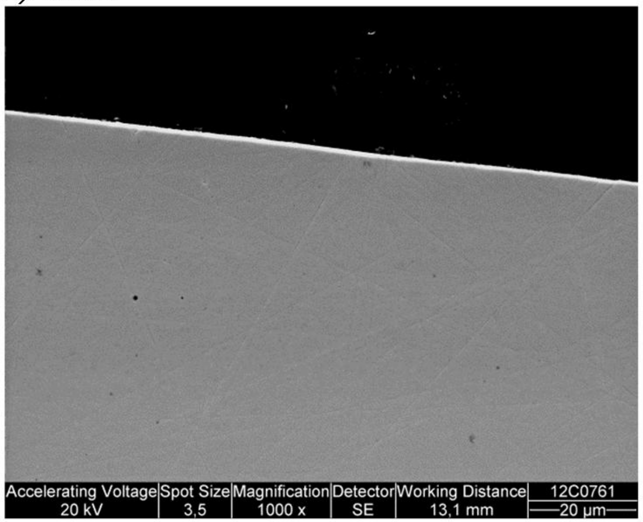
Probe test No. 5 – Metallography



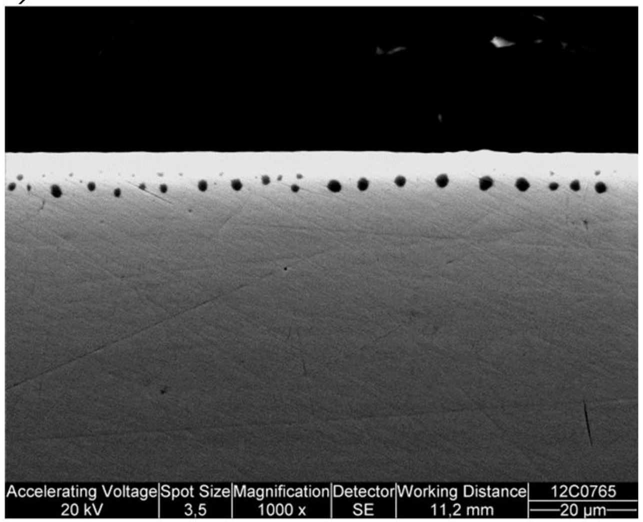
a) 3R12



b) Sanicro 28

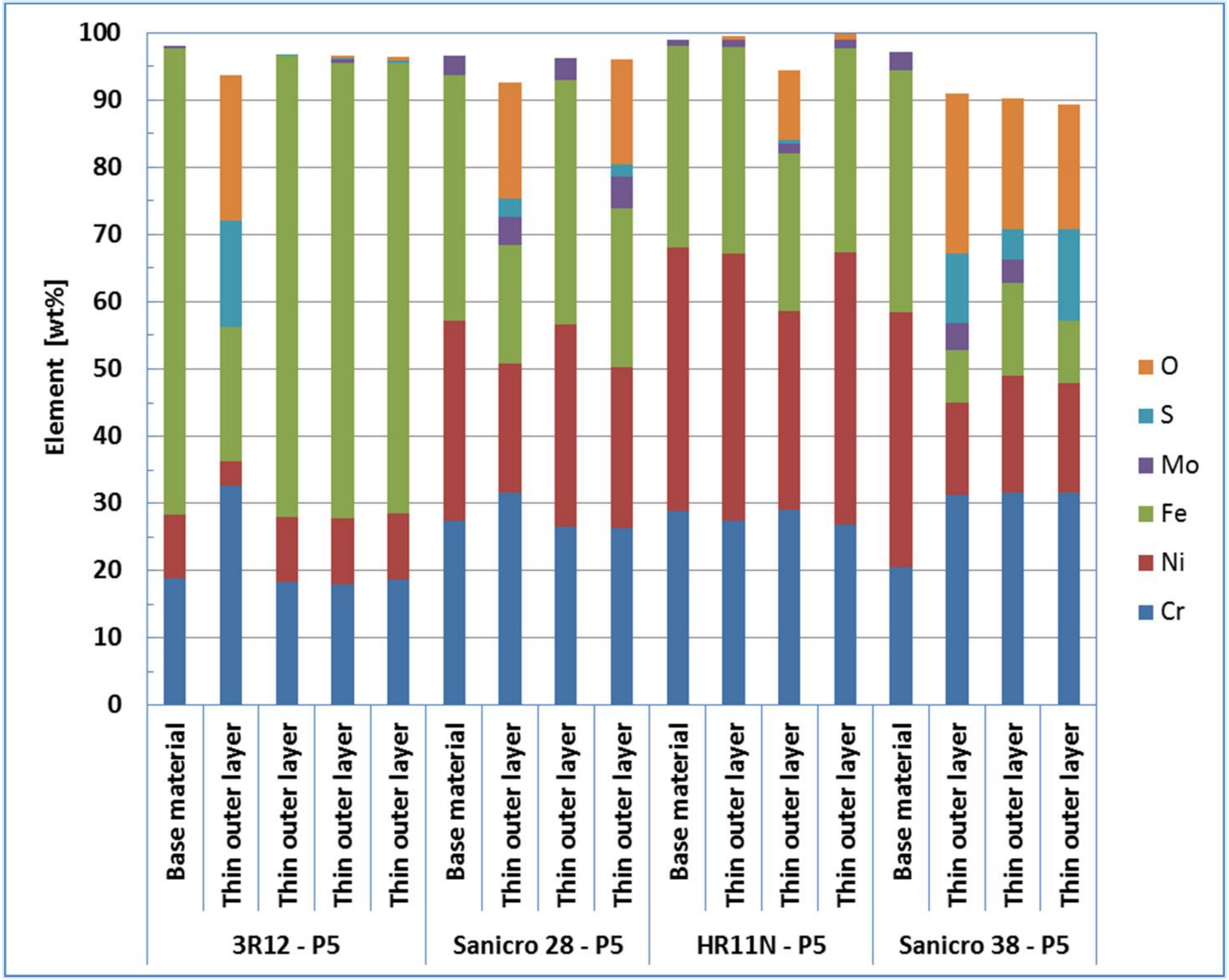


c) HR11N



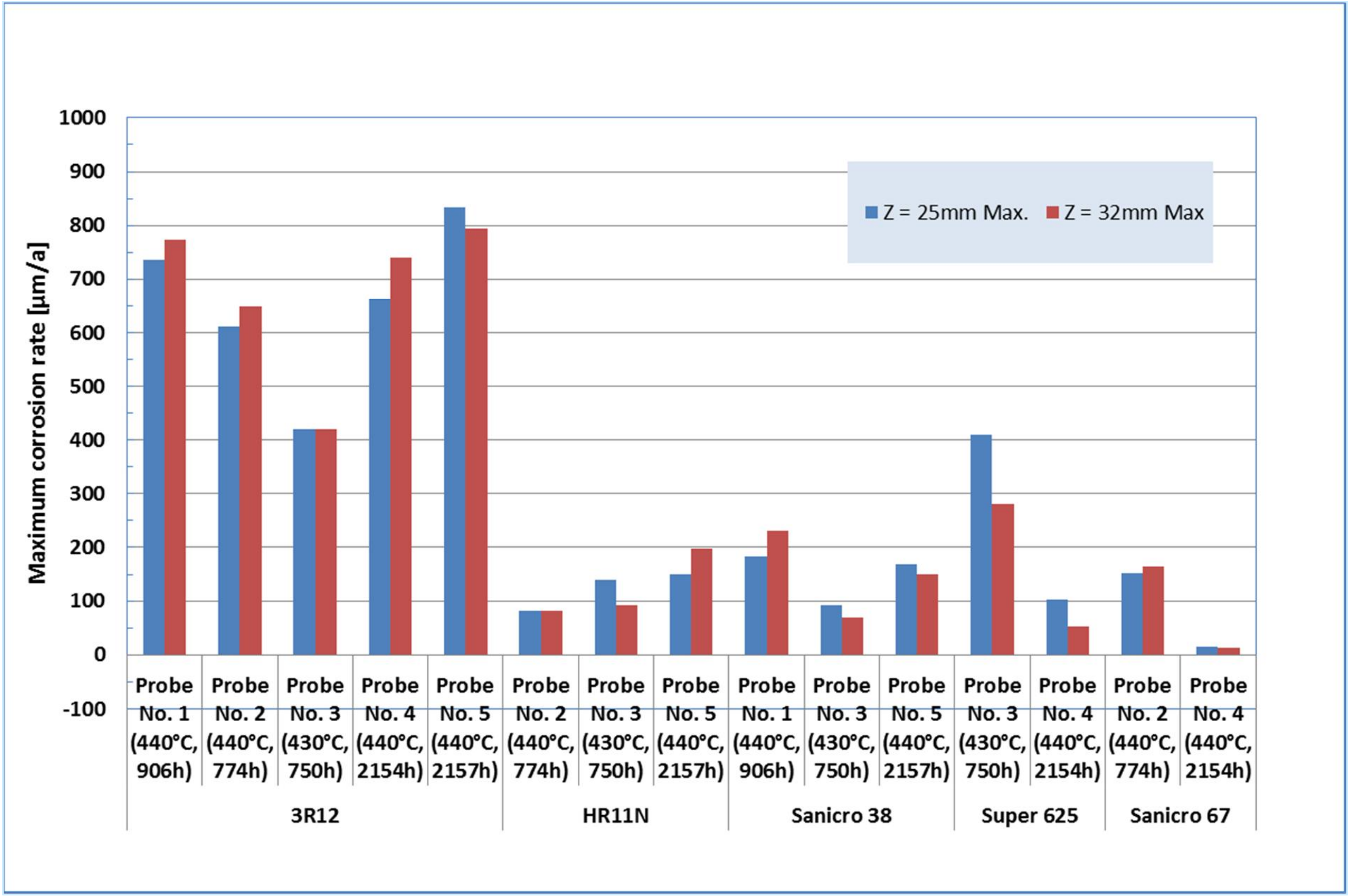
d) Sanicro 38

Probe test No. 5 – EDS analysis



Summary

Summary


Maximum corrosion rate [µm/a]
1000
900
800
700
600
500
400
300
200
100
0
-100
Z = 25mm Max.
Z = 32mm Max
Probe No. 1 (440°C, 906h)
Probe No. 2 (440°C, 774h)
Probe No. 3 (430°C, 750h)
Probe No. 4 (440°C, 2154h)
Probe No. 5 (440°C, 2157h)
Probe No. 2 (440°C, 774h)
Probe No. 3 (430°C, 750h)
Probe No. 5 (440°C, 2157h)
Probe No. 1 (440°C, 906h)
Probe No. 3 (430°C, 750h)
Probe No. 5 (440°C, 2157h)
Probe No. 3 (430°C, 750h)
Probe No. 4 (440°C, 2154h)
Probe No. 2 (440°C, 774h)
Probe No. 4 (440°C, 2154h)
3R12
HR11N
Sanicro 38
Super 625
Sanicro 67

Summary

Z = 25mm Max.
Z = 32mm Max
Maximum corrosion rate [µm/a]
500
400
300
200
100
0
-100
Probe No. 2 (440°C, 774h)
Probe No. 5 (440°C, 2157h)
Probe No. 1 (440°C, 906h)
Probe No. 5 (440°C, 2157h)
Probe No. 1 (440°C, 906h)
Probe No. 2 (440°C, 774h)
