RESEARCH REPORT | Nr VTT-R-07360 | 30 October 2006

The Recovery Boiler in the Future II – Material Sulphidation Tests, Analysis of Probe Samples

Authors Sanni Yli-Olli, Pekka Pohjanne, Tuomo Kinnunen

Confidential Confidential

Title

The Recovery Boiler in the Future II – Material Sulphidation Tests, Analysis of Probe Samples

Client name, contact person and contact information Finnish Recovery Boiler Committee Esa Vakkilainen c/o Jaakko Pöyry Oy PB 4, 01621 Vantaa	Client reference 16A0913/S60
Project name SOTU sulfidi	Project no./short name 9597
Author(s)of the report) Sanni Yli-Olli, Pekka Pohjanne, Tuomo Kinnunen	Number of pages/appendices 15/
Key words Sulphidation, recovery boiler probe	Report number VTT-R-07360-06

Abstract

The objective of this subproject was to analyse recovery boiler probe samples from two tests and compare the results with the laboratory tests performed in the previous subproject [1]. The management group of the Recovery Boiler in the Future project decided to use Sanicro 41 (UNS N08825mod), 3R12 (AISI 304L), Sanicro 63 and Sanicro 36 Mo (UNS N08036-2) as test materials. Boildec Oy (Timo Karjunen) performed the probe measurements. This report shows the results of Probe Test 3 (~ 400°C/1006 h) and 4 (~ 440°C/488 h).

In Probe Test 3, materials Sanicro 63, Sanicro 38 and Sanicro 36 Mo cracked near the hole drilled for the thermo sensor. In material Sanicro 63 serious cracking was observed also after the shorter test.

Thickness measurements did not produce the desired information on corrosion resistance. The thickness measurement results of Test 3 could not be utilised because of intermediate grounding. Unfortunately, very little can be concluded based on the thickness measurement results of Test 4, since the major part of the changes in thickness consisted of salt deposit.

The deposits in Test 3 and 4 consisted primarily of potassium, sodium and sulphur compounds. In many deposits, especially after the longer test (Test 3), the layer closest to the metal surface contained chromium, nickel and iron.

These deposits could not be compared directly with the results of the previous laboratory tests, but similarities in corrosion progress were observed in many samples.

Based on the probe tests, the materials could be listed in the following order of superiority as to corrosion resistance, from left to right:

Sanicro 63 > Sanicro 41 (38) > Sanicro 36Mo > 3R12 (304L).

The order is largely influenced by the extent of cracking and the interreaction between the surface deposit formed and the metal as concluded based on the composition of the deposit. The results are consistent with the previously obtained laboratory test results, the differences in results depending primarily on the cracking of materials occurred in the probe tests.

Based on the tests and analyses, we recommend that further tests be carried out of the influence of molten salt on corrosion and cracking. The tests could be made under salt deposits and with controlled gas atmosphere. In addition, additional tests are recommended to clarify the influence of gas vapour content, exposure time and carbon monoxide on sulphidation.

Confidentiality	Confidential

Espoo, 30 October 2006

Liisa Heikinheimo Research Manager	Sanni Yli-Olli Researcher	Satu Tuurna Researcher

VTT contact information

PB 1000, 02044 VTT (postal address Kemistintie 3)

Distribution (clients and VTT)

Finnish Recovery Boiler Committee, Esa Vakkilainen 3, VTT 3

Preface

This report is a part of the project The Recovery Boiler in the Future II of the Finnish Funding Agency for Technology and Innovation (Tekes), commissioned by the Finnish Recovery Boiler Committee (Suomen Soodakattilayhdistys ry).

Espoo, 30 October, 2006

The authors

Table of contents

1 Introduction

The objective of this subproject was to analyse recovery boiler probe samples from two tests and compare the results with the laboratory tests performed in the previous subproject [1].

2 Methods

The project management group of the Finnish Recovery Boiler Committee selected Sanicro 41 (UNS N08825mod), 3R12 (AISI 304L), Sanicro 63 and Sanicro 36 Mo (UNS N08036-2) as sample materials to be tested. Boildec Oy (Timo Karjunen) carried out the probe measurements, the objective of the first test being to reach a surface temperature of the samples of 400°C (Test 3) for 1000 hours and of the second test a temperature of 440°C (Test 4) [2].

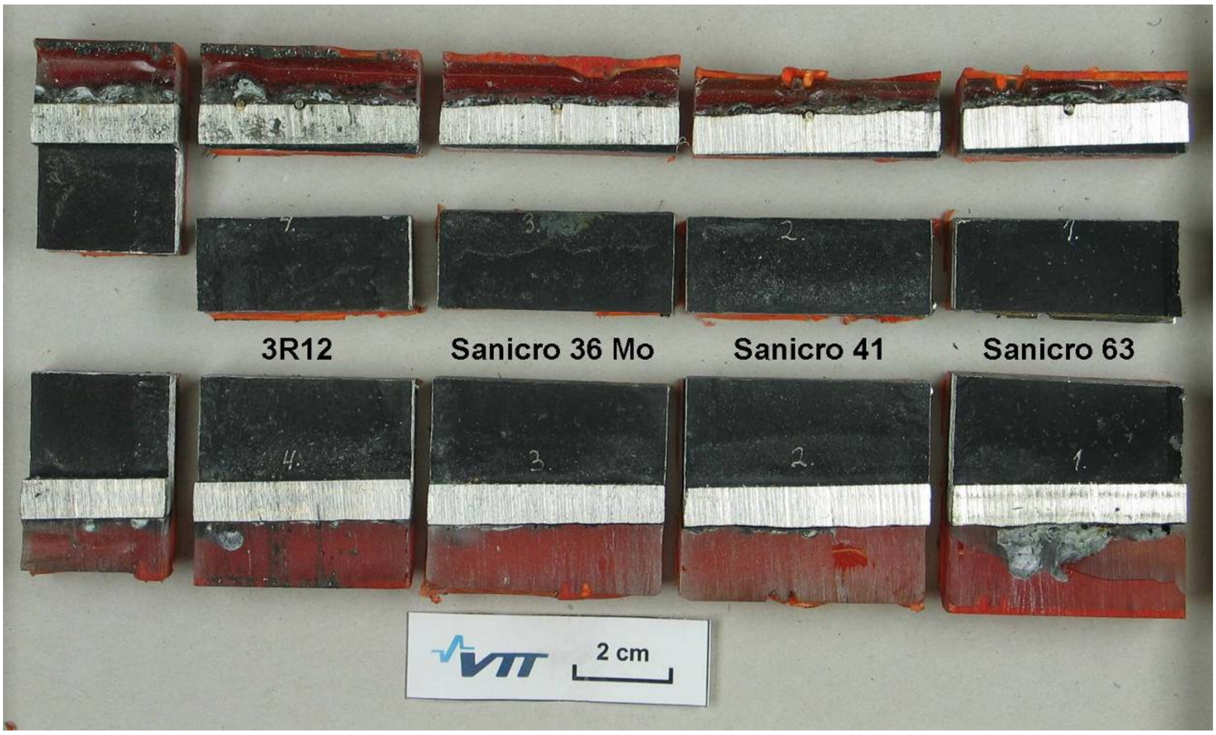
Table 1 presents the mean temperatures reached in the probe tests of each test material.

