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Summary of steel pre-coating materials, characterization and coating and manufacturing process

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Materials and Manufacturing Processes

Stainless Steel Substrates

There are several specialized ferritic stainless steel grades with a chemical composition specially designed to be used as interconnects in solid oxide fuel cell applications in a temperature interval of 600-850°C. Two examples are the steel grades Sandvik Sanergy HT and Thyssen Krupp's Crofer 22 APU (EN 1.4760). These steels have good high-temperature mechanical properties and corrosion resistance as well as acceptable electron conductivity in the formed oxide scale.

However, these specialized steels have a high production cost due to alloying elements. Two less expensive steels AISI441 (EN 1.4509) and Outokumpu 4622 (EN 1.4622) were selected (see Table 1) for use in combination with Sandvik Materials Technologies precoating concept.

Table 1. *Composition steels 1.4622 and 1.4509*

	Outokumpu 4622	AISI441	Crofer 22 APU
Element	1.4622	1.4509	1.4760
C	0,019	0,014	0,03
Si	0,45	0,59	0,5
Mn	0,38	0,35	0,5
P	0,032	0,03	0,05
S	0,001	0,001	0,02
Cr	20,8	17,56	20-24
Ni	0,2	0,26	
V	0,07		
Ti	0,12	0,173	0,2
Cu	0,38		0,5
Al		0,006	0,5
Nb	0,25	0,39	
N	0,023	0,017	
La			0,2

(weight-%) of stainless used in the project.

Coating Process

Sandvik Materials Technology has developed a PVD (physical vapor deposition) process with roll to roll type continuous evaporation coating of full width strip steel. The process significantly shortens the value chain for bipolar plate/interconnect production. It also ensures homogenous coating of the whole strip surface and repeated quality from batch to batch.

Complex coatings with multiple-layer options are applied to a strip in motion. The pre-treatment ensures a clean metallic surface, with a good adhesion between the substrate and the coating. All coatings are characterized by very low content of impurities and foreign elements. The coating process also assures close thickness tolerances of the surface layer. For solid oxide fuel cells the standard coating is cerium (Ce) and cobalt (Co).



Figure 1. Sandvik's production facility TERRA for precoated strip products located in Sandviken, Sweden.

Sandvik's coating technology is environmentally friendly, with no discharge to water or air, and no toxic residues. The coating process is also energy efficient compared to electroplating, which consumes approximately 60% more energy. A schematic overview of the process is displayed in Figure 2. The connection in the project between Sandvik and Borit and the total production route benefits are explained in Figure 3.

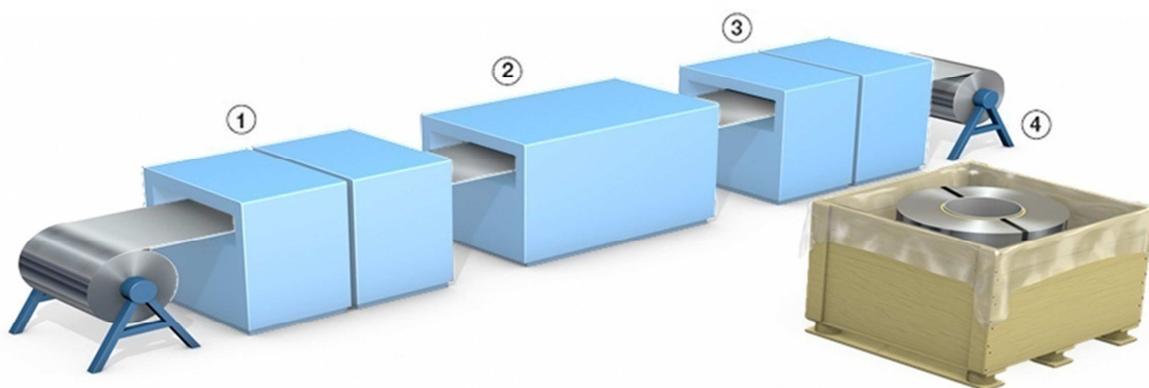


Figure 2. Schematic overview of the pre-coated strip production at Sandvik.

Process steps in Sandvik's coating process (Figure 2) are as follows:

1. Cleaning/inspection

Cleaning is important for good adhesion. To avoid harmful defects, the whole area of the strip surface is inspected – both sides.

2. Coating

Coating of metal layers by Sandvik's continuous evaporation coating process.

3. Inspection

Automatic X-ray inspection devices measure the thickness and quality of the coating.

4. Testing, slitting and packaging

After coating, the steel strip is inspected and tested (for example tensile, hardness and surface properties). The process is completed by slitting to the required width, control of burr height, width and shape, and finally by packaging and shipment.

