SmartInnovation

Pulse Plating

DTU MEK – A.H. Nichro Haardchrome A/S

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1 PREFACE

DTU MEK has chosen to write this report in English and a. h. nichro HAARDCHROM A/S has chosen to back up this line except for the Summary which includes a Danish written Summary as well.

This report is created to summarise the most essential findings in the Smart Innovation project on pulse plated hard chrome. The project is carried out in collaboration with DTU MEK and a.h. nichro HAARDCHROM A/S. This report is written as an overview for someone who has access to detailed information on the process parameters of each test series, as this is not described in depth here.

Full documentation for the findings claimed in the Conclusion will not be available in this report.

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2 SUMMARY

I perioden 2008 – 2011 gennemførte Nichro en række vellykkede forsøg med at udfælde hårdkrom fra et seksgyldigt krombad ved hjælp af pulserende strøm. Vi erfarede, at pulspletteringen gjorde det muligt at indbygge revnefri lag i krombelægningen. Lagene bestod af metallisk krom, men krystalstrukturen og egenskaberne var meget forskellig fra en traditionel hårdkrom. De pulspletterede lag forbedrede tilsyneladende belægningens korrosionsegenskaber markant. Vi erfarede at flere prøver kunne modstå mere end 500 timer i salttågetest. Vi kunne med rimelighed kontrollere antallet af pulslag i belægningen samt deres placering og lagtykkelse.

Dette arbejde gav imidlertid kun begrænset indsigt i sammenhængen mellem pulsmønstre og de resulterende belægningers struktur og egenskaber. Det er derfor nødvendigt at kortlægge og dokumentere disse sammenhænge for at kunne sammenligne pulspletteret hårdkroms egenskaber med konventionelle belægningers egenskaber; belægninger som f.eks. alm. hårdkrom, kemisk nikkel, hårdkrom på kemisk nikkel og tilsvarende.

Formålet med nærværende projekt er derfor at designe og producere pulspletterede hårdkrombelægninger i pilot skala for efterfølgende at kortlægge belægningernes egenskaber. Kortlægningen udføres på DTU af en uvildig tredjepart og resultaterne fremstilles som en teknisk dokumentation, der viser sammenhængen mellem pulsmønster, struktur og egenskaber. Dog, sådan gik det ikke !

Nichro producerede en række prøvebelægninger på såvel skiver (test serie 1) som indvendige røroverflader (test serie 2). Belægningerne omfattede traditionel hårdkrom, hårdkrombelægninger med et eller flere pulslag samt rene pulspletterede hårdkrombelægninger. Nogle af belægningerne blev pletteret direkte på grundmaterialet (Ovako 280), mens andre blev pletteret på et spærrelag af kemisk udfældet nikkel.

DTU gennemførte forskellige tests på belægningerne, herunder korrosionstests, der blev udført i et salttågekammer efter retningslinjerne givet i ASTM B117, ISO 9227 samt ISO 10289, Anneks A. Disse tests gav et uventet resultat. Det viste sig at prøvernes korrosionsbestandighed varierede meget på en ret uforudsigelig måde. Vel lykkedes det os at producere belægninger, der kunne modstå 1000 timer i salttåge, men de pulserede spærrelag kunne sagtens indeholde makrorevner, der ødelagde holdbarheden i salttåge. Samtidig lykkedes det os at producere en traditionel hårdkrombelægning uden spærrelag, der også kunne modstå 1000 timer i salttåge.

Forsøgene viste, at strømtætheden, lagtykkelsen og koncentrationen af brint i overfladen har vital betydning for belægningernes korrosionsbestandighed. Samtidig tyder meget på at grundmaterialet og grundmaterialets historie samt parametrene for den første plettering (kaldet aktivering) ligeledes har en vital betydning. Og det lader til at badets balance, forureningsgrad og katalysatorindhold også har stor betydning (måske vital).

Hårdkrombelægningers korrosionsegenskaber påvirkes altså af mange parametre på en kompleks og uforudsigelig måde. Det er ret let at designe og udfælde en flerlagskrom med indbyggede pulslag. Vi kan styre lagtykkelsen og lagenes placering, idet pulslagene består af metallisk krom arrangeret i en finkornet nano-krystallinsk nærmest amorf struktur, mens traditionel hårdkrom er metallisk krom udfældet i en mikro-revnet søjlestruktur.

Men vi kan ikke styre grundmaterialets historie eller badets tilstand med en sådan nøjagtighed, at opskalering af processen til fuld kommerciel skala vil være tilrådelig på nærværende grundlag. Vi vil ikke kunne give kunderne en garanti for belægningens korrosionsbestandighed.

English summary

In the period 2008 - 2011 Nichro conducted a series of successful attempts to precipitate hard chrome from a chromium (VI) bath using pulsating currents. We learned that the pulse plating made it possible to build in crack-free layers in the chrome coating. These layers consisted of metallic chrome but the crystal structure and properties differed a lot from the traditional hard chrome. The pulse-plated layers seemed to improve markedly the corrosion properties of the coating. We learned that several samples could withstand more than 500 hours in salt spray testing. We could reasonably control the number of layers in the coating as well as their location and their thickness.

However, this work provided only limited insight into the relationship between pulse patterns and the structure and properties of the resulting coatings. Therefore we found it necessary to map and document these relationships in order to compare the properties of pulse plated hard chromium with the properties of conventional coatings; coatings such as traditional hard chrome, chemical nickel, hard chrome on chemical nickel and the like. Thus the purpose of this project is to design and produce pulse-plated hard-chromium coatings on a pilot scale in order subsequently to map the properties of the coatings. The mapping is carried out at DTU by an independent third party and the results are presented as a technical documentation that shows the relations between pulse pattern, structure and properties. However the outcome of the project turned out to be much different!

Nichro produced a number of test coatings on panels (test series 1) as well as internal pipe surfaces (test series 2). The coatings included traditional hard chrome, hard chromium coatings with build in layers of pulse plated hard chrome, and clean pulse plated hard chromium coatings. Some of the coatings were plated directly on the base material (Ovako 280), while others were plated on a barrier layer of electroless nickel.

DTU conducted various tests on the coatings, including corrosion tests performed in a salt spray chamber according to the guidelines given in ASTM B117, ISO 9227 and ISO 10289, Annex A. These tests gave an unexpected result. It was found that the corrosion resistance of the samples varied greatly in a rather unpredictable manner. Well, we succeeded in producing coatings that could withstand 1.000 hours of salt spray, but the pulsed barrier layers could easily contain macros cracks that destroyed the corrosion resistance. At the same time, we succeeded in producing a traditional hard chrome coating with no barrier layer, which also could withstand 1.000 hours in salt spray.

The experiments showed that the current density, the layer thickness and the concentration of hydrogen in the surface are vital to the corrosion resistance of the coatings. At the same time it is likely that the basic material and its history as well as the parameters of the activation also are of vital importance. Furthermore it seems that the bath's balance, the degree of contamination and the catalyst content are of great importance as well; perhaps vital.

The corrosion properties of hard chromium coatings are thus influenced by many parameters in a complex and unpredictable way. It is quite easy to design and plate a multilayer chrome coating with pulse layers build-in. We can control layer thicknesses and their locations. The pulse layers consist of metallic chromium arranged in a fine-grained nano-crystalline, almost amorphous structure, while traditional hard chrome is metallic chrome deposited in a micro-cracked pillar-like structure.