The total duration of Test 3 was 1006h. However, the problems present at the start of the test led to the samples being exposed to unplanned conditions immediately at the beginning of the test. In order to normalise the situation, the probe was taken out of the boiler and the surfaces of the samples were lightly ground, after which the probe was put back into the boiler (duration of this step?). As a result of Test 4 being interrupted by a technical fault, the duration of the test was only 484 h.

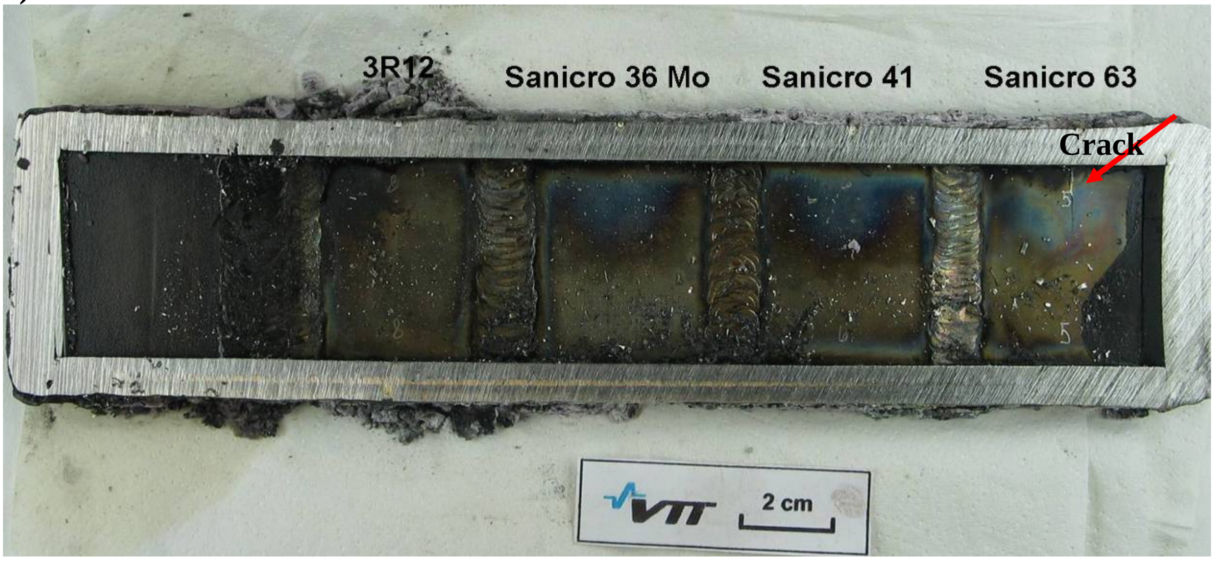
Table 1. Results of the probe tests carried out by Boildec.

	Test 3 T (°C)	Test 4 T (°C)
Sanicro 63	401	432
Sanicro 41	397	444
Sanicro36 Mo	405	437
3R12	391	431

When the probe reached VTT after Test 3, the thin salt deposit on the surface of the samples was protected from vibration caused by sawing by casting the samples in epoxy. Thereafter the probe was taken to Protoshop to separate the samples. After returning to VTT, the samples were cut (Figure 1a) and analysed with an optic and a scanning electron microscope as well as with an energy-dispersive X-ray spectroscopy (EDS) connected to the latter. Casting in epoxy did not produce the expected result, but the brittle salt deposit was separated from the metal remaining adherent to the epoxy. The epoxy also disturbed the analysis of the surface layer. For these reasons the probe samples of Test 4 were no longer cast in epoxy for protection. The samples of Test 4 were separated at VTT. They were also cut into pieces and analysed at VTT as in the previous test (Figure 1b).



a)



b)

Figure 1. Separated probe samples a) after Test 3 cast in epoxy, and b) after Test 4.

The corrosion resistance of the samples was estimated also with thickness measurements. For this purpose sample thicknesses were measured before and after the tests (Table 2). Table 2 also shows the thickness measurement results of Test 3, although they could not be used in the corrosion resistance assessment, since the samples had to be intermediately ground due to the problems occurred at the start-up of the probe test.

Table 2. Probe sample thicknesses

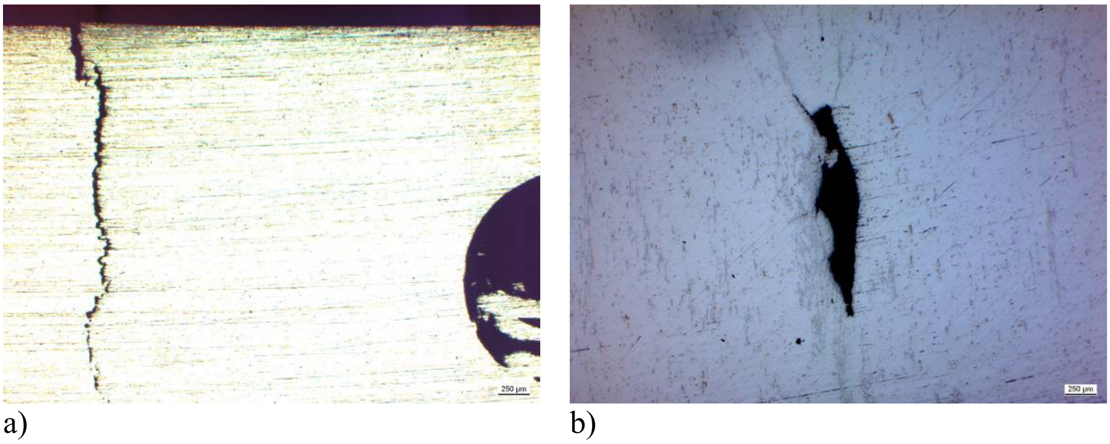
Test 3[A)]	**Before ka (mm)**	**After ka(mm)**	**Difference (mm)**
Sanicro 63	6,95	6,92	-0,02
Sanicro 41	7,57	7,47	-0,10
Sanicro 36 Mo	7,82	7,85	0,02
3R12	7,88	7,94	0,06
Test 4			
Sanicro 63	5,31	5,44	0,13
Sanicro 41	6,69	6,81	0,13
Sanicro 36 Mo	6,40	6,46	0,06
3R12	7,85	7,97	0,13

[A)] Since the samples had been intermediately ground, the results do not give an indication of corrosion resistance.