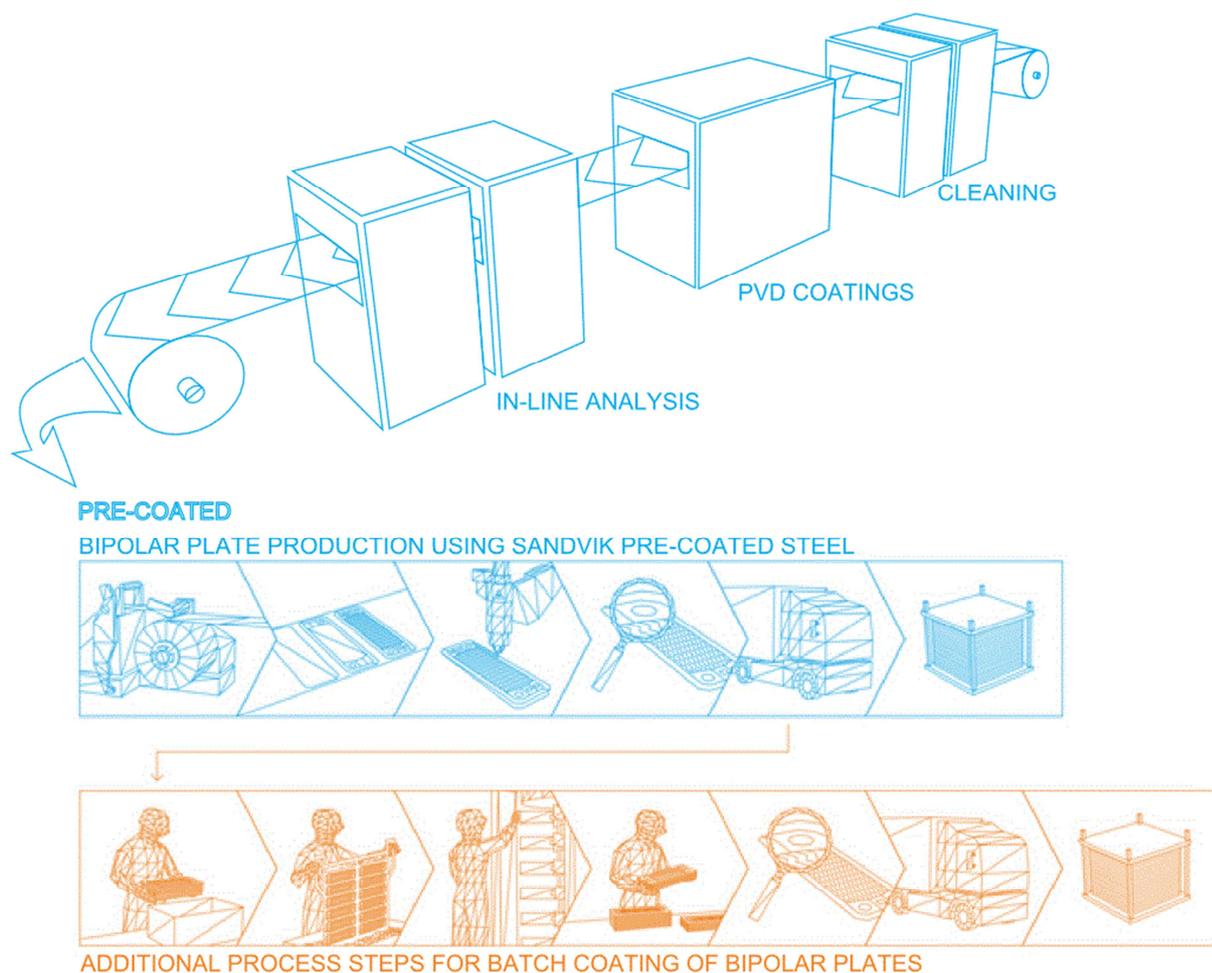


Figure 3. Blue route: The steel coil is first cleaned, then coated in one or multiple steps, analyzed and then shipped for shaping at Borit. The Sandvik coil-coating concept together with Borit’s hydroforming enables an industrial interconnect production process that shortens the entire value chain by eliminating the costly need of coating of individual plates i.e. the additional process steps (in orange above). The principal difference in manufacturing flows from raw material coil to final fuel cell stack can be described as in the illustration above.

Hydroforming Process

Based on the experiences gained in the project, the process flow to produce welded bipolar plates for fuel cells at Borit is presented below in Figure 4.

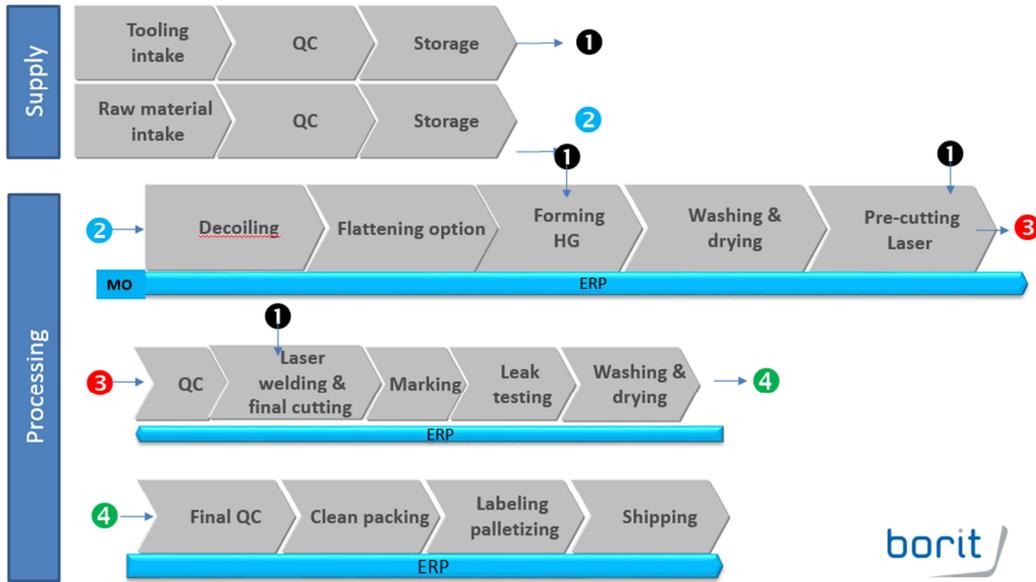


Figure 4. Process flow for production of welded bipolar plates

Using the proprietary forming process called *Hydrogate*, the individual parts are formed using a forming tool as shown below. The inherent gentle nature of the hydroforming process guarantees good compatibility with coated (and uncoated) raw materials.



Figure 5. Die for hydroforming interconnects

The forming pressure used in the *Hydrogate* process is 1750 bar. After laser cutting, where a dedicated cutting tool is used, 2 parts with an additional insert have been welded together. A dedicated laser welding tool and set-up has been manufactured in order to enable welding of the separate plates. After welding, all interconnects are leak tested to ensure the quality of the welded contour. Due to some height differences in the sealing contour, the standard leak test is not possible. The plates have been leak tested using a bubble test.

After this significant initial set-up phase for the laser welding process, the yield during production is close to 90%. Based on the current process flow, and with further automation of the welding assets, Borit is ready to start ramping up the production volume of welded bipolar plates. The capacity for the year 2017 is estimated at around 500 000 pieces.

Experimental Methods & Results

Long Term Oxidation Tests

All exposure tests at VTT were done at the temperature of 700 °C. Dry air was fed into the furnace with the rate of 1 l/min. Both Ce/Co-coated and uncoated samples with all three steel grades (AISI441, Outokumpu 4622, Crofer 22 APU) were analysed. Tests were carried out in pipe furnace at VTT Technical Research Centre of Finland Ltd and parallel samples were analysed with SEM/EDS by Sandvik Ltd and Juhan Subbi from KBFI. Two rounds of tests were performed. First one lasted 1000 h and second one 5000 h. In the second test one batch of samples was removed already after 1000 h in order to repeat the first test.

After 1000 h of exposure, in most of the samples no Cr diffusion to the coating was seen which indicates that coating is working as wanted. Only in second test with Crofer 22 APU samples there was some Cr diffusion as there was Cr-rich crystals detected in the surface of the samples after 1000 h (**Figure 6**). Also, in the first 1000 h test with Crofer 22 APU samples, significant Fe diffusion from steel to coating was seen as after exposure the top layer of the coating was CoFe-spinel. In the second 1000 h test Fe-diffusion was no more detected which could be due to better sample treatment.

Contrary to Cr- and Fe-diffusion, manganese diffusion to the coating is desired in order to attain the MnCo-spinel structure. The diffusion of manganese was varying quite a lot depending on the steel material. After 1000 h of exposure Mn/Co-ratio in the coating was about 1/40 with AISI441, 1/8 with Outokumpu 4622 and 1/5 with Crofer 22 APU.

