Multilayered Precoated AISI 441 for Solid Oxide Fuel Cell Interconnects

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Sandvik Materials Technology develops nanocoatings for SOFC stainless steel interconnects. In this study a multilayered PVD-coating has been investigated. Cyclic oxidation for more than 20,000 hours at 800°C, chromium volatilization and area specific resistance studies have been conducted on three different coatings and compared with the uncoated steel, in this case AISI441 (EN 1.4509). In this work we have shown that pre-coated AISI 441 shows very promising results for SOFC interconnectors at 800°C. We have studied and compared state of the art CeCo coating with a new four layered coating that shows slightly higher cumulative chromium volatilization, similar ASR values and reduced mass gain in the cyclic oxidation experiments. SEM micrographs show that for the multilayered coating the total oxide layer is less than 10 microns after more than 20,000 hours of exposure.

Introduction

Metallic interconnects in solid oxide fuel cell applications (SOFC) are almost exclusively ferritic stainless steels. Steel producers and other developers have developed alloys with an expected lifetime of 40,000 hours, a coefficient of thermal expansion compatible with the ceramic components of SOFCs, good surface conductivity in the formed oxide scale etc. Among these specially developed alloys are: Sandvik Sanergy HT (1), ThyssenKrupp Crofer 22 APU (2), ThyssenKrupp Crofer 22 H (3), Hitachi ZMG232 (4), Hitachi ZMG232L (5), Allegheny Ludlum ATI E-Brite (6), and Plansee Ducrolloy Cr-5 Fe-1 Y_2O_3 (7). Presently, the alloy composition and properties are similar, i.e. the interconnect steel has physical and mechanical properties which are well suited for use in SOFCs and generally these commercial alloys meet the desired properties. The general trend previously was to build fuel cell systems operating at temperatures around 700-800°C but today even lower temperatures are commonplace among stack builders, and the use of metallic materials will increase as compared to ceramic material in interconnects. However, the specialized interconnector steel grades are still costly to manufacture due to the alloying elements and production routes and as a result, other ferritic stainless steel grades spanning from AISI430 to 446 have been considered and EN 1.4622 by Outokumpu released October 2013, is an interesting newcomer. In this study we focus on the properties of pre-coated AISI441 (EN 1.4509).

In the future, most work in improving the properties of interconnects will probably be focused towards exploration of different coatings and/or coating systems. Co coatings, for instance, can be used to minimize detrimental chromium evaporation from ferritic stainless steel and to improve the electrical conductivity of the formed oxide scale (8).

Many types of coatings have been investigated with the aim of reducing the chromium evaporation and oxidation rate and increasing the conductivity of the oxide scale. The coatings are usually deposited on a formed interconnect by various batch coating techniques such as sol-gel coating, pulsed laser deposition, plasma spraying, RF-magnetron sputtering, electrodeposition, etc. (9,10). However, the use of batch coating processes is rather unproductive and expensive which will lead to undesired increase of the overall cost for the production of interconnects. The ability to coat the steel surface or even surface alloy the strip steel in a roll to roll process will greatly reduce the overall cost for the interconnect (11).

The idea is to deposit a metallic Co coating which will oxidize and react with Mn that diffuses from the substrate to the Co coating, resulting in a CoMn-spinel at the surface on the interconnect. Except from substantially reducing the Cr evaporation (8) the formed CoMn-spinel will have a relatively good electrical conductivity (12). The thickness of the CoMn-spinel will be dependent on the initial thickness of the Co coating and it has been shown that up to a cobalt thickness around 600-800 nm the Cr evaporation is suppressed linearly with Co layer thickness.

It has been shown that a small amount of Ce added to the spinel improves the ASR as well as reduces the mass gain due to less oxidation (12). In this study a four layered PVD coating on AISI441 is presented displaying excellent ASR, chromium evaporation and oxidation properties. SEM micrographs show that for the multilayered coating the total oxide layer is less than 10 microns after more than 20,000 hours of exposure.

Experimental

Cold rolled steel strip with a thickness 0.2 mm of a commercial ferritic stainless steel AISI441 were used in the present study. The nominal chemical composition is (in wt%): 17.8 Cr, 0.48 Nb, 0.26 Mn, 0.55 Si, 0.01, Ni 0.013, Ti 0.139. Three different metallic coatings were prepared, see Table 1 for details. The double sided coatings were deposited with a PVD technique on 15 cm × 30 cm substrates cut from the steel strip. Before coating, the substrates were cleaned in acetone and ethanol followed by alkaline cleaning at 60°C for 10 min. After alkaline cleaning the substrates were rinsed in hot tap water, deionized water and finally in ethanol. The uncoated substrates were cleaned in the same way before the oxidation experiments.