But we cannot control the history of the base material or the state of the bath with such accuracy that scaling up the process to full commercial scale will be advisable on the present basis. We will not be able to give customers a guarantee of the corrosion resistance of the coating.

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4 BACKGROUND

The hard chrome plating process is characterized by low current efficiency and poor throwing power. The main characteristics are described below.

The current efficiency of the process is low. Depending on various process parameters the current efficiency will be no more than 10 – 30 pct. of the current input. The rest of the current consumption is mainly used for dissociation of water leading to formation of hydrogen and oxygen in the form of free radicals and as gases in the end.

The chromium is plated as chromium hydride molecules. These are layered at the component surface and arranged in a hexagonal lattice structure. This means that it is not possible to avoid build in of hydrogen in the coating. This is a serious challenge because the hydrogen might lead to hydrogen embrittlement destroying the coating. The electroplater must ensure that as much hydrogen as possible is released during the process to avoid hydrogen embrittlement.

The bath additives and the choice of process parameters allow the electroplater to get rid of the hydrogen during the process. Using these tools correctly leads to a recrystallization of the surface crystals; i.e. the hexagonal chromium hydride crystals are transformed into hydrogen gases and metallic chromium arranged in body-centred cubic crystals. The metallic chromium crystals are however smaller than the chromium hydride crystals. The recrystallization will generate an internal stress in the coating. The bath catalyst ensures that this tensile stress is released regularly during plating forming micro-cracks in the coating. The micro-cracks will be perpendicular on the surface of the component being coated. The crack-depth will typical be in the range of 1 – 5 my and it will not normally penetrate from the topcoat to the base material. The crack-depth however depends on the chosen process parameters and might evolve into macro-cracks going through the coating to the base material. The sizes of the chromium crystals are closely linked to the current density.

The surface of the chromium crystals surrounding these cracks are however subject for oxidation leading to formation of chromium oxide (Cr_2O_3) in the grain boundaries. The electric conductivity of chromium oxide is less than that of the metallic chromium leading to formation of a hard chrome coating ending up in a pillar structure. This structure is responsible for the hardness of the coating. In general – the more cracks, the harder chrome coating. The cracks are unfortunately also weak points where corrosion might start. In general – the more cracks, the shorter lifetime of the hard chrome coating due to corrosion attack.

The throwing power of the hard chrome electrolyte is poor meaning that the electric current always chooses the shortest distance on its way from the anode to the cathode (the component to be plated). This is challenging because part of the electricity is used to reduce hexavalent chromium (Cr^{6+}) to metallic chromium (Cr^0) as described before.

The challenge relates to the fact that the current density varies over the component to be plated. The anode-cathode distance is not the same at all locations of the surface meaning that the amount of chromium plated at the component surface varies from location to location. Most chromium is plated at high current density areas leading to variations in the layer-thickness of the hard chrome coating. The variation can easily be more than 100% if no care is taken.

The main key to successful hard chrome plating is creation and preparation of the anodes ensuring that the anode-cathode distance is as uniform as possible. The distance is crucial; i.e. bad hard chrome plating can deliver chrome coated components with excess chrome at high current density areas such as edges and pipe-ends and at the same time leave low current density areas (f. x. recesses) without chrome at all.

The poor throwing power of the hard chrome electrolyte also explains why the surface roughness will be no better after plating. The electrolyte does not possess the ability to level out a surface. On the contrary the roughness of the surface will increase during plating; a fact that the electroplater must be aware of when creating the anodes and choosing the process parameters after careful examination of the component to be plated. Doing this the electroplater might ensure that the roughness of the component will be no worse than it was before plating.

The above background knowledge seems to possess an opportunity for more efficient hard chrome plating if pulsating currents are used in combination with conventional plating using direct current; indeed not only pulsating current but also pulse reverse current because reversing the current might favour driving out the dissolved hydrogen. Current patterns changing frequently between pulsating current and pulse reverse current might be constructed in such a way that recesses can be plated (short pulses with high current density followed by long reverse pulses with low current density). Such a pattern might also possess the ability to level out the coating. It might be possible to ensure a growth of very fine chromium crystals forming a dense chromium coating using the correct mix between metal precipitation and metal dissolution.

In 2009 Nichro successfully completed experiments in the lab. scale with pulse and pulse reverse plating combined with conventional direct plating. We could design and plate multilayer coatings containing a controlled mix of pulse plated chromium layers and direct plated layers of chromium. We could control the layer types (DC / pulse), number of layers, the thickness of each layer and their location in the plated coating. It seemed that the pulse plated layers were without cracks. Some of the multilayer coatings showed an excellent corrosion resistance (more than 500 hours in salt spray test) but we found that the corrosion resistance very much depends on the multilayer design and the process parameters chosen for the plating.

The upscaling from lab. tests to commercial operation was however not completed because our main investor lost interest in the project. New queries on corrosion-resistant hard chrome coatings suggests that time is ripe for the scaling up. However we need technical documentation comparing the corrosion resistance, the hardness and the roughness with our existing metal coatings. The purpose of the Smart Innovation project is to provide this knowledge allowing Nichro to improve the customer service and to develop the market for corrosion resistant hard chrome.

5 EXPERIMENTAL

The different test series are shown below in Table 1.

Cross sections and layering were examined using bright-field light optical microscopy (BF LOM), and layers brought to appear by etching using aqua regia.

Crack density was examined using dark-field light optical microscopy (DF LOM)

Corrosion resistance testing was performed in accordance to ISO 9227 and ASTM B117 and the coatings were evaluated after the ISO 10289, Annex A.

The effect of prior pulse plating and stripping of this plating before pulse plating again was done using GD-OES for compositional analysis and BF LOM to investigate the thickness of the layer.

Table 1: Showing the different test series produced

Test Series	**1A**	**1B**	**1C**	**1D**	**1E**	**1F**	**2B**	**2C**	
Coating Type	Nickel	Nickel + DC chrome	DC chrome	DC chrome with 2 pulse layers	DC chrome with 6 pulse layers	Pulse plated chrome	Nickel + DC chrome	DC chrome	
Panel ID's	1-2-3-4-5-6	11-12-13-14-15-16	21-22-23-24-25-26	31-32-33-34-35-36	41-42-43-44-45-46	51-52-53-54-55-56	111-112-113-114	121-122-123-124	
Test Series	**2D**	**2E**	**2F**	**3C**	**3D**	**3F**	**4DA**	**4DB**	**5DB**
Coating Type	DC chrome with 2 pulse layers	DC chrome with 6 pulse layers	Pulse plated chrome	DC chrome	DC chrome with 2 pulse layers	Pulse plated chrome	DC chrome with 2 pulse layers and ramp up	DC chrome with 2 layers and just current switch	DC chrome with 2 layers and just current switch
Panel ID's	131-132-133-134	141-142-143-144	151-152-153-154	3C1-3C2-3C3-3C4-3C5-3C6	3D1-3D2-3D3-3D4-3D5-3D6	3F1-3F2-3F3-3F4-3F5-3F6	4DA1-4DA2	4DB1-4DB2	5DB1-5DB2-5DB3-5DB4

6 RESULTS

6.1 COATINGS

6.1.1 Layers and thickness

Each coating is comprised of different combinations of layers, and these layers are documented here using BF LOM. Series 1B (see fig.1) has a layer of nickel below the hard chrome layer plated with direct current (DC-plating or just DC).