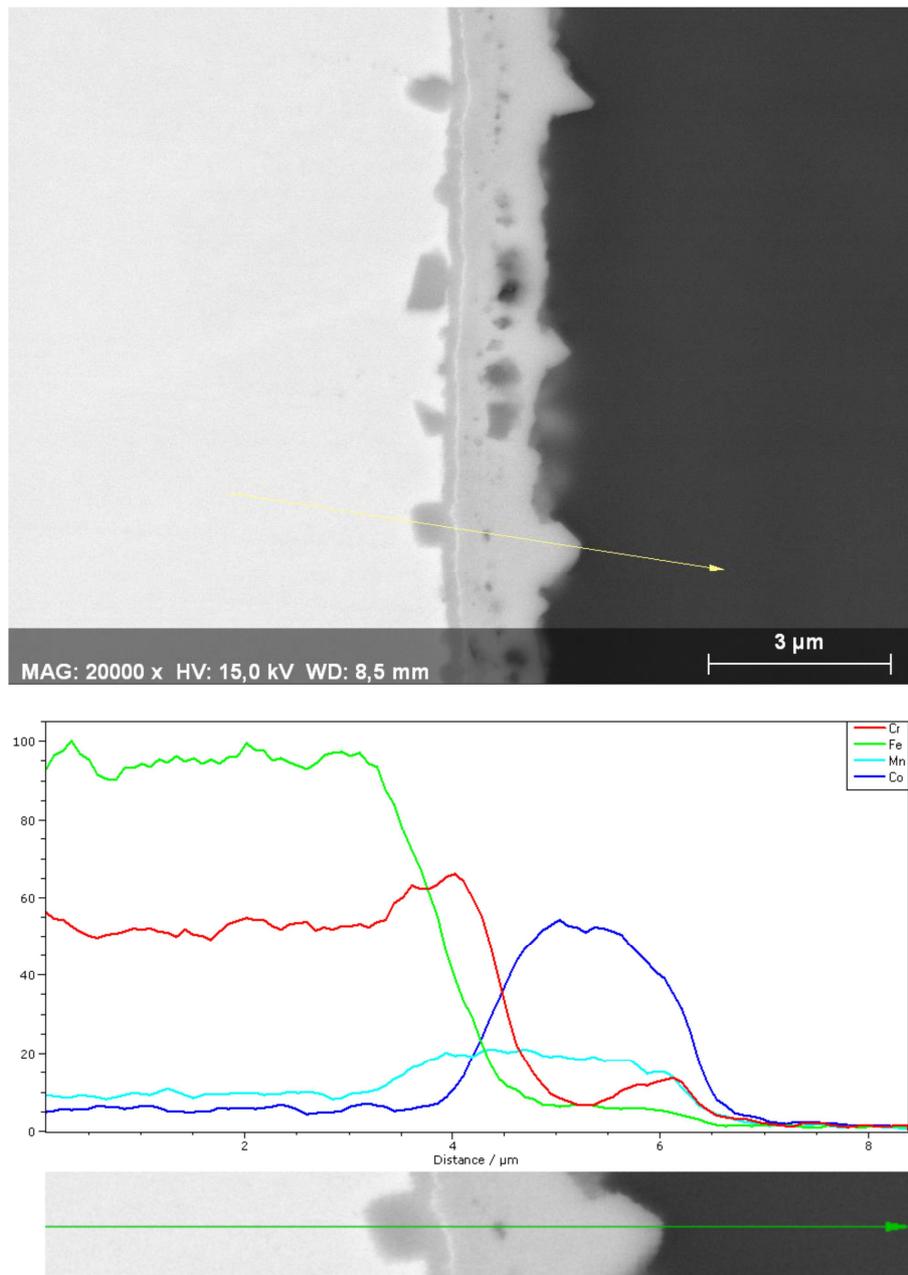


Figure 6. SEM picture and EDS linescan of coated Crofer 22 APU after 1000 h of exposure at 700 °C in dry air.

The results from the longer 5000 h test were in line with the shorter tests. Co/Ce-coating prevents the diffusion of chromium effectively. Only in the case of Crofer 22 APU some local chromium diffusion was detected. Also, no Fe-diffusion was seen with Crofer 22 APU in the 5000 h test as can be seen in **Figure** . Amount of manganese in the coatings continued to increase as exposure time increased as suspected. After 5000 h Mn/Co-ratios in the coating were 1/7 with AISI441, 1/4 with Outokumpu 4622 and close to 1/2 with Crofer 22 APU. Thus, in the Crofer 22 APU samples compositions would already be that of MnCo-spinel.

With uncoated Outokumpu 4622 after 5000 h there was some Si and Cu detected in the surface as well. The higher mobility of silicon in Outokumpu 4622 could be due to lower Nb/Si-ratio compared to AISI441. Nevertheless, Co/Ce coating was discovered to be effective in preventing the unwanted diffusion of these elements as well.