3 Results and discussion

3.1 Sanicro 63

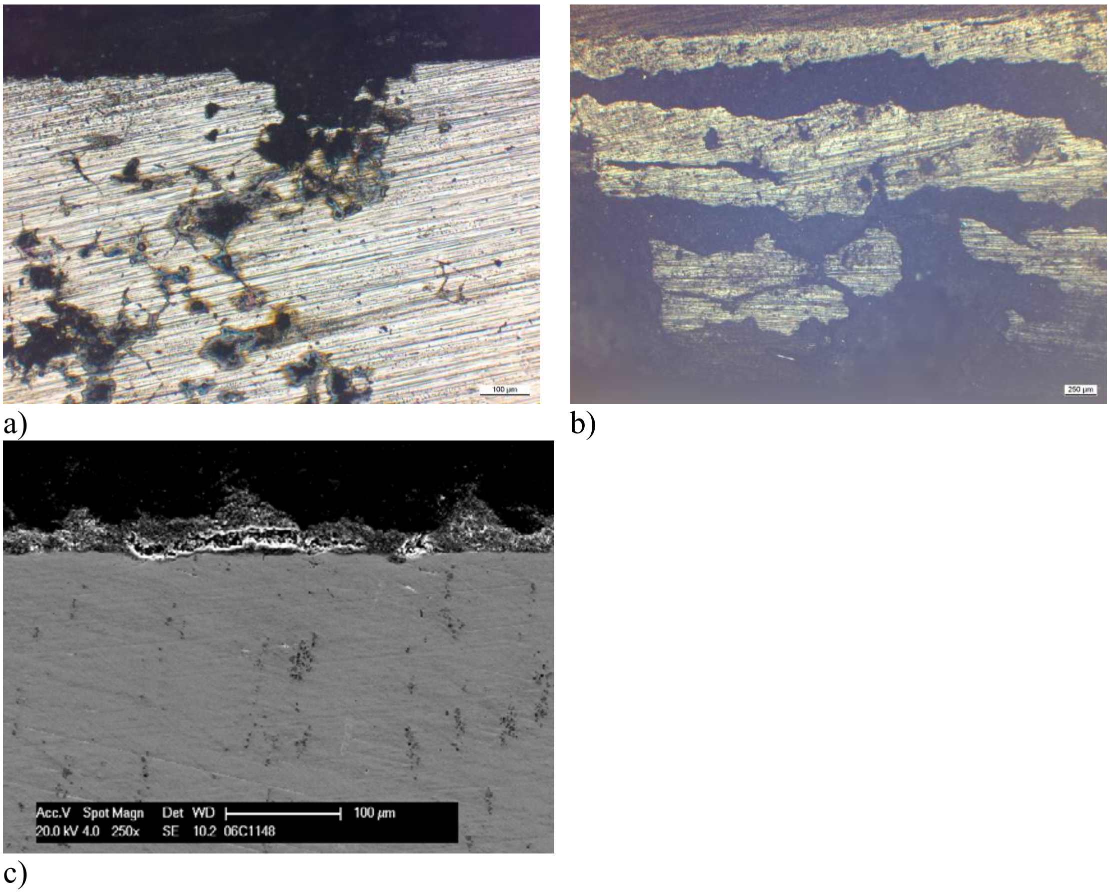
Sanicro 63 had cracked around the drill hole in both tests (Figure 2 a and b). In Test 4 the material had cracked visibly, as seen in Figure 1b). The crack continued deep inside the sample (Figure 2b).



a) b)

Figure 2. Cracking of the Sanicro 63 sample a) Test 3 and b) Test 4.

In addition, in Test 3 surface corrosion was observed (Figure 3a) and at the sample surface there was a thick and brittle salt deposit (Figure 3b). The deposit consisted primarily of salt accumulated on the surface of the sample, but the layer closest to the surface also had a high content of chromium, as well as traces of nickel and iron (Figure 4). Based on this, the conclusion can be drawn that the salt deposit formed during Test 3 had started to corrode the surface, in places even severely.



a) b)

c)

Figure 3. Salt deposit and corrosion at the surface of the Sanicro 63 samples a) and b) after Test 3 and c)after Test 4.