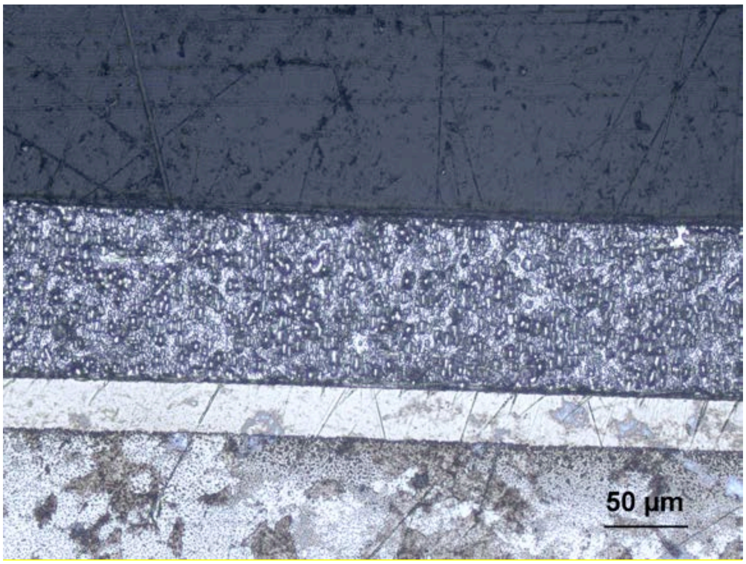

Figure 1: BF of etched sample 14 – DC hard chrome on nickel layer (200x)

4DB1 and 4DB2 are the two halves of the same pipe. The samples were exposed for salt-spray. 4DB2 starts to corrode after 168 h. It was removed from the salt-spray chamber and a sample was cut for LOM images. The thickness of the individual layers in the two coating was found to be the same (fig.3 and fig.4). The 4DB – coating consists of DC-plated hard chrome with 2 build-in layers of pulse reverse plated hard chrome (PR-plated or just PR).

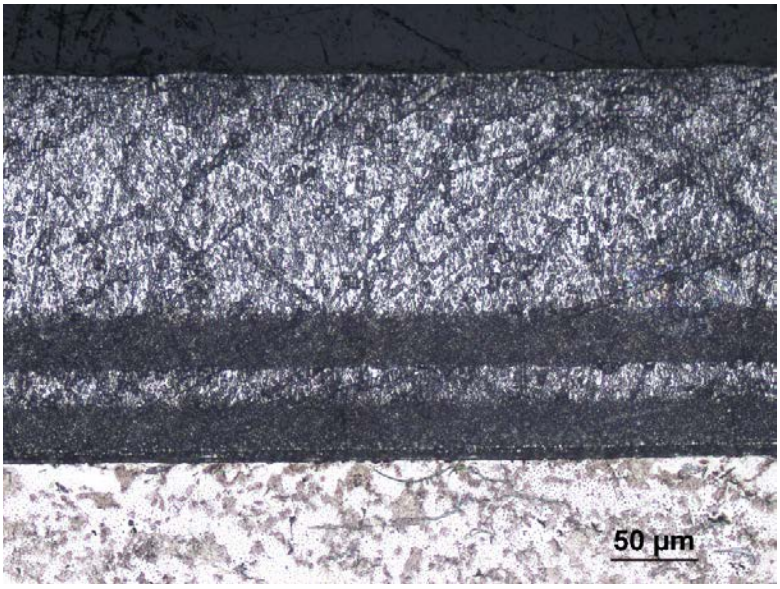

Figure 2: BF of etched 4DA – unexposed sample - DC with 2 PR layers (200x)

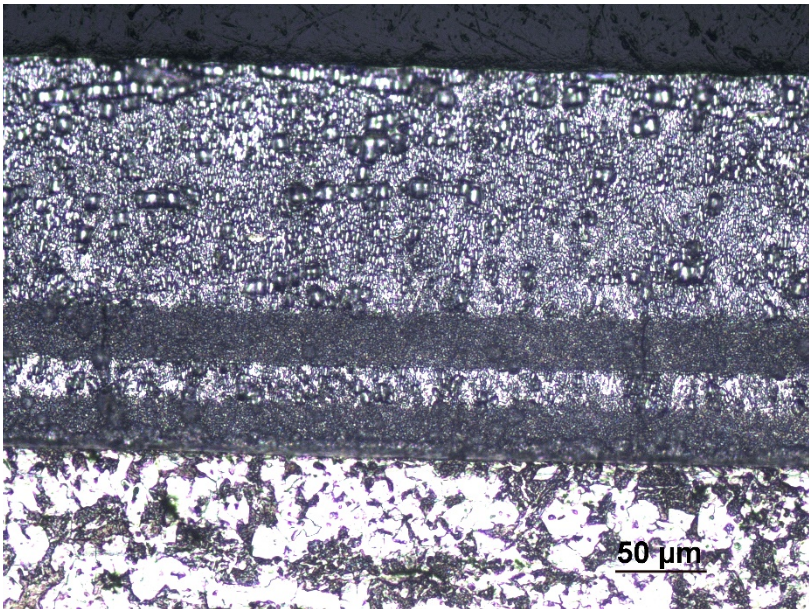

Figure 3: BF of etched 4DB1 – DC with 2 PR layers (200x)

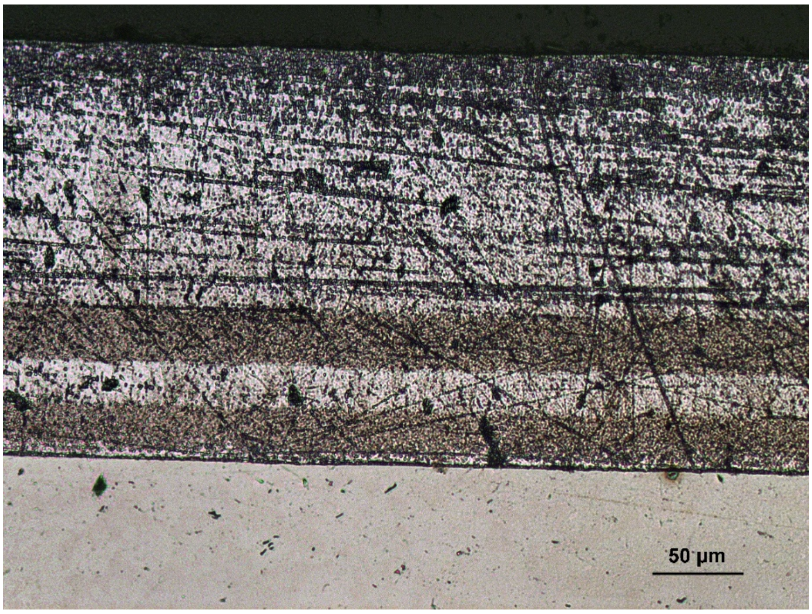

Figure 4: BF image of etched 4DB2 after 168 h exposure in accordance to ISO 9227 (200x)