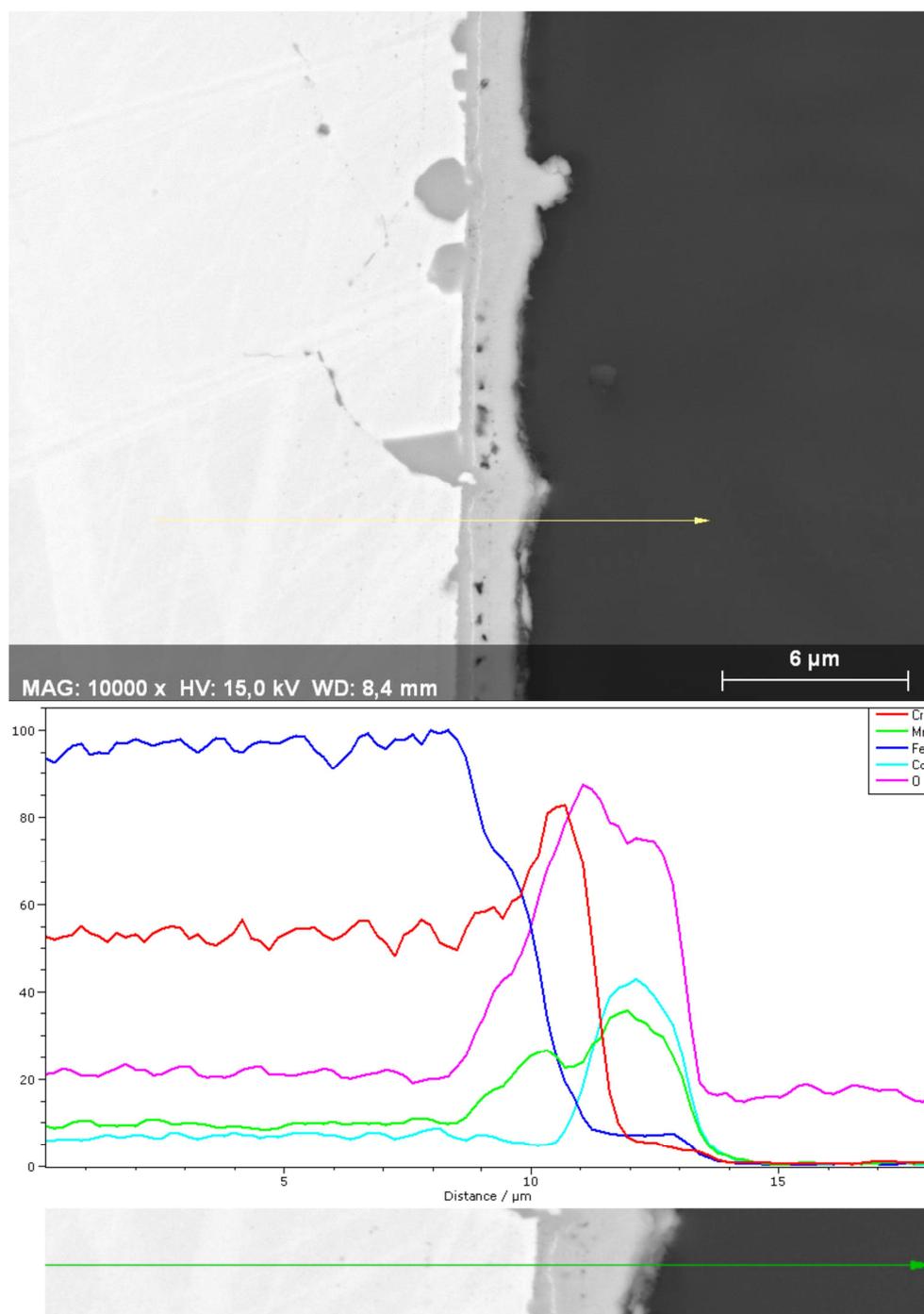


Figure 7. SEM picture and EDS linescan of Co/Ce-coated Crofer 22 APU after 5000 h of exposure at 700 °C in dry air.

There were some drawbacks with the coated steels as well. All the coatings had rather high porosity after heat-treatment due to Co-diffusion from coating to steel. This was especially the case with 441 steel. Also, it seems that coating enhances the formation of Si-rich layer in the interface between metal and oxide scales. However, this was not detected with Crofer 22 APU samples. It was also seen that the adhesion of coating to metal was much better with Crofer 22 APU than with AISI441 and Outokumpu 4622. This is

probably due to lack of Si-rich layer. Also the composition of coating in Crofer 22 APU is closer to spinel which could also lead to better adhesion.

Total thickness of oxide layer and coating is of course relevant as well. In Table 2 all thicknesses after 5000 h of exposure are listed. In all steels Co/Ce-coating reduces the thickness of the oxide scales. Thinnest it was with Crofer 22 APU and thickest with Outokumpu 4622.

Table 2. Thicknesses of oxide layers and coatings after the 5000 h exposure at 700 °C in dry air.

sample	thickness of oxide layer (µm)	thickness of coating (µm)
uncoated AISI441	1.0-1.5	
coated AISI441	0.5-0.7	1.1-1.3
uncoated Crofer 22 APU	1.0	
coated Crofer 22 APU	0.5	1.0-1.3
uncoated Outokumpu 4622	0.8-1.3	
coated Outokumpu 4622	0.6-0.8	1.0-1.3

Cyclic Oxidation

Cyclic oxidation for more than 15,000 hours of pre-coated AISI441 (EN 1.4509) and Outokumpu 4622 (EN 1.4622) at 800°C is displayed in Figure 8. Coupons of the materials exposed and the mass gain is measured by weighing of the coupons at different exposure times. In Figure 9 cross sections of selected samples were examined by light microscopy and scanning electron microscopy with energy dispersive spectroscopy (SEM+EDS) to understand if long term exposure of the steels changes the microstructure as well as the coating. The micrographs in Figure 9 show grain growth of Outokumpu 4622 with increased exposure time, which is not seen in AISI441 (1.4509). In SOFC applications lifetime of the stack of beyond 40,000 hours is desired and the grain growth seen in Outokumpu 4622 is a problem for long term exposures.

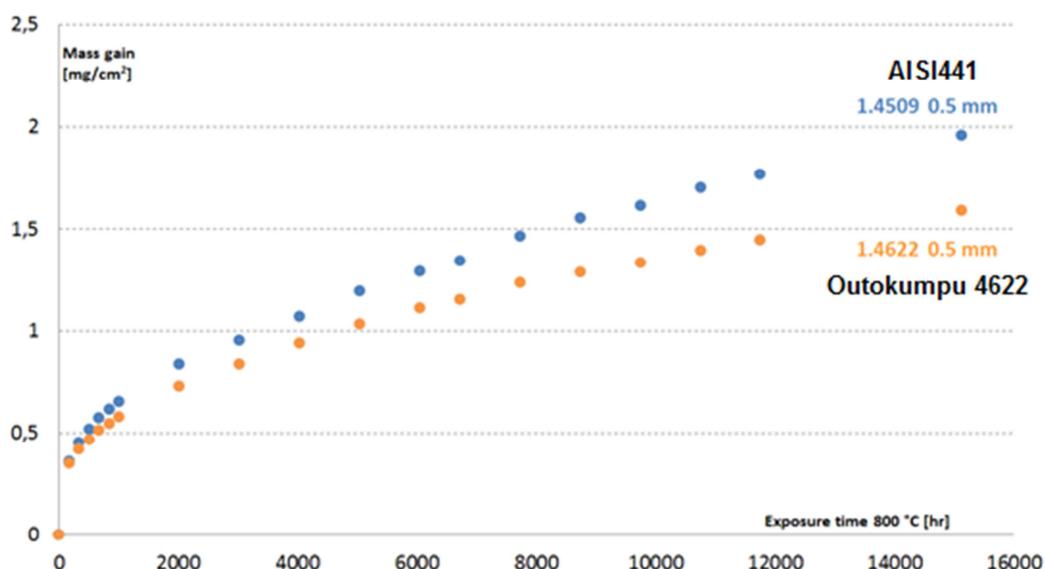


Figure 8. Cyclic oxidation of Ce 10 nm/Co 600 nm pre-coated 0.5mm stainless steels at 800°C in ambient air.