TABLE I. Investigated Samples And Details Regarding Coating Thicknesses

Sample Name	1st Layer (nm)	2nd Layer (nm)	3rd & 4th Layer (nm)
Co	Co (800)	N/A	N/A
CeCo	Ce (10)	Co (600)	N/A
CeCrCeCo	Ce (10)	Cr (450)	Ce (10) Co (600)

From the coated samples, coupons with a size of 30 mm × 40 mm were cut, and pierced with a hole with a diameter of 3 mm used for hanging the samples during high temperature cyclic oxidation in ambient air. The coupons were oxidized in a muffle furnace and during the oxidation experiments the coupons were hanging on a platinum thread to avoid contract with other coupons and to expose the same surface area. Three

coupons of each coating type were oxidized at 800°C for 20,160 hours corresponding to 120 weeks. The weight increase was recorded after cooling the coupons to room temperature. At each measurement the coupons were also visually inspected for delamination or peeling off of the coating.

For comparison, sample coupons of CeCrCeCo were cut with the dimensions 15 mm × 15 mm. A hole with 3 mm in diameter was punched into the sample for sample handling. Before exposure the samples were degreased and cleaned as previously described. The samples were mounted vertically, three at a time on an alumina sample holder, and positioned parallel to the gas flow, in the center of a horizontal tube furnace. The furnace was operated at 800°C. The reaction gas consisted of 20% O_2, 77% N_2 and 3% H_2O. The volumetric flow rate was 1000 ml/min, giving a linear flow rate of approximately 3.8 cm/s. Digital mass flow controllers were used for the dry carrier gases. For adding the water vapor, the dry gas flow was bubbled through a humidifier and cooled to the correct dew point (24.4°C for 3% water vapor) in a condenser, before being led into the furnace. All parts of the system downstream of the condenser were kept above the relevant dew point, in order to prevent condensation.

The chromium volatilization experiments were performed using the denuder technique described in more detail elsewhere (13). To quantify the chromium volatilization the samples were exposed to 850°C in air with 3% water vapor and flow rate of 6000 ml/min.

Area Specific Resistance (ASR) was measured at the FCH Test Center at DTU Energy Conversion (DTU Risø Campus, Denmark), for samples CeCo and CeCrCeCo at 800°C±7 for 1500 hours in air. A standard LSM cathode contact component was used in building the mini stacks of the coupons of the coated material. The current density was 0.5 A/cm^2 and no thermal cycling was conducted. The heating/cooling rate was 100°C/h.

The electron micrographs and EDS analysis were collected using a Zeiss Crossbeam 1540EsB equipped with an Oxford Instruments X-Max[N] system with 80mm^2 detector. The SEM cross sections were prepared using Hitachi IM4000 Ion Milling system. The samples presented here were examined after 20,160 hours of cyclic exposure.

Results and Discussion

Gravimetrical Measurements

The initial rapid oxidation for all samples, seen in Figure 1, is attributable to the Co being oxidized. After the initial oxidation of the cobalt layer, the mass gain rate shows a similar behavior as the uncoated sample. The combination of Ce and Co reduces the mass gain significantly and has been shown previously (14). In the four layered structure the mass gain is further improved. For comparison the total weight gain at 10,000 hours for CeCrCeCo is similar to what is measured for a Co coating after roughly 1,800 hours and the CeCo sample after 4,500 hours.