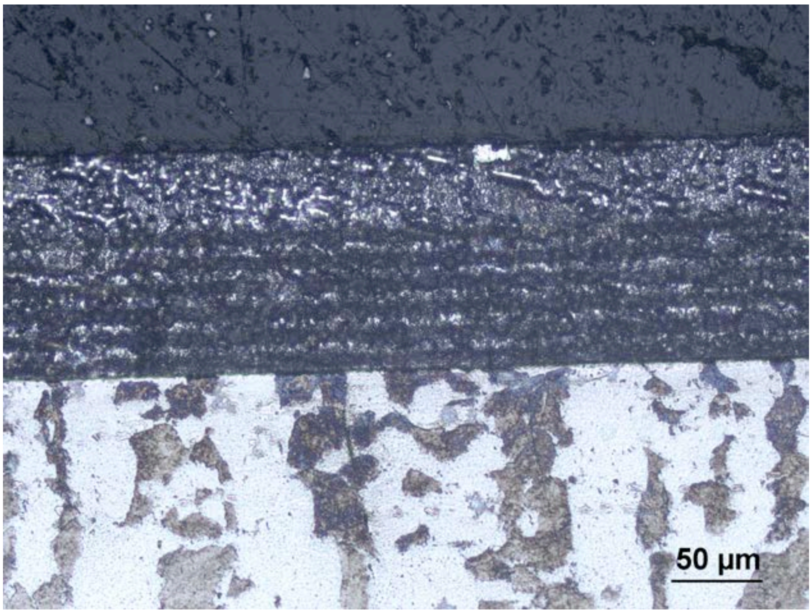

Figure 5. BF of etched sample 46 – DC with 6 PR layers (200x)

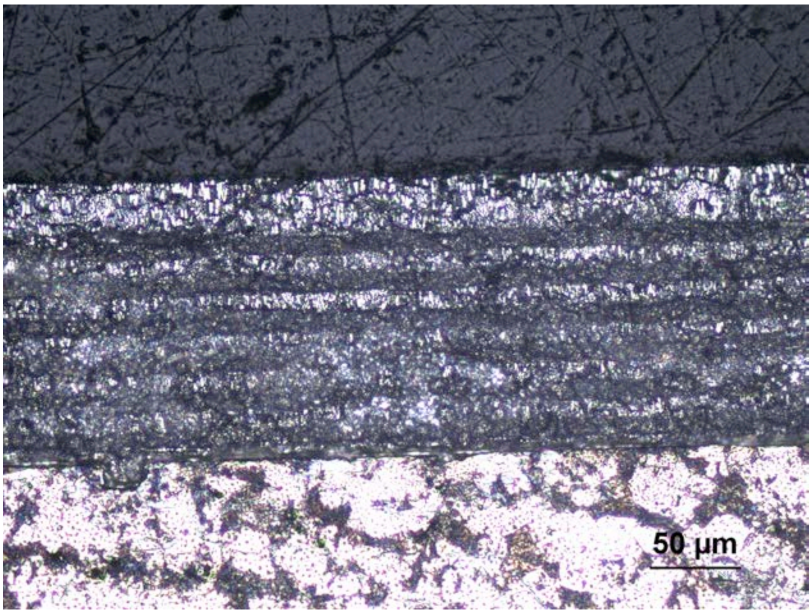

Figure 6: BF of etched 2E2 – DC with 6 PR layers (200x)

Table showing thickness measured for individual test plates:

Table 2: Thickness of individual layers on test plates, measured in BF LOM

Panel ID	**Layer thickness (Ni - Cr - Puls Cr) [micrometer]**
6 – nickel coating	27.6
14 – DC hard chrome on Ni-layer	29.7 + 102.8
26 – DC hard chrome	103.8
36 – DC hard chrome with 2 PR layers	due to over etching it needs to be redone
46 – DC hard chrome with 6 PR layers	3.8 + 8.6 + 6.2 + 8.9 + 5.5 + 9.7 + 5.5 + 9.3 + 5.2 + 8.9 +5.5 + 8.3 + 44.8
56 – PR hard chrome	2.8 + 82
2D2 – DC hard chrome with 2 PR layers	8.3 + 23.8 + 5.9 + 25.9 + 39.7
2E2 – DC hard chrome with 6 PR layers	4 + 13 + 9.7 + 11.7 + 10.7 + 11 + 9 + 11.4 + 11 + 11 + 10 + 11.7 + 30.7
2F2 – PR hard chrome	112.4
4DA – DC hard chrome with 2 PR layers	7.6 + 25.7 + 20.7 + 31 + 136.9
4DB – DC hard chrome with 2 PR layers	5.5 + 23 + 22 + 29 + 135

6.1.2 Cracking

The investigation of cracks in the coating surface was done to understand the connection between vulnerability to corrosion and the coating morphology.

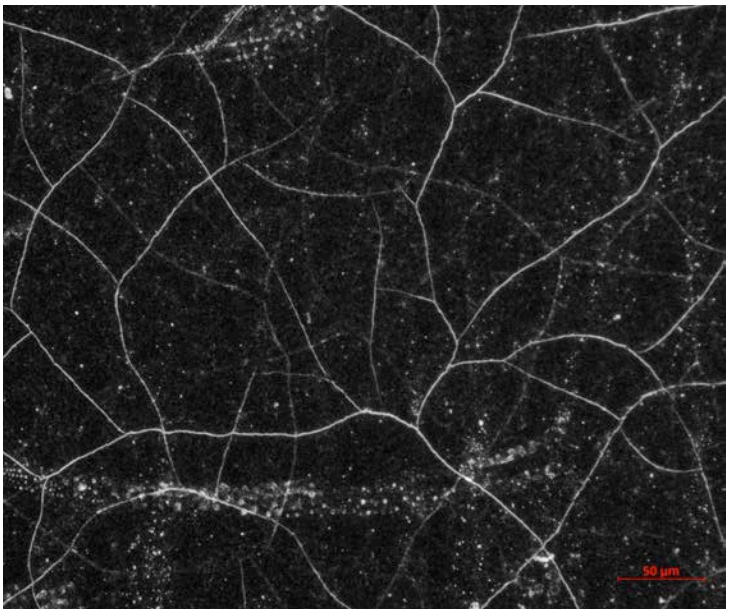

Figure 7: DF image of panel 14 – DC plated on nickel layer (200x)

Surface samples for crack analysis of panel 26 (DC plated hard chrome on panel) and 3C6 (DC plated hard chrome on panel) are cut from the exact same position of their respective test plates. Despite this, it is evident that the crack density on 3C6 is higher than that of plate 26. I could also appear that 3C6 has more knobs on the surface. However, the number of knobs varies from test plate to test plate within the same batch of a series. The cracking of these are the same as that of panel 14 being

DC plated chrome with an underlying nickel layer. Thus, the nickel layer does not alter the cracking density of the coating. It merely acts as a barrier layer at the bottom preventing the corrosive species from reaching the underlying substrate.