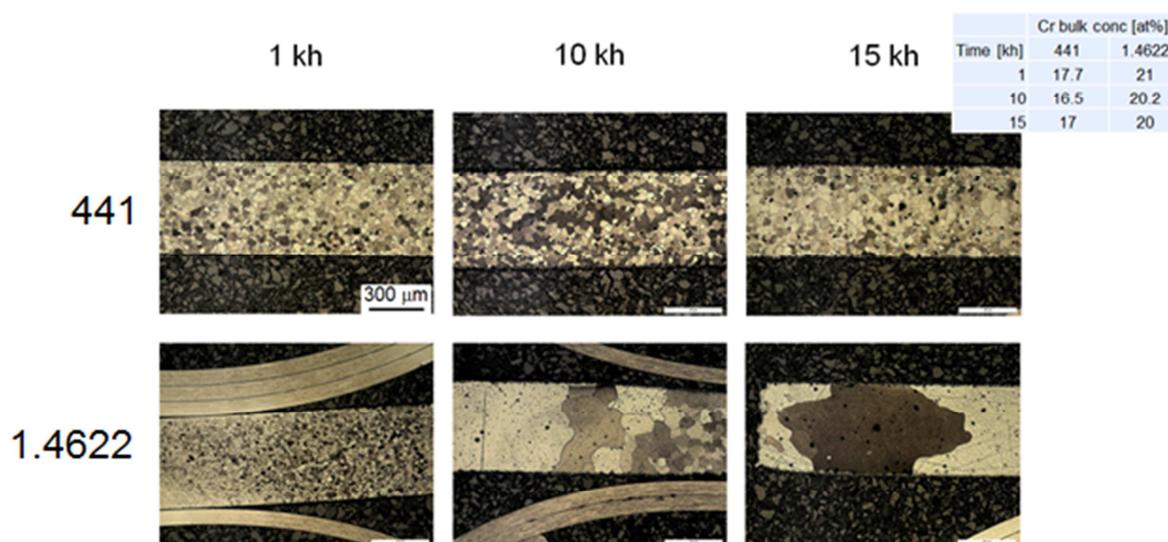


Figure 9. Cross sections examined by light microscopy of precoated stainless steels exposed to cyclic oxidation at 800°C in ambient air. The different exposure times of 1000, 10,000 and 15,000 hours show grain growth of Outokumpu 4622 with increased exposure time, which is not seen in AISI441. The chromium (Cr) bulk concentration is measured by SEM EDS.

Forming Trials

During forming operations of the pre-coated steel the coating is bound to crack when the substrate material is stretched. Earlier studies have shown that thin cracks (few micrometer) in the coating will become enclosed due to the instant volume expansion that follows when the metallic cobalt becomes oxidized [1,2].

A cerium cobalt coated AISI441 steel sheet was cut to 240×240 mm². The sample was biaxially formed in a conventional deep drawing cup test set up (Erichsen). The bottom surface of the cup was subjected to biaxial straining in the plane. The steel sheet was strained to roughly 10%, which was found to be the limit before the steel would fracture.

The strained sample was examined in a scanning electron microscope (SEM). It was seen that the coating had cracked during the forming operation. Parts of the cracked surface can be seen in Figure 10 in the upper left image. None of the examined cracks on the sample exceeded 5 μm in width. This figure can be thought of as an approximate upper limit for the crack width because the sample was strained to the very limit before the steel would rupture. Despite the cracks, no delamination could be observed on the surface, indicating good adhesion between the substrate and the coating.

The cobalt maps shown in Figure , recorded with energy dispersive x-ray spectroscopy (EDS), confirm that no or only very little cobalt was present in the cracks after forming. During the initial oxidation the smallest cracks (< 1 μm) would become enclosed due to the volume expansion of the metallic cobalt coating when

this was oxidized. At 800 °C the oxidation of 600 nm cobalt happens within a couple of minutes. After an hour of oxidation, small (~100 nm) oxide grains protruding from the cobalt coating became evident but no further sealing of the cracks was observed. When the sample had been exposed for 168 hours (one week) at 800 °C the entire sample surface had become clearly oxidized with oxide grains, ranging from a few hundred nanometers to a couple of micrometers. At this stage no traces of the cracks were seen and the EDS map indicated that cobalt was now present over the entire surface.

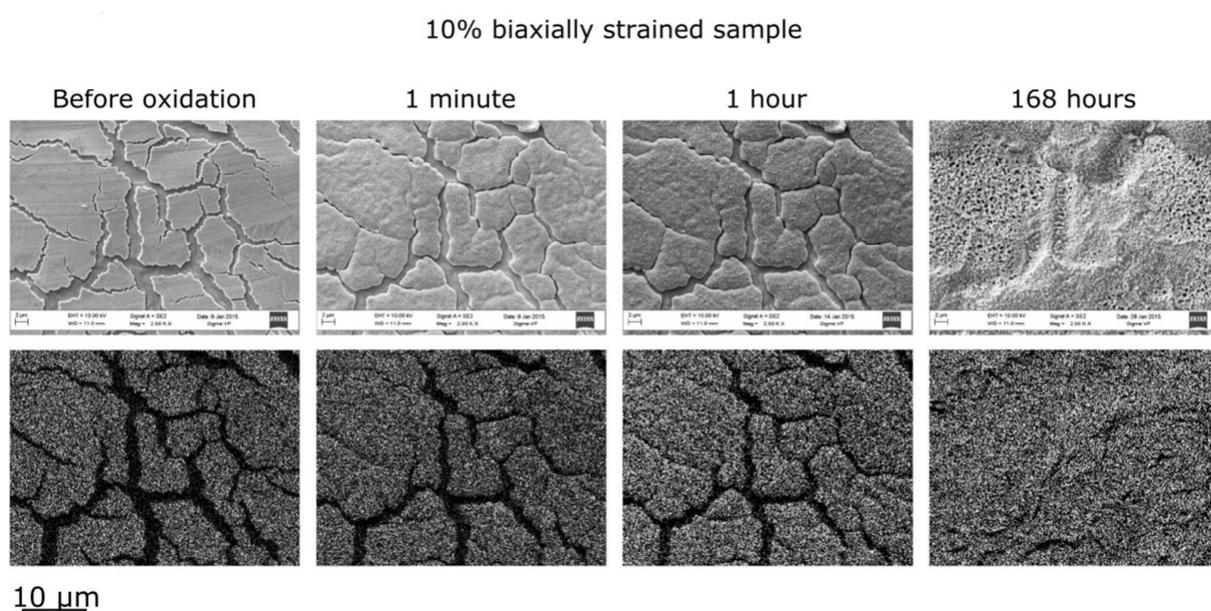


Figure 10. SEM images of strained and oxidized (800 °C) samples (top), EDS cobalt maps from corresponding areas (bottom).

Surface Diffusion of the Coating

Before coating the sheets, one of the samples was marked with a thin line, drawn with a felt pen. After the coating step the line (and the coating on top of it) was removed using an ethanol soaked cotton q-tip. This would create a well-defined stripe where no coating was present on the surface. In this uncoated region a trench was milled at a set distance (13 μm) away from the coated border using a focused ion beam (FIB), see Figure 11. This trench could then be used as a reference point during oxidation trials.

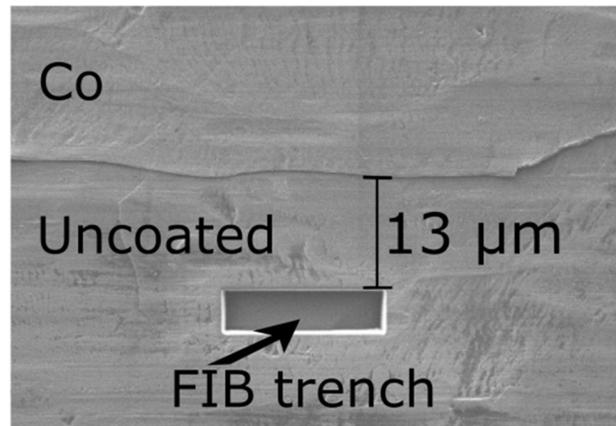


Figure 11. A FIB trench was milled as a reference point close to the edge.