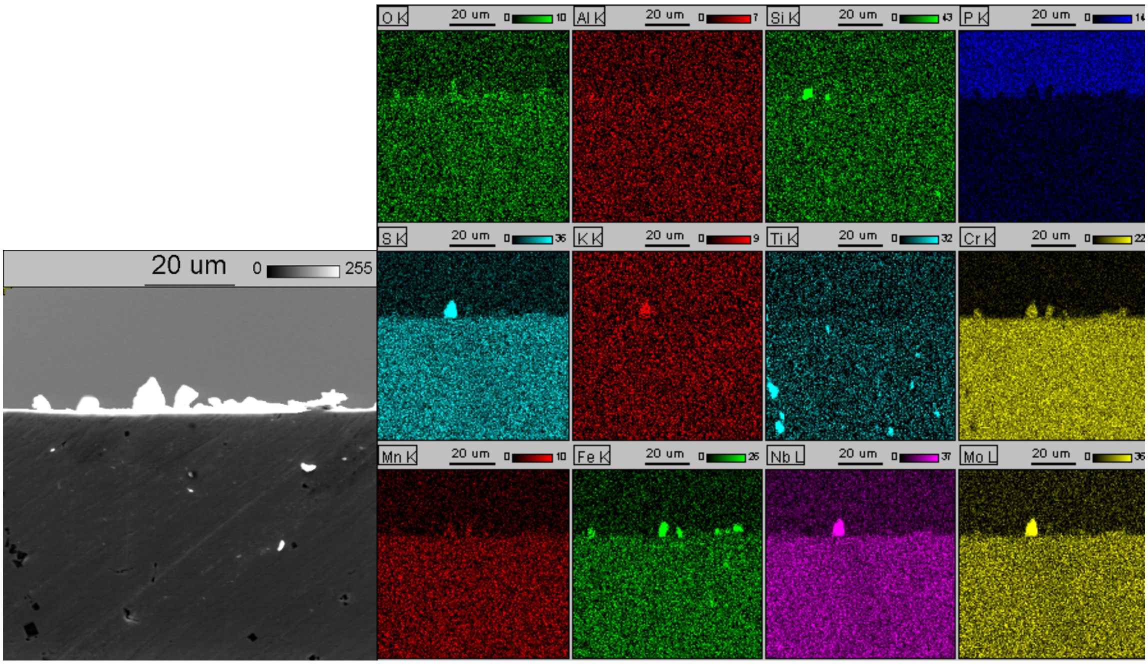


Figure 4. Element map of the surface of the Sanicro 63 sample after Test 3.

In Test 4, equally severe surface corrosion was not observed; however, there were signs of corrosion as well as a clear deposit (Figure 3 c). As in the previous test, this deposit was formed mainly by salt (K, Na, S), although the innermost layer also contained small amounts of metals (Ni, Cr, Fe) (Figure 5).

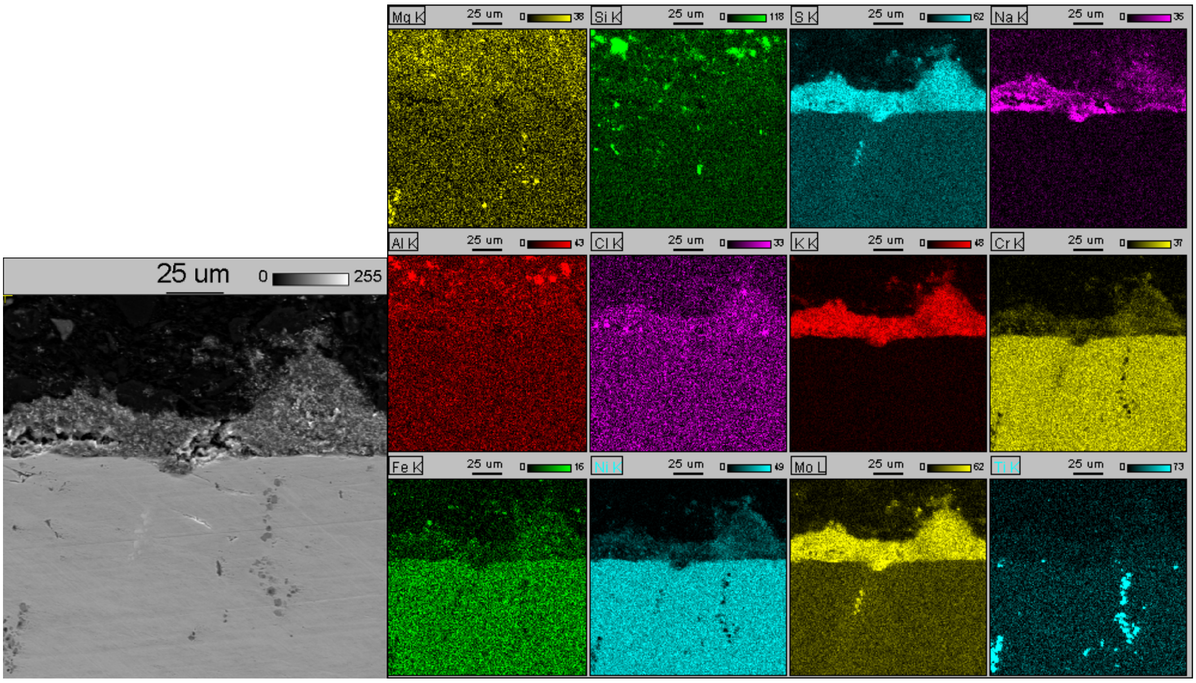


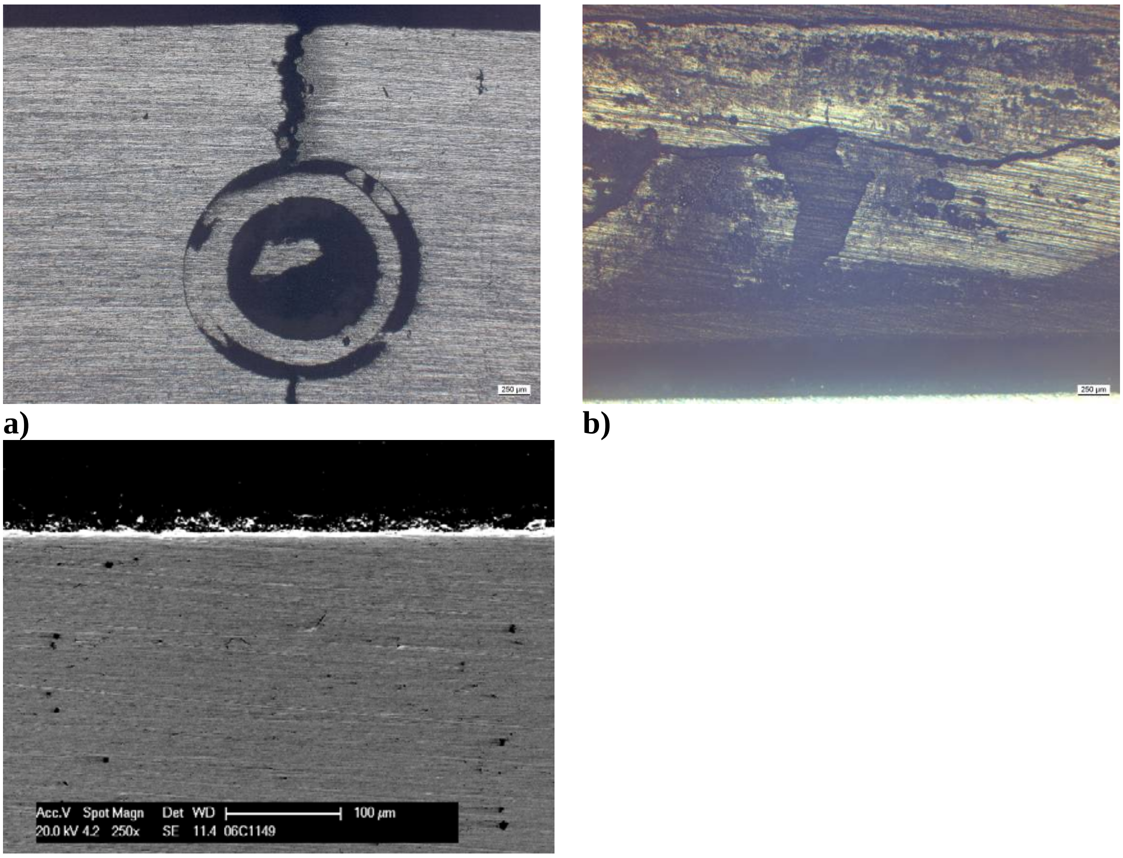
Figure 5. Element map of the surface of the Sanicro 63 sample after Test 4.