At each measurement the coupons were also visually inspected for delamination or peeling off of the coating.
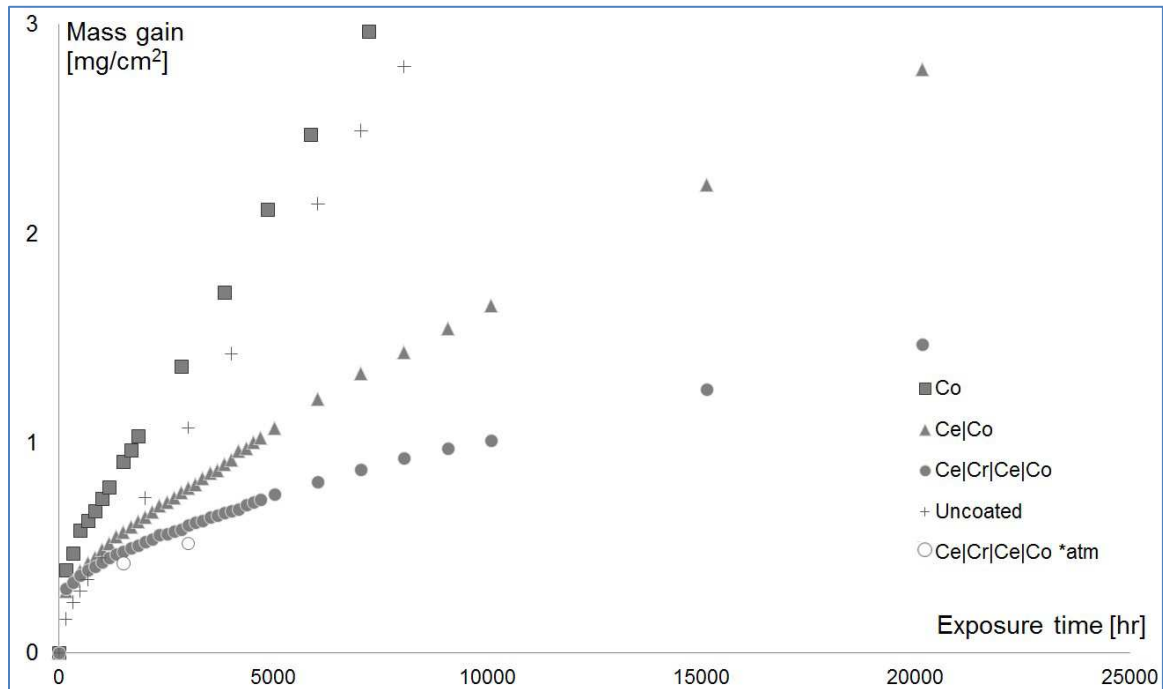
Figure 1. Mass gain from cyclic oxidation at 800°C in ambient air. The open circles show CeCrCeCo sample in the controlled air composition. The mass gains are not corrected for Cr evaporation.

The muffle furnace in ambient air in comparison to a furnace with flowing and controlled air composition generates different results, as seen in Figure 1. Generally the mass gains are higher for ambient air. This, however, does not necessarily mean that the ambient air generates a more aggressive environment. Instead, in controlled atmosphere, the partial pressure of water vapor is generally higher than normal air humidity (as the reaction gas is saturated with water vapor at 24.4°C). It is reasonable to assume that this combined with the fact that the gas is flowing in the exposures with controlled atmosphere (rather than being more or less stagnant as in the exposures in ambient air), would result in increased evaporation of chromic acid in these exposures, which gives a negative contribution to the recorded mass gain. It is expected that this more closely resembles the conditions in an actual fuel cell.

The results from the muffle furnace for the samples, however, show the relative performance of the samples which is sufficient for comparison.

Chromium Volatilization

Figure 2 shows the cumulative chromium evaporation of the three different coatings. Also, for comparison, the Cr volatilization of uncoated AISI441 has been added to Figure 2. The multilayered CeCrCeCo-sample shows a slightly higher value in comparison to Co and CeCo. Still, the presence of the Co coating reduces the Cr evaporation by roughly a factor of 10 as compared to the uncoated stainless steel.
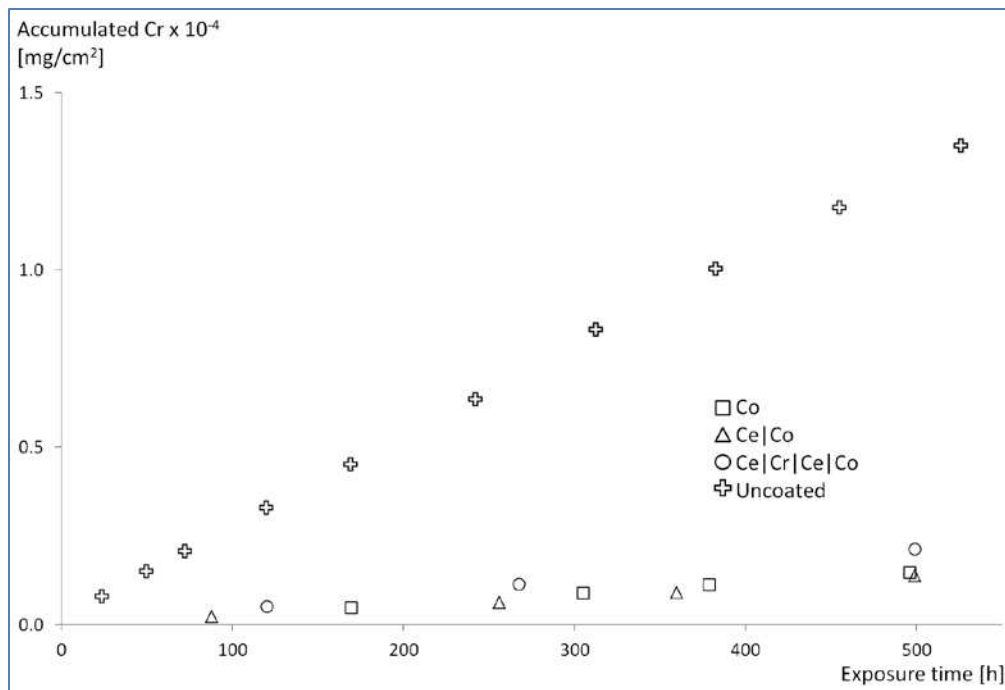
Figure 2. Cumulative Cr evaporation for coated and uncoated AISI 441.