When stretching the coated steel in the deep drawing cup test or in a tensile test rig cracks were generated in the coating up to 5 μm wide. After that point the steel would fracture. The masking approach described above was therefore used to produce larger areas without any coating. The masked sample with the FIB trench milled into it was oxidized and examined in the SEM. After 504 hours (three weeks) of oxidation at 800 °C a second FIB trench was milled at a right angle towards the first trench. This second trench, which was about 26 μm wide, stretched from one of the short ends of the first trench and roughly 13 μm into the coated part of the steel, shown in Figure .

The second trench therefore showed both the previously uncoated area and the coated part of the sample. Interestingly the oxide formation of the two had much resemblance. As commonly seen for these cobalt coated steels the upper oxide scale was dominated by two fairly distinct layers. These have been shown to consist of an upper spinel type oxide and beneath a chromia layer [3].

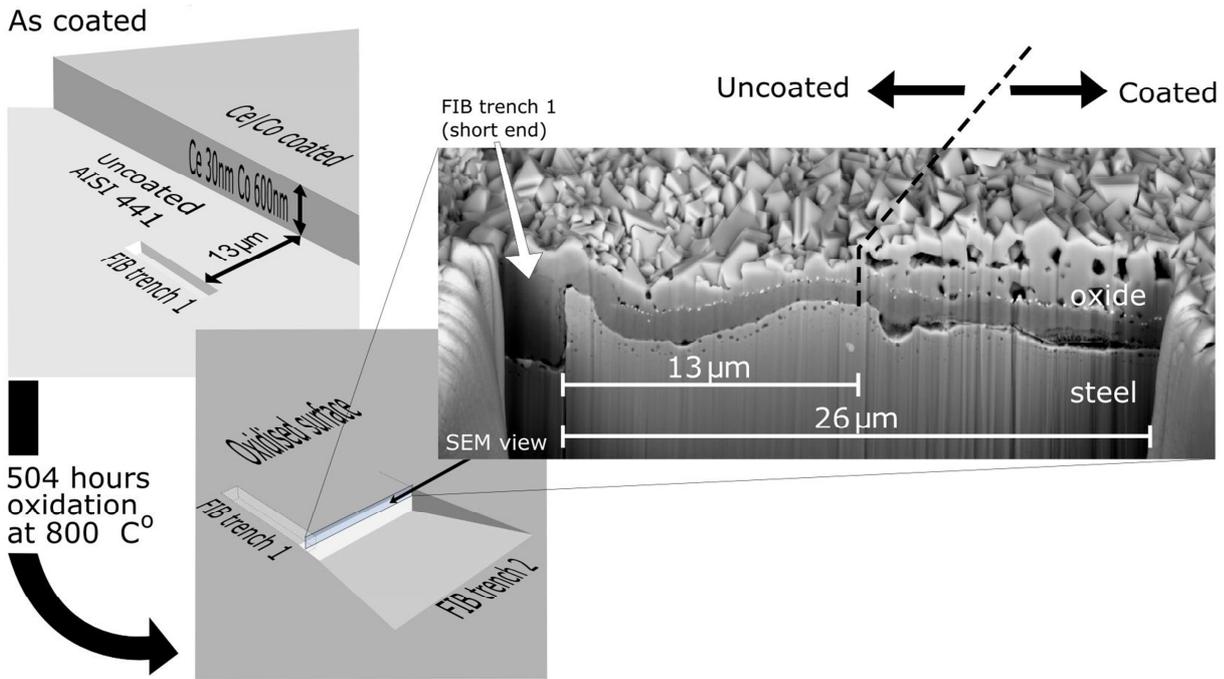


Figure 12. The AISI441 sample was masked before being coated with 30 nm cerium and 600 nm cobalt, respectively. With the mask removed a sharp border between coated and uncoated surface was created. After oxidation at 800 °C the formed oxide of the uncoated part was examined. Cerium rich particles were detected in the scale as far as 10 μm away from the coated area.

In Figure 13 the progression of the cobalt diffusion is shown by EDS maps collected at different exposure times. As discussed earlier, when stretching the coated steel in the deep drawing cup test or in a tensile test rig the cracks generated in the coating had widths up to 5 μm. This demonstrates how diffusion from one side of a crack would progress. However, in a real application the cobalt would diffuse from both sides of the crack on the sample surface. Consequently, cracks up to 25 μm could be self-healed based on the cross-sections in Figure 13 given enough exposure time and temperature is supplied.

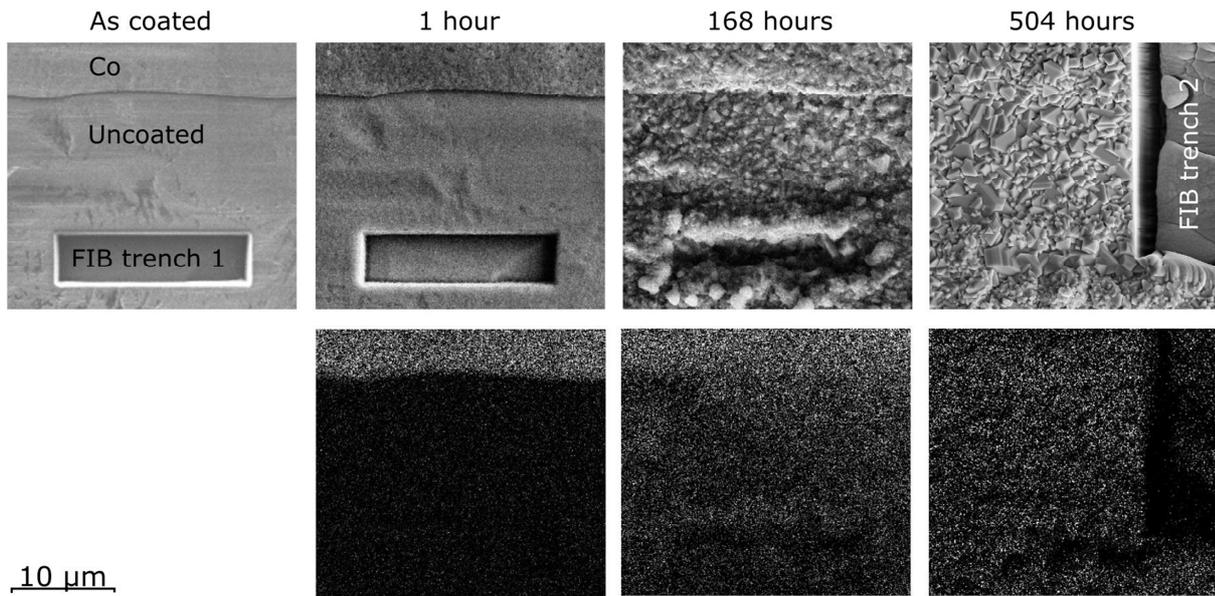


Figure 13. Top row shows SEM images of the investigated area before and after 1 hour, 168 hours and 504 hours of oxidation at 800 °C. The bottom row shows cobalt EDS maps of the oxidized samples.