Since material Sanicro 63 was not tested in the previous laboratory tests [1], there is no direct comparative information available. In composition the material is close to Sanicro 65, which has been used in laboratory tests, revealing similar behaviour. In both cases, corrosion starts at the surface, continuing to spread irregularly in the thickness direction of the material.

Admittedly, the corroded products cannot be compared with each other, since the laboratory tests were made only with gas atmosphere, i.e., not under salt deposits.

3.2 Sanicro 41

In Test 3, Sanicro 41 had cracked at the upper part of the drill hole? (Figure 6a). The sample was covered with a thick layer of brittle salt after Test 3 (Figure 6b). The deposit closest to the metal surface also consisted primarily of salt (S, Na, K), containing, however, also small amounts of nickel, iron and chromium (Figure 7). Some irregularity was also observed in the surface, which is an indication of early surface corrosion.



a)

b)

c)

Figure 6. Sample of Sanicro 41 a) and b) after Test 3 and c) after Test 4

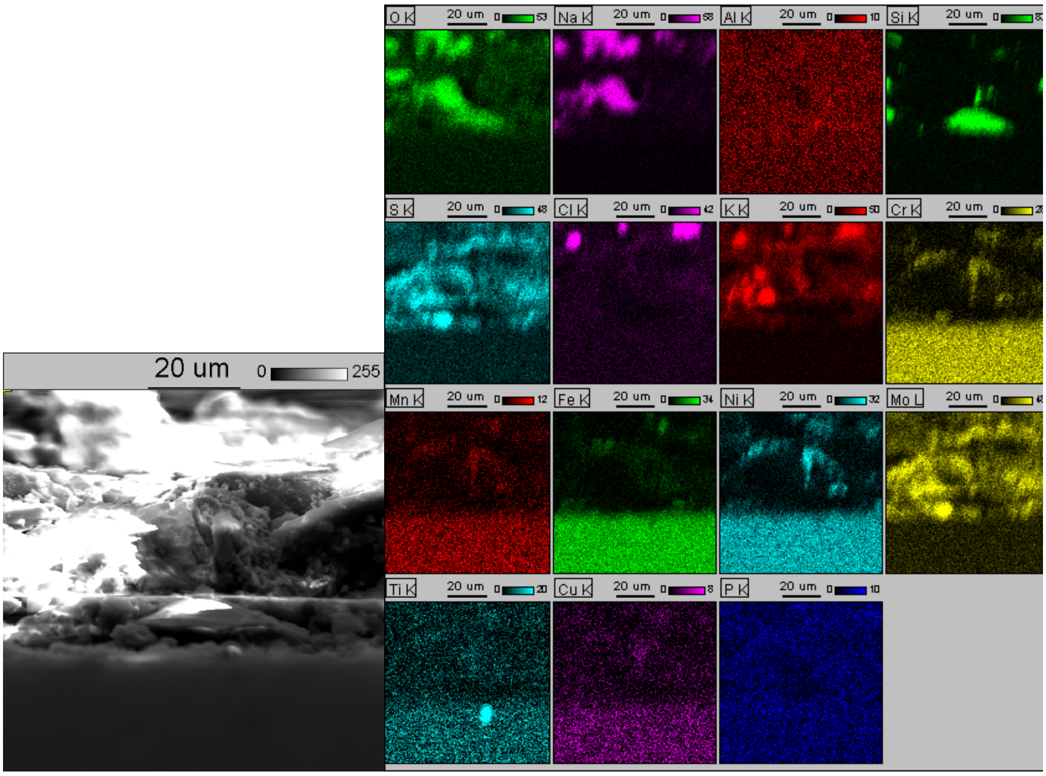


Figure 7. Element map of the surface of the Sanicro 41sample after Test 3.

After Test 4, no cracking close to the drill hole was observed in the Sanicro 41 sample, or at least not to the extent shown in Test 3. At first, a thick brittle salt layer covered the sample also after Test 4. However, in the process of preparing the sample, only the thickest layer was left on the surface of the sample (Figure 6c). In addition to salt, this dense layer also contained in particular chromium. The surface of this sample was also irregular, indicating early corrosion.