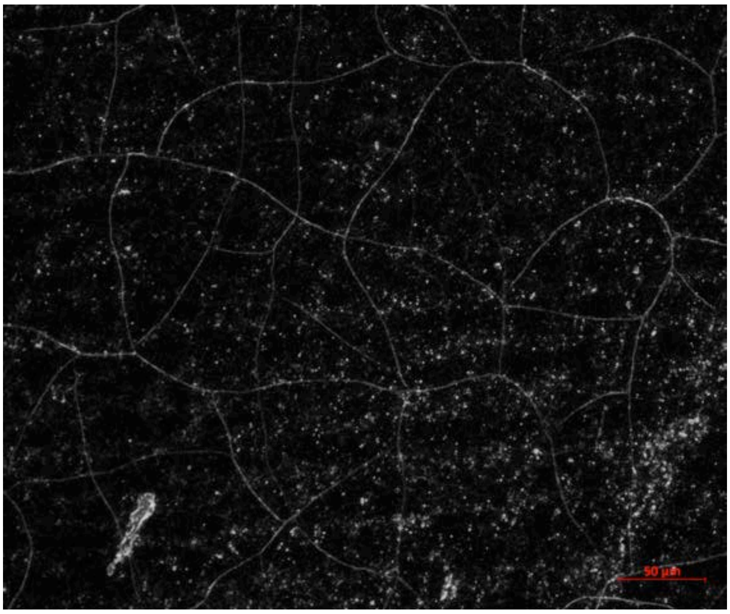

Figure 8: DF image of panel 26 – DC plated hard chrome (200x)

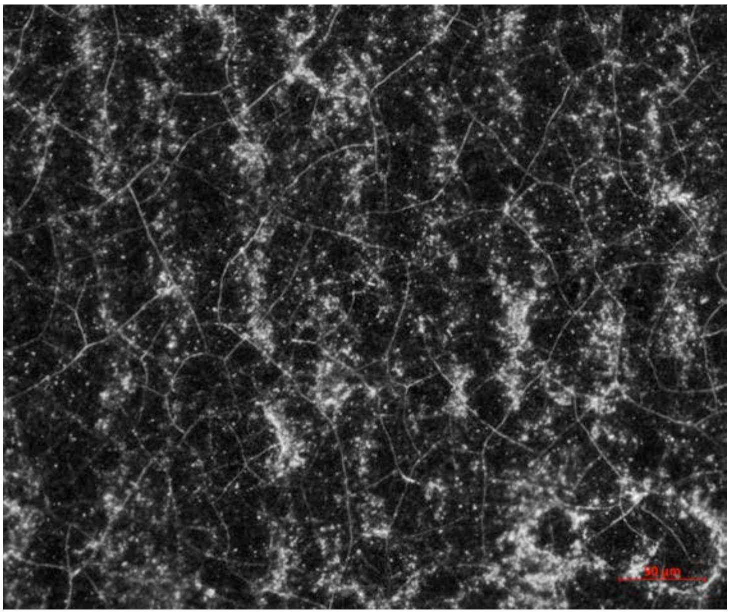

Figure 9: DF image of panel 3C6 – DC plated hard chrome (200x)

The surface sample from panel 36 (DC with 2 PR layers) and 3D1 (DC with 2 PR layers) has been cut from almost the same location of their respective test plates. There appears no significant difference in the crack density of the upper most DC chrome layer on the two.

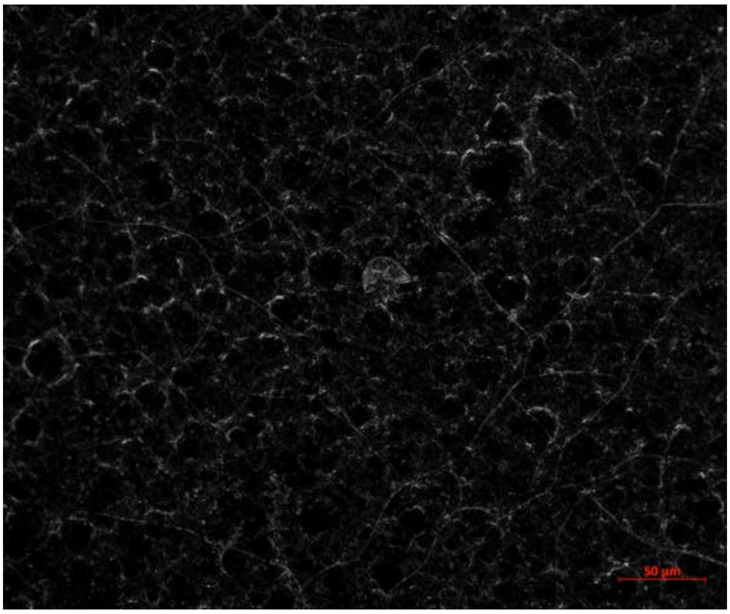

Figure 10: DF image of panel 36 – DC with 2 PR layers (200x)

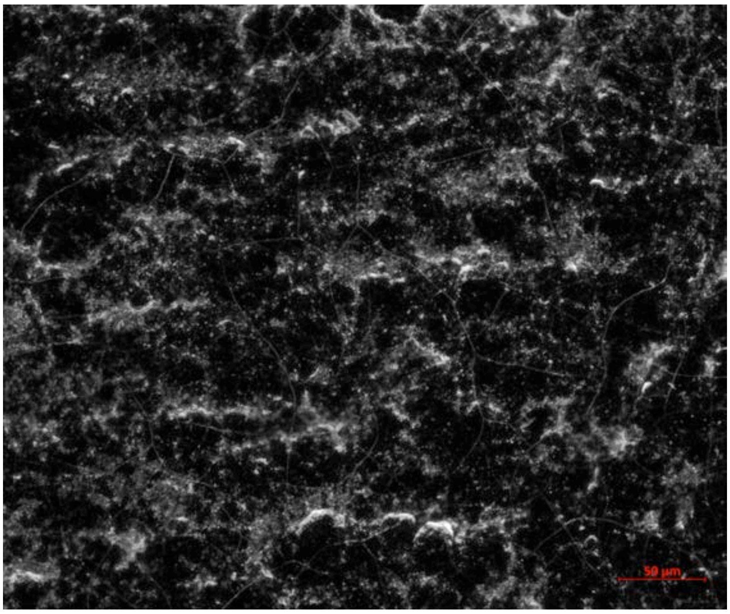

Figure 11: DF image of panel 3D1 – DC with 2 PR layers (200x)

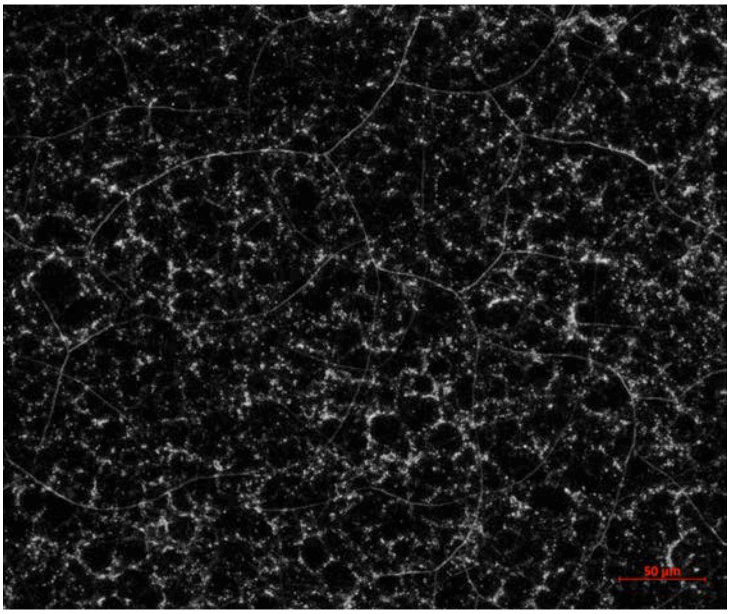

Figure 12: DF image of panel 46 – DC with 6 PR layers (200x)

The investigation of the solely pulse plated, test plate 56, show a much lower crack density. The surface appears less smooth and the cracks wider. The width and depth of the cracks are indicated by the fact that the light in DF LOM is not reflected by the sides of the cracks like it is seen for the other samples; simply because the crack size and shape swallow up the light.