Dual-Atmosphere (air/fuel) oxidation tests

Dual-atmosphere oxidation tests were conducted at 650 °C up to 1000 h at ENEA CR Casaccia premises. Uncoated Crofer 22 APU samples from a thin foil (0.2 mm thickness) were cut to a round shape (20 mm diameter) and mounted into a conventional single fuel cell test system, which allowed a continuous monitoring of contact resistance during the dual-atmosphere oxidation exposure (Figure 14). Humid air was fed at the air-side of the steel sample at 100 ml/min, while fuel gas was fed at the opposite side of the steel sample at a rate of 25 ml/min. Two different fuel gas compositions were used for these tests:

- 1) humid hydrogen gas (97 H₂ – 3 H₂O)
- 2) simulated syngas (5 CH₄ – 5 CO – 27 CO₂ – 18 H₂ – 44 H₂O)

The temperature profile chosen for conducting the experiments is illustrated in Figure 15. During heating up of the cell, the anode side of the cell was fed with dry nitrogen flowing at 25 ml/min. Change to fuel gas was done at the beginning of the dwell 650 °C segment. Contact resistance between the sample surfaces and gold current collectors was measured every 24 h and reported in terms of Area Specific resistance (ASR) by using Electrochemical Impedance Spectroscopy (EIS). The impedance at high frequency was used to estimate the ASR values. No duplicate exposure tests were performed. Post-mortem analysis was performed with SEM/EDS and X-Ray Diffraction (XRD) analysis.

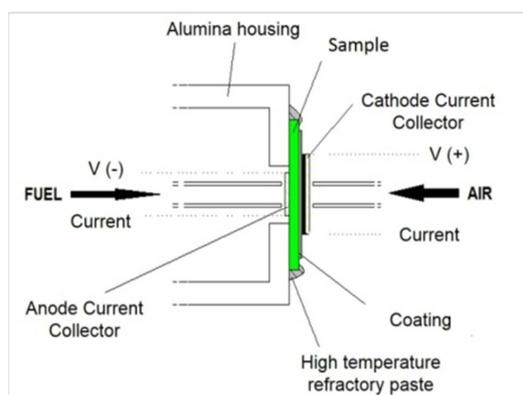


Figure 14. Schematic representation of the single cell system used for the dual-atmosphere oxidation tests.

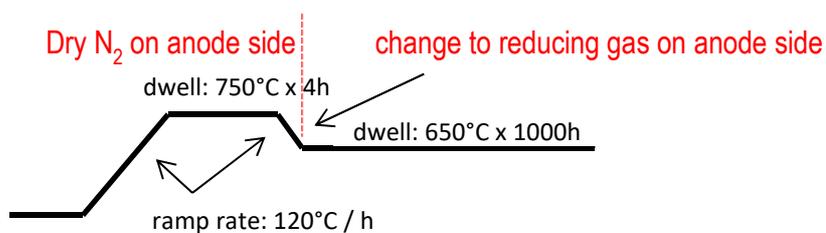


Figure 15. Temperature profile program for the dual-atmosphere single cell tests.

Figure 16 reports the ASR contact resistance results. It is seen that contact resistance evolves gradually in both the cases, although higher resistances are obtained when humid hydrogen was chosen as fuel gas. No breakaway corrosion degradation features are observable from the ASR values.

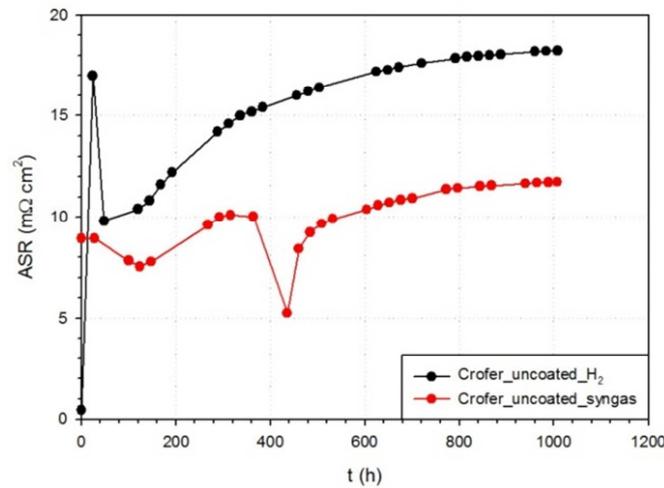


Figure 16. Evolution of ASR contract resistance values during dual-atmosphere oxidation in single cell tests.

After 1000 h exposure at 650°C, post-mortem analysis indicated a severe corrosion degradation on the air-side of the uncoated Crofer 22 APU steel. The oxidized surface on the air side of the steel samples was covered with a continuous, homogeneous and thick layer of hematite. However, thickness of the hematite layer was significantly higher in case of humid hydrogen chosen as fuel gas.

XRD spectra of the air-side surface of samples after 1000h exposure at 650°C is illustrated in Figure 17. Hematite is the main phase present in both the cases. However, substrate signal is detected only in the case of syngas fuel gas suggesting that thickness of the hematite layer is much higher when humid hydrogen is used as fuel gas.

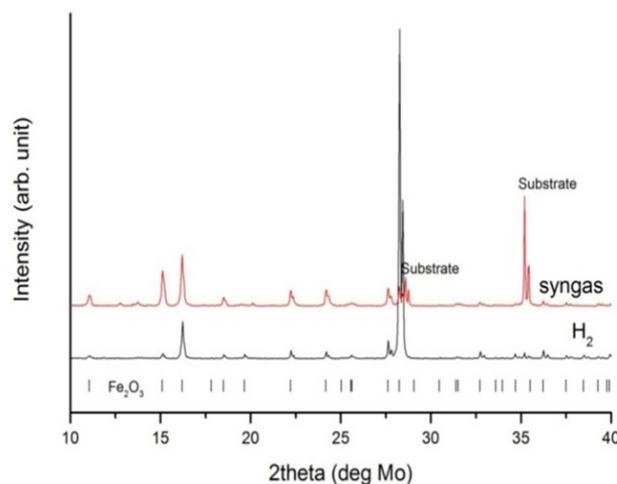


Figure 17. XRD spectra of uncoated Crofer 22 APU after 1000h exposure at 650 °C in dual-atmosphere oxidation conditions using syngas and humid hydrogen as fuel gases

Metallographic cross-sections of the oxide scale grown on the air side of the Crofer 22 APU samples (Figure 18) were in line with the XRD results indicating the formation of a continuous hematite layer with a thickness of about 50-60 μm when the anode side was exposed to humid hydrogen and 10-15 μm when exposed to syngas.