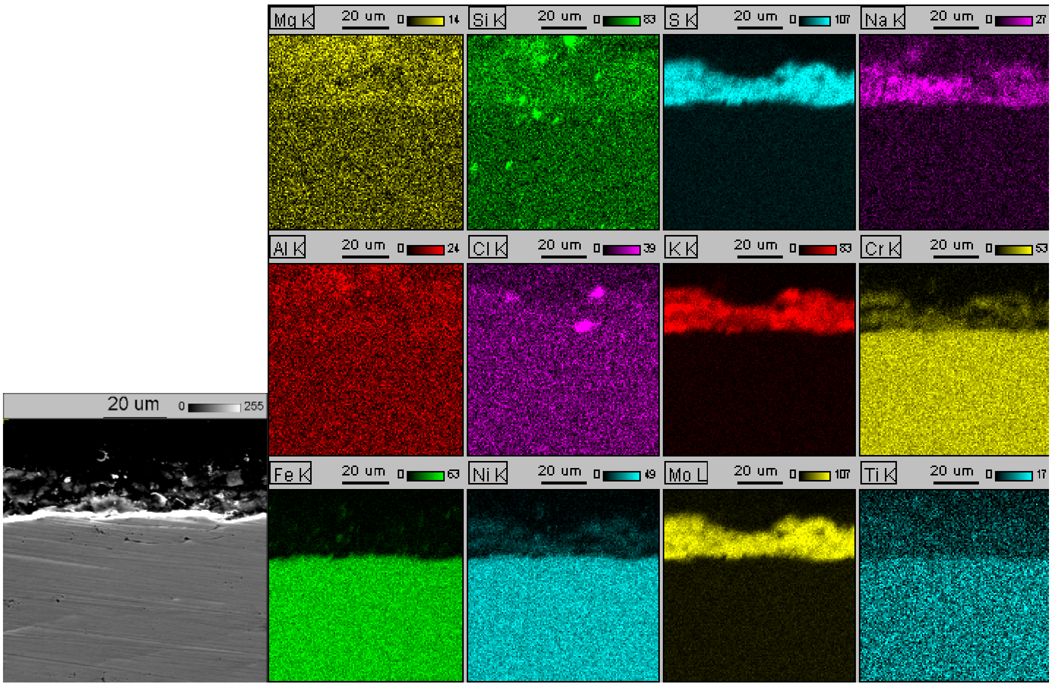


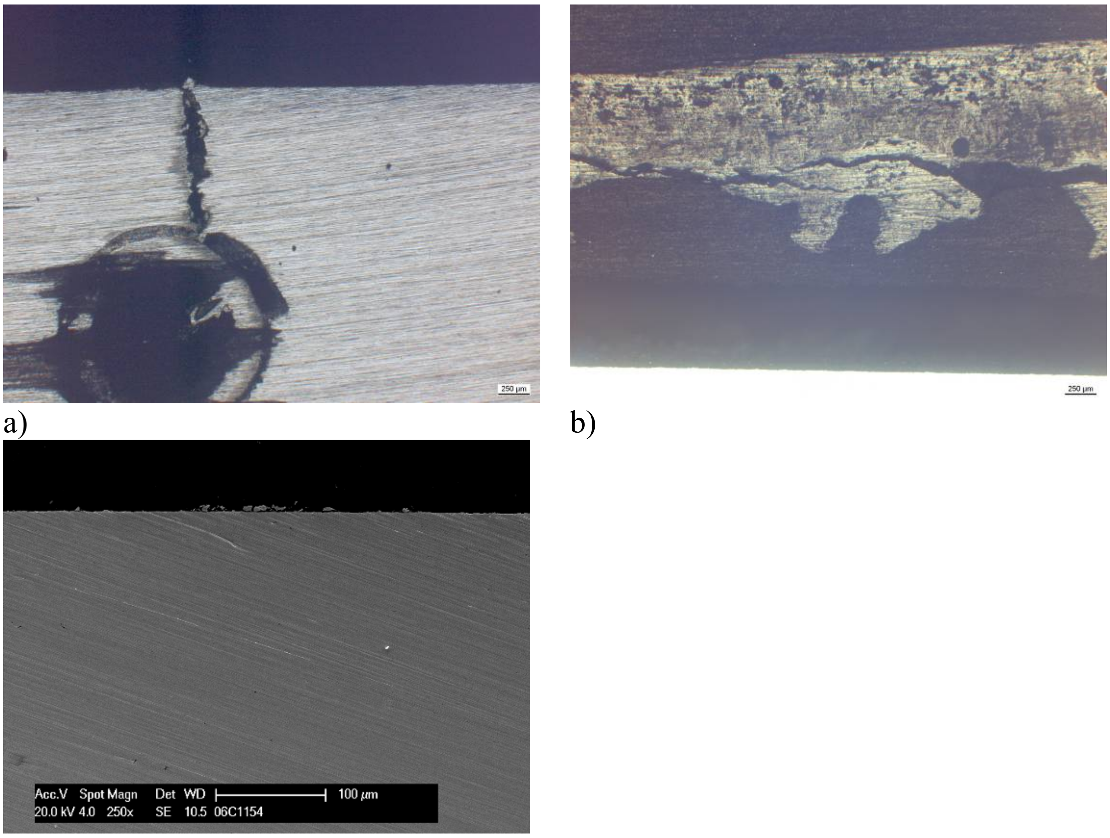
Figure 8. Element map of the surface of the Sanicro 41sample after Test 4

When comparing the results of Sanicro 41 with those of Sanicro 38 present in the laboratory tests, similarities in corrosion spread are observed. The salt in the deposit prevents a direct comparison of deposits, but, as expected, chromium and nickel were found in the probe test deposits, however, as different compounds.

3.3 Sanicro 36 Mo

Also Sanicro 36 Mo had cracked at the forepart of the drill hole (Figure 9a) in Test 3. In Test 4 no similar cracking was observed. The sample was covered by a thick brittle salt layer after Test 3 (Figure 9b). The deposit closest to the metal surface was also principally composed of salt (S, Na, K), containing, in addition, also much chromium and small amounts of nickel and iron (Figure 10).

After Test 4 there was also a thick layer of salt in the sample, but the salt had not yet reacted with the metal, since after the preparation of the metallographic sample no significant deposit at the surface of the sample and no corrosion of the surface were observed (Figure 9c). The deposit formed may have scaled off from the metal surface. Since there was no deposit, no element map was made of the material after Test 4.



a) b)

c)

Figure 9. Sample of Sanicro 36 Mo a) and b) after Test 3 and c) after Test 4.