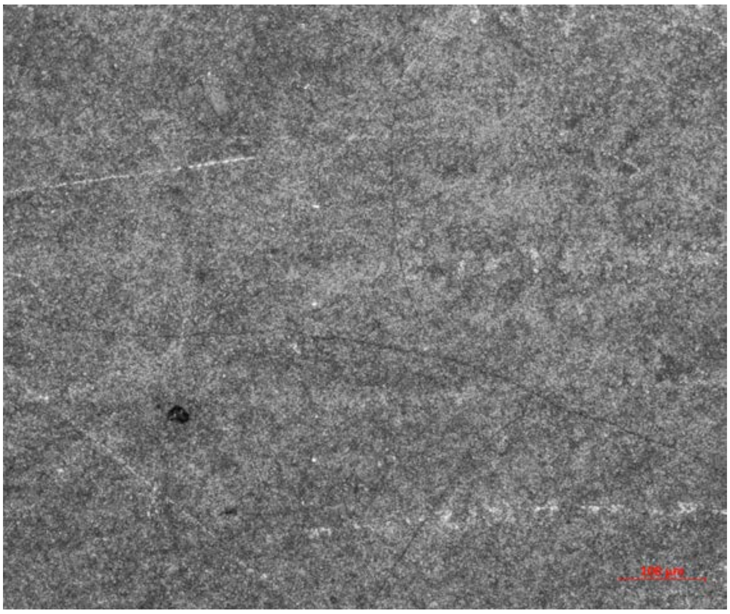

*Figure 13: Df image of panel 56 – PR plated hard chrome (100x).
Cracks are seen as dark lines*

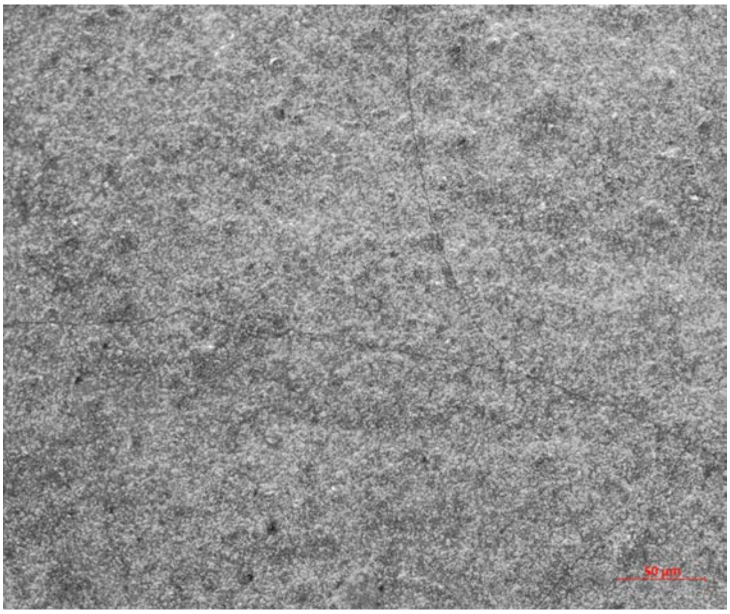

*Figure 14: DF image of panel 56 – PR plated hard chrome (200x).
Cracks are here seen as dark lines*

6.2 PLATING EFFECT ON BASE MATERIAL

All panels are made of stainless steel grade 19MnV6 (Ovako 280). The composition of the substrate or base material, Ovako 280, is given in the table below.

Table 3: Typical composition of Ovako 280

C	Si	Mn	Other	Balance
0.2	0.4	1.5	0,7	Fe

In the case of the 3F series (100% PR-plated hard chrome), several plates had previously been plated with a sole layer of pulse plated chromium. They had then been stripped and prepped before being pulse plated again. The resulting coating, 3F, however showed extremely bad adhesion to the substrate. A ring of approximately 20 mm around the edge of the plate appeared to have proper adhesion and then a relatively sharp line separated this part of the coating from the centre part that peels off very easily. An adhesion test has not been performed as it was evident the adhesion was inadequate. As plates in the 3F series, that had not been previously plated, showed no indication of similar problems it appears to be an issue with alteration of the substrate. Therefore, has the substrate been analysed using GD-OES. A few results of this are shown in Figure 16: Chart showing the contents of alloying elements (wt%) of 3F1 substrate measured using GD-OES From this it is evident that towards the centre of the plate (spot 3F1_01 and 3F1_02) there is much more hydrogen in the substrate. This appears to decrease gradually to be very limited towards the edge where proper adhesion was seen (3F1_04 and 3F1_05).

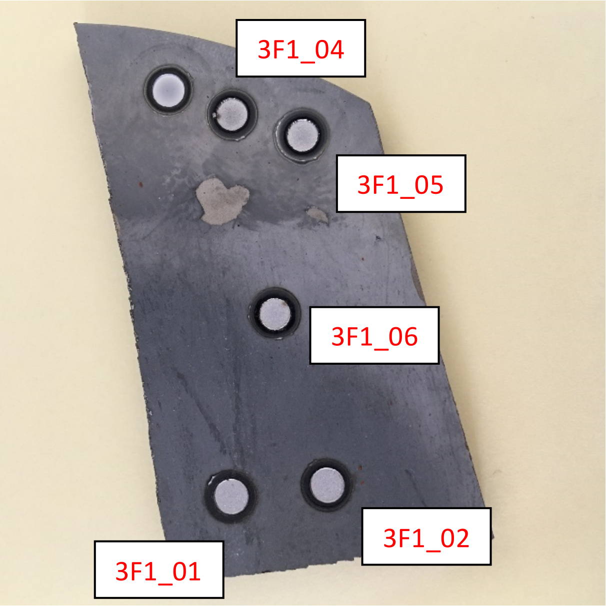

Figure 15: Image showing the spots after GD-OES analysis on panel 3F1 – PR plated hard chromium