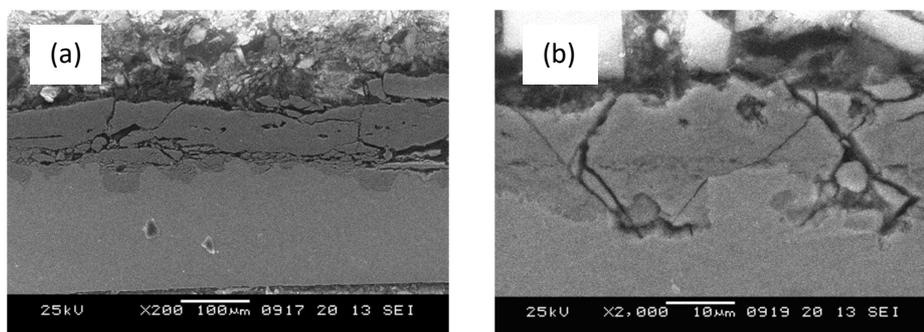


Figure 18. Metallographic cross-section of uncoated Crofer 22 APU after 1000 h exposure at 650 °C with two different fuel gases: (a) humid hydrogen; (b) syngas

The surface morphology along with EDS mapping of Fe and Cr elements of the air-side oxide scale is seen in Figure 19. A more porous and apparently less protective oxide structure is visible in the case of humid hydrogen as fuel gas. Element mapping clearly indicates that Fe covers homogeneously the entire surface in both the cases with no distinct differences in the surface composition of the oxide scale.

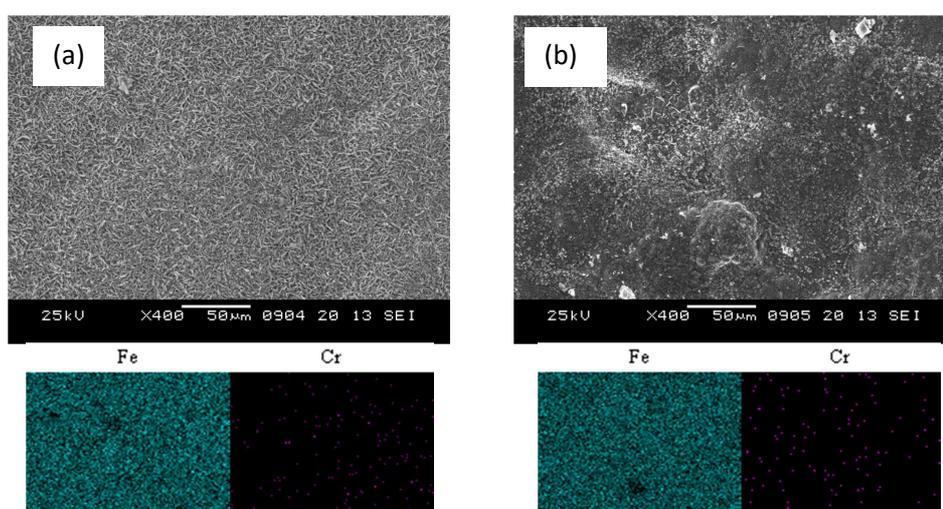


Figure 19. Surface morphology of the air-side oxide scale of uncoated Crofer 22 APU after 1000 h exposure at 650 °C with two different fuel gases: (a) humid hydrogen; (b) syngas

Figure 20 shows that no significant differences can be observed in the morphology of the fuel-side surface after testing. In both the cases, the surface appears decorated by lines of oxide particles grown along the grain boundaries of the steel. The oxide particles are essentially formed of Cr,Mn-oxides (presumably, with spinel structure) containing some Si and Nb and even minor amounts of La and Al.

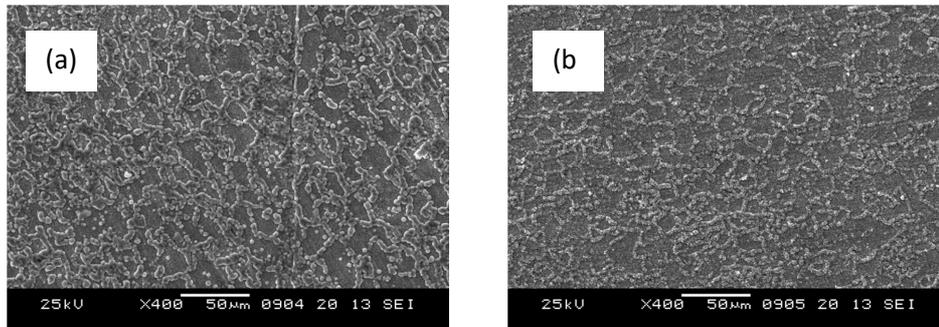


Figure 20. *Surface morphology of the fuel-side oxide scale of uncoated Crofer 22 APU after 1000 h exposure at 650 °C with two different fuel gases: (a) humid hydrogen; (b) syngas*

Summary

A variety of tests were conducted for different steel grades with and without coating. Long term oxidation tests for coated and uncoated AISI441, Outokumpu 1.4622 and Crofer 22 APU steels were performed at 700°C with dry air. Considering the exposure test results, the most promising Co/Ce-coated steel material for solid oxide fuel cell interconnect material would be Crofer 22 APU. It had best coating adhesion and thinnest oxide layers. Also the formation of MnCo-spinel was one of the benefits of Crofer 22 APU. In addition, there was porosity problem with AISI441 which was not as big with Crofer 22 APU. Nevertheless, there were some local defects in oxide/coating layers with Crofer 22 APU and some Cr-rich crystals were observed locally in coated Crofer 22 APU, which must be taken into account.

In addition, cyclic oxidation tests for more than 15 000 hours were conducted for coated AISI441 and Outokumpu 1.4622 steels at the temperature of 800°C. Mass gain was somewhat larger for AISI441 than Outokumpu 1.4622. Nevertheless, there was significant grain growth detected in Outokumpu 1.4622 steel which could be problematic for long term exposures.

Also, dual-atmosphere oxidation tests for uncoated Crofer 22 APU samples were conducted at 650 °C up to 1000 h. Results indicate that exposure to a dual atmosphere at 650 °C induces a dramatic change of the air-side oxide scale on the uncoated Crofer APU steel promoting a change from a chromia-rich thin protective layer to a hematite-rich, thick and non-protective oxide layer. The effect of the fuel gas is apparently related to the hydrogen concentration of the fuel gas so that degradation effect is most severe when humid hydrogen is chosen as fuel gas. Another series of exposure tests is currently in progress to evaluate the behavior of Ce/Co coated steel interconnects at 650 °C in dual-atmosphere oxidation environments.

Finally, the surface diffusion of the coating was studied in 800 °C. By stretching the coated AISI441 steel sheet, cracks with the width up to 5 µm were formed. It was seen that after 168 h of exposure at 800 °C even the largest cracks were oxidized. It was also seen that at this point cobalt was present over the entire surface, albeit no or only very little cobalt was present in the cracks after stretching. Surface diffusion was also studied by coating the steel only partially and then following the progression of the cobalt diffusion during exposure. These results suggest that even larger cracks, up to 25 µm, could self-heal given enough time in the temperature of 800 °C. These findings are very encouraging since they suggest that cracks introduced in the coating during stamping and/or forming, which are usually in the 1-3 µm range, are very likely to self- heal (i.e. become enclosed by the forming Co, Mn, Cr-spinel) upon oxidation.

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