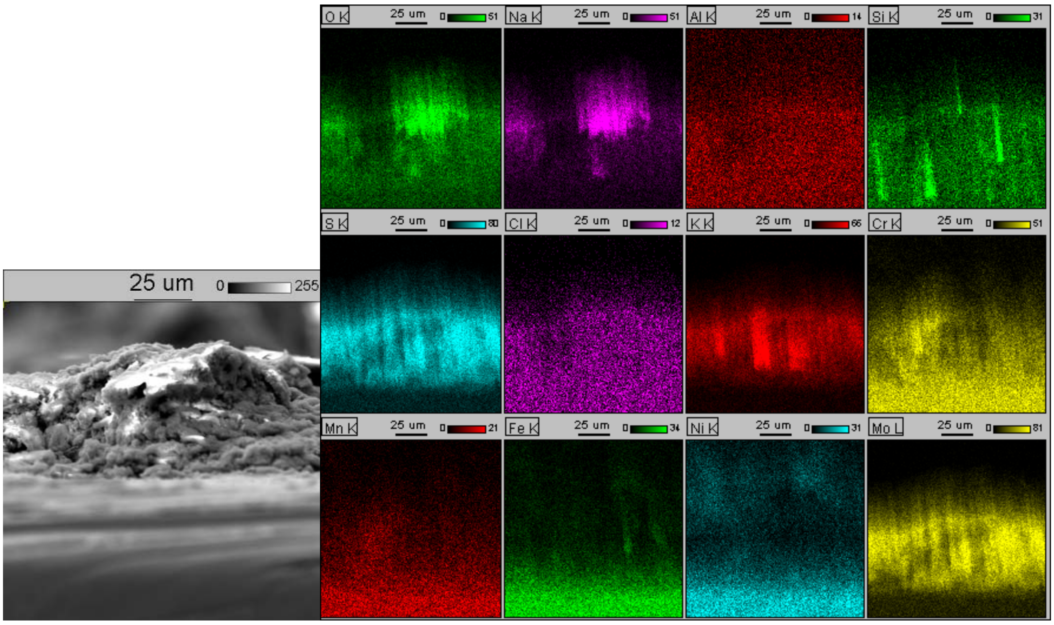
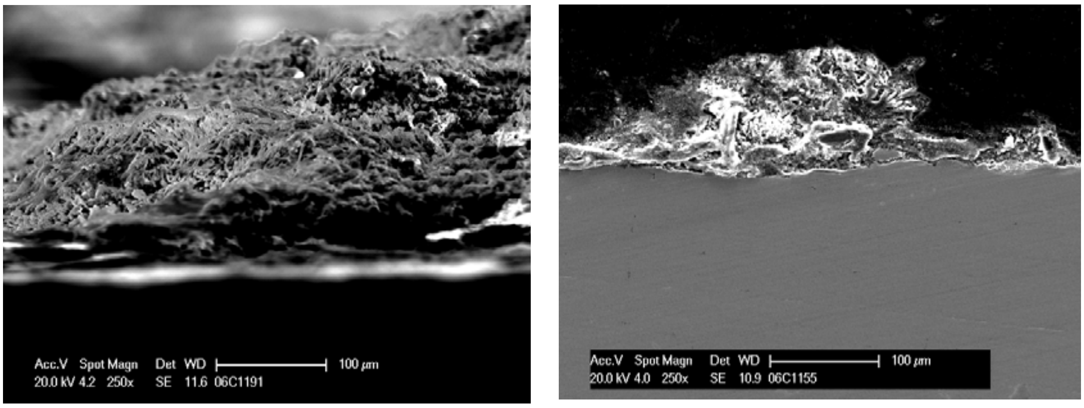


Figure 10. Element map of the surface of the Sanicro 36 Mo sample after Test 3

When comparing the results of the Sanicro 36 Mo sample with the laboratory tests, similarities in corrosion progress are observed. The deposit was predictably smaller than that of the other materials, although the salt contained in the deposit prevents any direct comparison of deposits. The laboratory results predicted that Sanicro 36 Mo is an easily flaking material, and possibly also for this reason there was no layer left to analyse in the Test 4 sample. From the Test 3 sample the salt layer had also partly separated particularly from this material already prior to casting in epoxy.

3.4 3R12

Material 3R12 (304L) was the only sample that did not present any cracking in either of the tests. Indeed, the sample was covered by a thick, brittle salt layer after Test 3 (Figure 11a). The deposit closest to the metal surface was composed of salt (K, S, Na) as well as of very small amounts of chromium, nickel and iron (Figure 12). However, the metal content of the deposit was very low, indicating an insignificant reaction between the salt deposit and the metal. Some surface irregularity was still observed, indicating early corrosion. In Test 4 the deposit was composed purely of salt (Figure 13). Admittedly, some surface irregularity was observed also after this test.



a) b)

Figure 11. Surface of sample 3R12 a) after Test 3 and b) after Test 4.

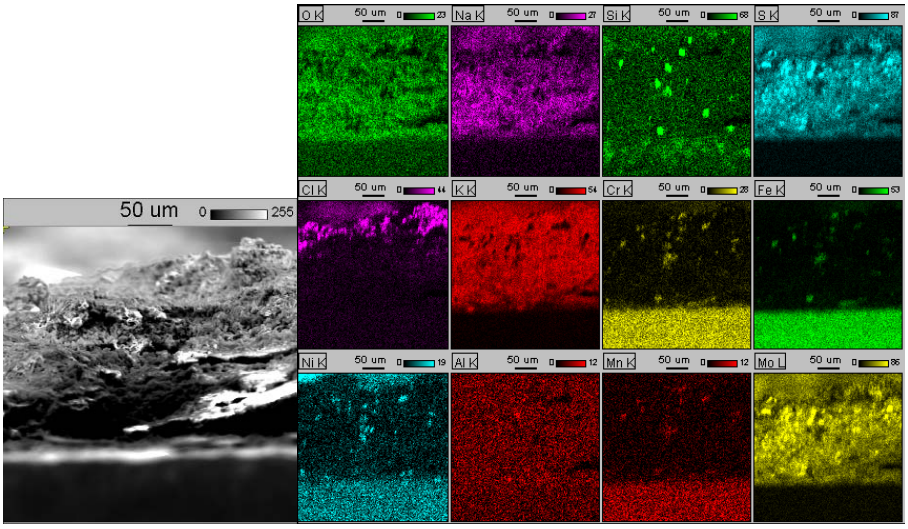


Figure 12. Element map of the surface of sample 3R12 after Test 3

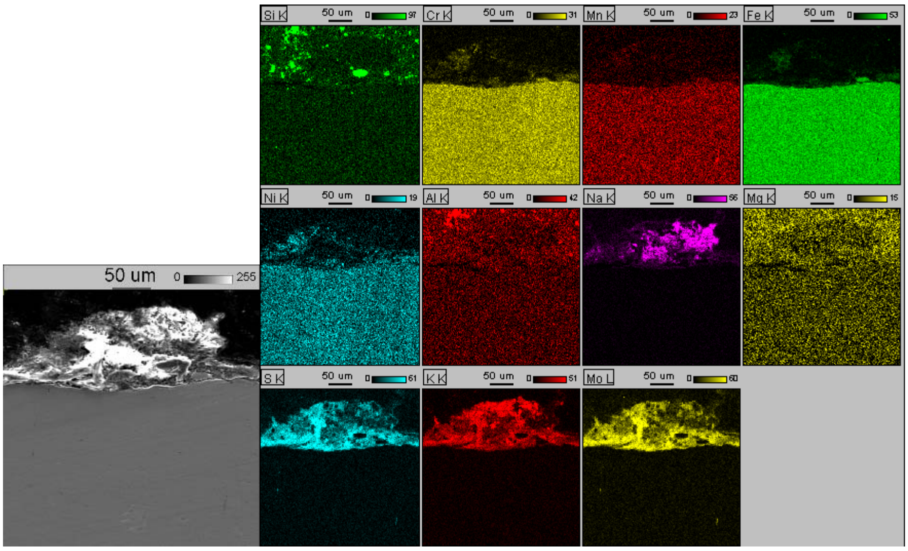


Figure 13. Element map of the surface of sample 3R12 after Test 4

When comparing the results of sample 3R12 (304L) with the laboratory tests, similarities are again observed in the corrosion progress. The salt in the deposit prevents, in principle, the comparison of the deposits. Surface irregularity due to corrosion was also observed in the laboratory tests at content 5000ppm H_2S (5 % CO, 0 % H_2O, 440 °C and 288h). The flaking observed in the same laboratory test was, however, not observed in the probe tests.