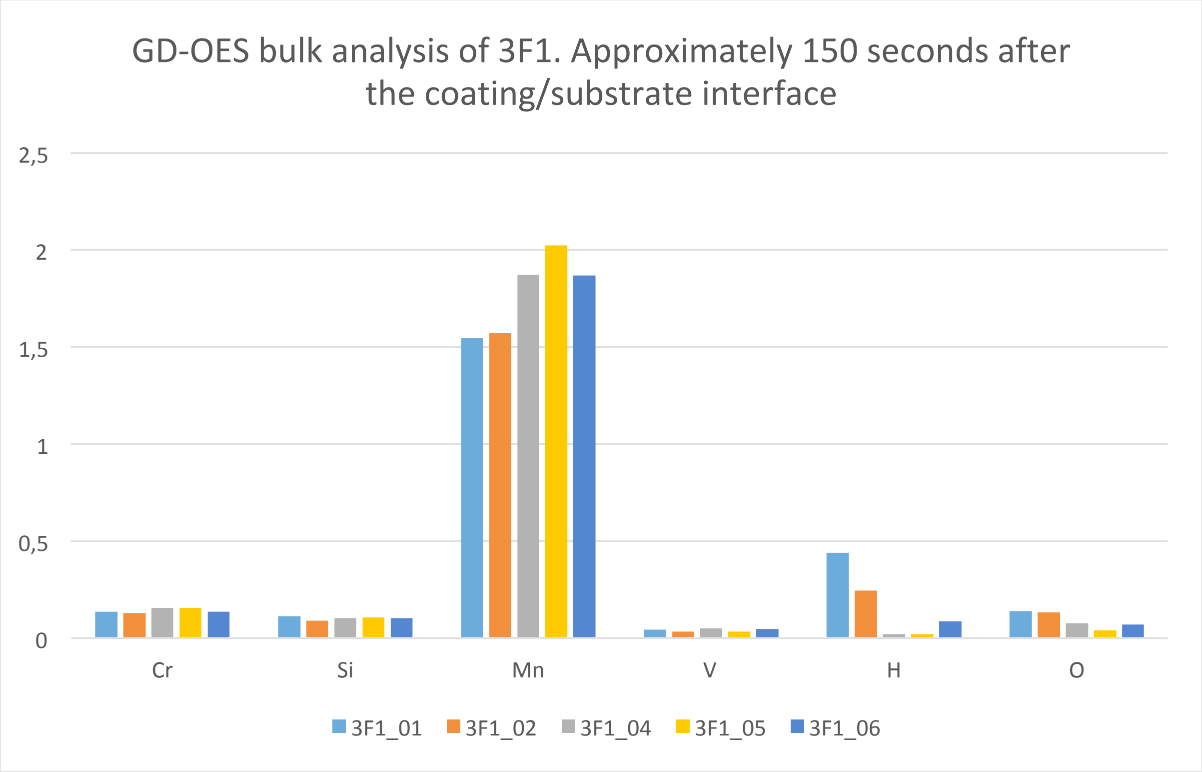

Figure 16: Chart showing the contents of alloying elements (wt%) of 3F1 substrate measured using GD-OES

6.3 CORROSION RESISTANCE

Photos of the most interesting test panels are here presented along with table 4 showing the ratings of the coatings in accordance to ISO 10289 Annex after exposure to neutral salt-spray as prescribed in ISO 9227.

Figure 17: 3F1 prior to NSS exposure

Figure 18: Zoomed image of 3F1 (PR plated) after 168 h exposure in NSS.

From Figure 18 it can be seen how the cracks in the coating has allowed the corrosive species to penetrate to the substrate and the dried-out river bed pattern is vaguely visible. Similar was seen on the plates in series 1F (100% PR). The performance of the combined layers of the D and E series (DC with 2 → 6 PR layers) were inadequate in comparison to that seen before in the 2008 - 2010 tests. At that time the samples were stopped after 504 h of NSS with no sign of corrosion. The difference between these tests was the current density and the adhesion procedure. It seems that the current density in the plating process affects the substrate irreversible if it is too high, (photo below).

Figure 19: 5DB3 (DC with 2 PR layers) prior to exposure (left) and after 672 h NSS exposure (right)

Figure 19 shows how the 5DB series (both 5DB2 and 5DB3) has been able to resist corrosion for 672 h – only 5DB1 showed 2 spots of corrosion after this time. Furthermore, 5DB2 and 5DB3 has been able to stay corrosion free for up to 766 h. Unfortunately the salt-spray chamber broke down at that time. This is a significant improvement over the previous panels of the D type. Below in Figure 20 is seen 3D4 before and after 720 h of exposure in NSS and it is clear how the altered initiation of 5DB improves the corrosion properties over the 3D series and its ramp-up initiation method.

Figure 20: 3D4 (DC with 2 PR layers) before NSS exposure (left) and after 720 h exposure (right)

The 3D series is however still better than the 1D series (DC with 2 PR layers) that had both ramp-up initiation and high current density for the pulse plated layers. It is worth mentioning that a plate from the 3C series has managed 1016 h exposure in NSS without corrosion (fig.21). This series was manufactured with very low current density. However, it shall be mentioned that 3C4 did not last this long and started showing corrosion after 336 h.

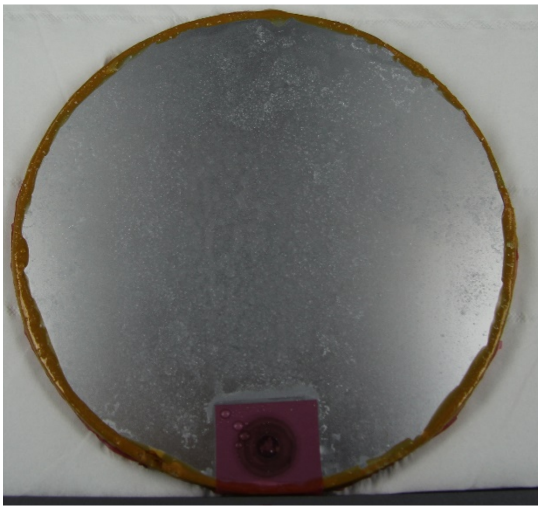

Figure 21: 3C5 (DC plated) after 1016 h exposure to NSS

The test results from the salt-spray test are found in the table below:

Table 4: Rating of the test panels in accordance to ISO 10289 Annex A, after exposure to neutral salt-spray following ISO 9227. (-) meaning test was discontinued. (n.a.) meaning non-available

Sample ID	Exposure time in neutral salt-spray in accordance to ISO 9227 [h]. Rated following ISO 10289, Annex A								
	24	48	72	168	336	672	720	766	1016
1	n.a.	n.a.	n.a.	8	-	-	-	-	-
3	n.a.	n.a.	n.a.	8	-	-	-	-	-
4	n.a.	n.a.	n.a.	8	-	-	-	-	-
13	n.a.	n.a.	n.a.	10	-	-	-	-	-
15	n.a.	n.a.	n.a.	10	-	-	-	-	-
16	n.a.	n.a.	n.a.	10	-	-	-	-	-
21	n.a.	n.a.	n.a.	3	-	-	-	-	-
22	n.a.	n.a.	n.a.	4	-	-	-	-	-
24	n.a.	n.a.	n.a.	6	-	-	-	-	-
31	n.a.	n.a.	n.a.	7	-	-	-	-	-
32	n.a.	n.a.	n.a.	4	-	-	-	-	-
33	n.a.	n.a.	n.a.	3	-	-	-	-	-
41	n.a.	n.a.	n.a.	8	-	-	-	-	-
42	n.a.	n.a.	n.a.	8	-	-	-	-	-
44	n.a.	n.a.	n.a.	9	-	-	-	-	-
51	n.a.	n.a.	n.a.	0	-	-	-	-	-
52	n.a.	n.a.	n.a.	0	-	-	-	-	-
55	n.a.	n.a.	n.a.	0	-	-	-	-	-