Probe No. 1 (440°C, 906h)
HR11N
Sanicro 38
3RE28
3XRE28
Sanicro 28

Summary

- Corrosion resistance in lower furnace conditions is improved by alloying, especially by chromium.
- According to the wall thickness measurements the test materials can be put in following order based on increased resistance:

  C-steel << 3R12 < HR11N ~ Sanicro 38 (~ Sanicro 28 ~ 3RE28/3XRE28) < Super 625 < Sanicro 67

- Carbon steel corroded at extremely high rate (>4 mm/a) at the temperature of 440 °C.
- 3R12 (AISI 304L) corrodes in such high rate (>0.6 mm/a) at 440 °C that it can’t be safely used in the lower furnace in the future high pressure recovery boilers,

Summary

- Performance of the Sanicro 38 and HR11N was satisfactory in long term test at 440 °C (CR_{max} ~ 0.1...0.2 mm/a), but it is recommended to verify their performance also at lower temperature (400 °C).
- The new material group which looks promising is the high chromium alloys 3RE28/3XRE28 and Sanicro 28, but their long term performance should be verified in the future.
- If the corrosion resistance is the determining factor, the Sanicro 67 seems to be a good material for future boilers, since its corrosion rate was lowest from the studied alloys.
- Based on the long term test the Super 625 is the second best choice for the future high pressure boiler, but because of its relatively high corrosion rate in short term test more and longer tests are needed to verify its performance.

Summary

- In current samples the biggest problem was the specimen alignment i.e. it was impossible to measure the thickness profiles exactly from the same location before and after the test.
  - Some error to the measurement results; especially to the maximum corrosion rates
  - Most significant when samples had surface scratches and dents.
- Another factor that affected to the accuracy was the surface deposits that were not completely removed during washing.
- Tests showed that polishing together with longer exposure time improves the accuracy, both of which are recommended to be used in future tests and especially when evaluating highly alloyed materials.

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