4 Conclusions

In materials Sanicro 63, Sanicro 41 and Sanicro 36 Mo cracking was observed after probe Test 3 near the hole drilled for the thermo sensor. Cracking was most pronounced with material Sanicro 63 and it was observed also in the shorter Test 4. This indicates that cold reduction exposes materials to cracking. At worst, cracks advanced through the 5.5 mm thick Sanicro 63 material in less than 500 hours. 3R12 was the only one of the materials in which no cracking was observed.

Thickness measurements did not produce the desired information on corrosion resistance. The thickness measurement results of Test 3 could not be utilised, due to the intermediate grounding performed. The results of the thickness measurements carried out in Test 4, unfortunately, reveal very little, since the major part of the change in thickness consisted of salt deposit. However, it can be concluded that the smallest change was observed in Sanicro 36 Mo, which also obtained good results in the laboratory tests. However, the small change in the material is partly due to flaking.

In Test 3 and 4, the deposits consisted primarily of potassium, sodium and sulphur compounds. In many deposits, especially after the longer test (Test 3), the layer closest to the metal surface contained chromium, nickel and iron. The corrosion products cannot directly be compared with the results of the sulphidation tests made in laboratory, since they were conducted only with gas atmosphere. Since material Sanicro 63 was not present in the previous laboratory tests [1], there are no comparison data as such. When comparing the results with the laboratory results of material Sanicro 65 it is observed that for both materials corrosion in reducing atmosphere starts at the surface, advancing unevenly in the thickness direction of the material. When comparing materials Sanicro 41 and Sanicro 38, it was observed that corrosion progressed in almost the same way. Flaking of Sanicro 36 Mo forecast by the laboratory tests was also observed in the probe tests. When comparing the results of material Sanicro 36 Mo with the laboratory tests, a predictably smaller deposit was observed in Sanicro 36 Mo than in the other materials, although the salt in the deposit prevents, in principle, the comparison of deposits. When comparing the results of sample 3R12 (304L) with the results of the laboratory tests, similarities in corrosion progress are detected, although the flaking occurred in the laboratory tests was not observed in the probe samples.

Based on the laboratory tests [1], the materials can be listed in the following order of superiority as a result of the weighing results:

Carbon steel << Sanicro 38 (41) < HR11N < Sanicro 65 ≤ 4C54 < Sanicro 36Mo ≤ 304L (3R12).

Based on the probe tests, the materials can be listed in the following order of superiority:

Sanicro 63 < Sanicro 41 (38) < Sanicro 36Mo < 3R12 (304L).

The cracking of the materials and the composition of the surface deposit formed have the greatest influence on order of superiority. The order was somewhat changed when comparing the probe tests with the laboratory tests, the greatest difference factor being material cracking.

We recommend that further laboratory tests be carried out under salt deposits and with controlled gas atmosphere using test coupons. In addition, we recommend stress corrosion tests under the same circumstances to investigate cracking. The additional tests recommended in the previous subproject [1] of the influence of water vapour content, time and carbon monoxide on sulphidation are also recommended.

5 Summary

The objective of the subproject was to analyse recovery boiler probe samples from two tests and compare the results with the laboratory tests performed in the previous subproject [1]. In the project The Recovery Boiler in the Future, the project management group selected Sanicro 41 (UNS N08825mod), 3R12 (AISI 304L), Sanicro 63 and Sanicro 36 Mo (UNS N08036-2) as materials to be tested. Boildec Oy (Timo Karjunen) carried out the probe measurements. The results of Probe Test 3 (~ 400 °C / 1006 h) and Probe Test 4 (~ 440 °C / 488 h) are shown in this report.

Probe Test 3 materials Sanicro 63, Sanicro 38 and Sanicro 36 Mo cracked near the thermo sensor drill hole. In material Sanicro 63 serious cracking was observed also after the test of shorter duration.

The thickness measurements did not produce the desired information on corrosion resistance. The results of thickness measurements in Test 3 could not be used because of the intermediate grounding carried out. Unfortunately, very little can be concluded based on the thickness measurement results of Test 4, since the major part of the thickness formation consisted of a salt deposit.

In Test 3 and 4, the deposits were composed primarily of potassium, sodium and sulphur compounds. In many deposits, especially after the longer test (Test 3), chromium, nickel and iron were observed in the layer closest to the metal surface. These deposits could not be directly compared with the previous laboratory results, but several samples showed similarities in corrosion progress.

Based on the probe tests, the materials can be listed in the following order of superiority as to corrosion resistance, from left to right:

Sanicro 63 > Sanicro 41 (38) > Sanicro 36Mo > 3R12 (304L).

The order is very much influenced by the extent of cracking and the interreaction between the formed surface deposit and the metal as concluded based on the composition of the deposit. The results are consistent with the previously obtained laboratory test results, the differences in results depending primarily on the cracking of material occurred in the probe tests.

Based on the tests and analyses, we recommend that further tests be carried out on the influence of molten salt on corrosion and cracking. The tests could be made under salt deposits and with controlled gas atmosphere. In addition, additional tests are recommended to clarify the influence of gas vapour content, exposure time and carbon monoxide on sulphidation.

References

1. Mustala S., Pohjanne P., Heikinheimo L., Pankakoski P., Kinnunen T., The Recovery Boiler in the Future – Sulphidation and Black Liquor Tests of Materials, VTT report TUO74 – 056625, 10.3.2006, s. 42
2. Karjunen T., Report on Furnace Probe Tests 3 and 4, 25.9.2006, s. 13