3D4	10	upper 1x10 is a 7, rest is 10	upper 1x10 is a 7, rest is 10	1/5 = 6, 4/5 = 10	Upper 2 cm = 6, rest = 10	-	Outer 3 cm =5, rest a 9 or 10	-	-
3D6	10	0.5x5 is a 7, rest is 10	0.5x5 is a 7, rest is 10	9	left edge = 5, rest = 9	-	Outer 1.5 cm = 5 or 6. Rest 10	-	-
3D5	9	upper 0.5x16.5cm is 4, rest is a 10	upper 0.5x16.5cm is 4, rest is a 10	2 cm half round = 5, rest 10	2 cm half round = 5, rest 10	-	Moon shape with 4. Rest 10	-	-
3F5	7	5	5	2	1	-	-	-	-
3C5	10	10	10	10	10	-	10	-	10
3C4	10	10	10	10	2cm half way round = 5, rest 10	-	10	-	10
2F1	4	2	2	1	-	-	-	-	-
2F1	4	2	2	1	-	-	-	-	-
2F2	4	3	3	1	-	-	-	-	-
2E2	9	7	7	5	3	-	-	-	-
2E1	8	7	7	5	4	-	-	-	-
2E1	8	7	7	5	4	-	-	-	-
2C1	10	8	8	2	1	-	-	-	-
2D2	7	5	5	2	1	-	-	-	-
2D1	5	3	3	2	1	-	-	-	-
2D2	5	4	4	2	1	-	-	-	-
2B1	10	10	10	10	10	-	-	-	-
2B2	10	10 (spots)	10 (spots)	9	9	-	-	-	-
2B1	10	10	10	10	10	-	-	-	-
2C2	1/3 6 rest 10	8	8	2	2	-	-	-	-
2C1	10	10	10	5	3	-	-	-	-
4DA1	8	7	n.a.	4	3	-	-	-	-
4DA2	8	7	n.a.	4	3	-	-	-	-
4DB1	10	10	n.a.	10	5	-	-	-	-
4DB2	10	10	n.a.	6	-	-	-	-	-
4DA1	8	7	n.a.	4	3	-	-	-	-
4DA2	8	7	n.a.	4	3	-	-	-	-
5DB1	10	10	10	10	10	9	n.a.	9	n.a.
5DB2	10	10	10	10	10	10	n.a.	10	n.a.
5DB3	10	10	10	10	10	10	n.a.	10	n.a.

7 DISCUSSION

The intention of the project was to find the characteristics of hard chrome coatings produced using various patterns of direct current pulse current and pulse reverse current. It did not succeed because the corrosion resistance of the various coatings showed up to be fluctuating in unpredictable ways.

We did succeed to produce hard chrome coatings being able to withstand the salt-spray test for more than 750 hours (3C5 and 5DB series). The coatings in the 5DB series are DC plated hard chrome with 2 PR chrome layers build in as designed. These coatings are fairly identical to the coatings produced at Nichro in 2009 withstanding the salt-spray test for more than 500 hours. The activation procedure however might not be the same.

The 3C5 coating (DC plated hard chrome) withstanding more than 1000 hours in the salt-spray chamber is unexpected. It is produce using our normal ramp-up activation followed by DC plating at fairly low current density. The same current pattern is used for producing the 1C coatings except that the current density has been increased. The DC plated hard chrome coatings of 1C only withstand the salt-spray test for less than 168 hours. The 1C and 3C series are plated on circular panels while the 2C series is plated on an inner pipe surface. The parameters for plating 2C and 3C are identical except for the coating thickness. It turns out however that the 2C withstands corrosion for less than 48 hours. The main difference plating panels versus inner pipe surfaces is the content of hydrogen in the plating electrolyte being much higher within the pipe.

It seems that the current density, the layer thickness and the hydrogen concentration is vital for the corrosion resistance of the plated hard chrome coatings.

The 4DA and the 4DB coatings (DC plated hard chrome with 2 PR layers build in) were produced with the same rectifier settings except for the activation procedure. The 4DA used our ramp-up settings whereas the 4DB was activated using reverse current only. It turned out that the 4DA could stand no more than 24 hours in the salt-spray chamber whereas one half of the 4DB pipe started corroding after 72 hours and the other half after 168 hours. The difference between the two 4DB half pipes might indicate that the one part is fresh material whereas the other part has been stripped before plating. This means that the plating process might lead to irreversible changes in the base material.

It seems that the activation procedure and the condition of the base material do have some impact on the corrosion resistance of the plated hard chrome coating; maybe a vital impact!

Series 1F (pure PR plated hard chrome) demonstrates in fact that the outmost surface of the base material is changed when being plated. The PR parameters used for plating the 1F series included a very high current density. The resulting hard chrome surface looked nice but could stand less than 24 hours in the salt-spray tests. The 6 panels of the 1F series were stripped for being reused in the next plating series. Four of the plates were used in series 3F together with 2 fresh panels. It turned out that the 4 panels being stripped could not be plated again. Of the 4 panels being stripped two of these has been tested in the salt-spray chamber whereas the other two has been kept as reference.

DTU performed GD-OES analysis on these panels trying to describe the changes of the base material. Unfortunately they did not perform a similar analysis reference measurement on a fresh Ovako 280 panel. Thus we do not have a description of the changes in the base material caused by PR plating parameters but the GD-OES did confirm that changes took place.

The few but large cracks of sample 56 (1F series – solely PR hard chrome) coincide with the dried-out riverbed pattern seen after the salt-spray testing. This bleeding from the cracks indicates that these fewer but wider cracks go all the way through to the base material. Thus fewer cracks itself are not necessarily preferable if these go straight through the coating and reach the base material. The base material itself is steel of the type Ovaco 280 containing manganese in the surface. It might be so that the manganese is involved in side-reactions forming stabile compounds preventing further plating. If this is the case it indicates that the base material itself affects the properties of the hard chrome.

All samples were plated in a hard chrome bath used for commercial production. The bath conditions and the bath composition are controlled periodically be means of lab-analysis. The lab-results are used for adjusting the plating electrolyte in such a way that the Cr^{6+} concentration ends at approx. 300 g/l and the ratio between chromic acid and sulphuric acid ends at approx. 100. The amount of impurities is kept below 3 g/l Cr^{3+} while impurities of iron and other metals are left in the plating bath as long as the throwing power is acceptable. The tests made at Nichro in 2008 – 2010 were all plated in a fresh lab-scale plating bath.

The difference between the commercial hard chrome plating bath and the lab-scale electrolyte used for sample plating in 2009 is that the chemistry of the commercial bath varies much more than the chemistry of the lab-scale plating bath. It might affect the corrosion resistance of the hard chrome coatings much more than expected. Sample 3C5 was plated just after adjustment of the plating bath, which indicates that the concentration of catalyst, chromium and impurities do have a vital impact on the corrosion resistance of the plated hard chrome coating.

8 CONCLUSION

The corrosion characteristics of the hard chrome coating are influenced by numerous parameters in very complex and unpredictable ways. It is quite easy to design and plate a multilayer hard chrome coating with build-in layers of pulse or pulse reverse plated layers. In contrast to the micro-cracked pillar structure of the direct plated hard chrome the PR-plated layers consists of a very fine nano-crystalline structure, crack-free or with a few cracks only. Unfortunately these cracks might go all the way through the coating down to the base material.

We have demonstrated that high current densities must be avoided as these favours formation of cracks through the whole coating. Furthermore such current densities might change the structure of the base material prohibiting future reprocessing. At the same time it is obvious that the PR-pattern cannot be chosen freely. The activation procedure as well as the PR-plating parameters must allow the build-in hydrogen to escape from the coating and enhance the re-crystallisation of the chromium lattice in such a way that the internal stress of the hard chrome coating is released.

Unfortunately it seems that the base material and its history affects the corrosion resistance of the hard chrome coating in an unpredictable and uncontrolled way. The same might be the case for the hard chrome electrolyte itself keeping sample 3C5 in mind. It seems that the concentration and the balance of chromium, catalyst and impurities are vital for the corrosion characteristics of the hard chrome coating (unless the lifetime of 3C5 in salt-spray is false owing a defect salt-spray chamber).

It seems correct to assume that the corrosion resistance is vulnerable to variations in the plating bath composition, concentration and condition and vulnerable to the base material and its history. Consequently it is not advisable to scale up the plating process to full-scale operation based on this investigation and maybe up-scale might not be possible at all.