Area Specific Resistance

Five independent ASR measurements were made for CeCo and CeCrCeCo samples and averages are presented in Figure 3. The ASR for both samples are stable and below 15 mΩ/cm^2 for the first 1500 hours. This work provides a baseline for future work involving in-situ tests with operating fuel cells.
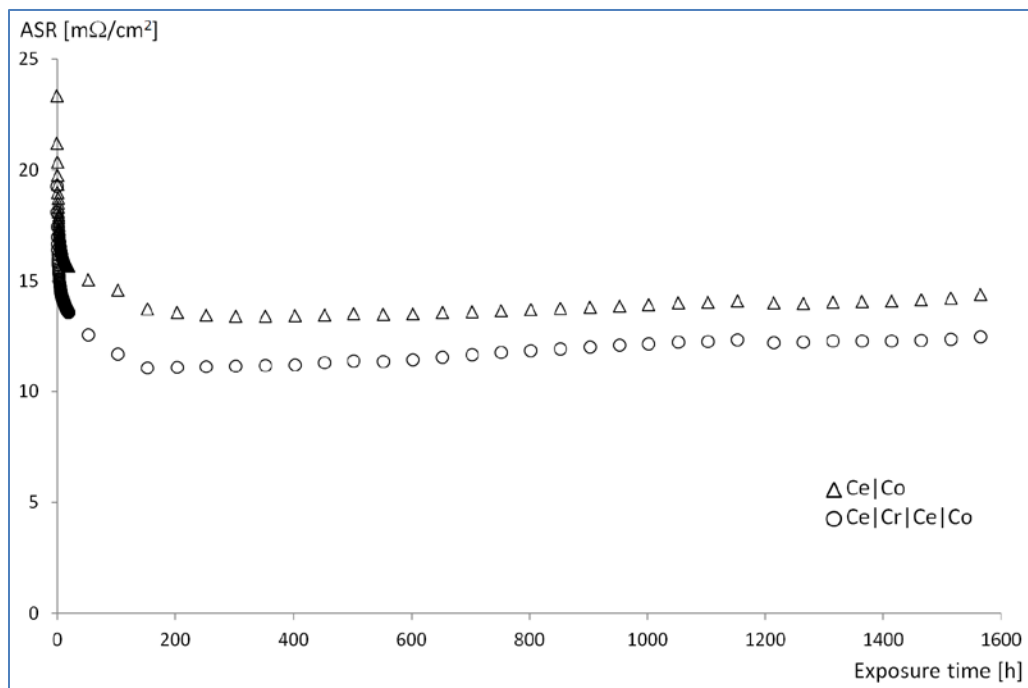

Figure 3. ASR for the CeCo and CeCrCeCo coatings on AISI441 steel grade measured at 800°C.

Scanning Electron Microscopy

Both the CeCo and CeCrCeCo-coated samples exposed for 20,160 hours exhibits a buckled oxide scale due to the formation and development of the oxide scale, clearly visible in Figure 4. No spallation was observed during the cyclic oxidation measurements and the samples were visually inspected at each measurement. No detectable effect of spallation is observed in the graphs from the gravimetrical measurements either, see Figure 1. Due to sample preparation using the ion milling system one side of cross-section will have artifacts, as displayed in the lower part in Figure 4, thus only one side of the coating was examined. The micrographs in Figures 4 to Figure 6 show that the oxide scales cover the steel substrate well and that the thickness of the total oxide scale is 13-17 microns for the CeCo samples and 7-9 microns for CeCrCeCo samples, effectively reducing the oxide scale thickness by almost half in comparison.

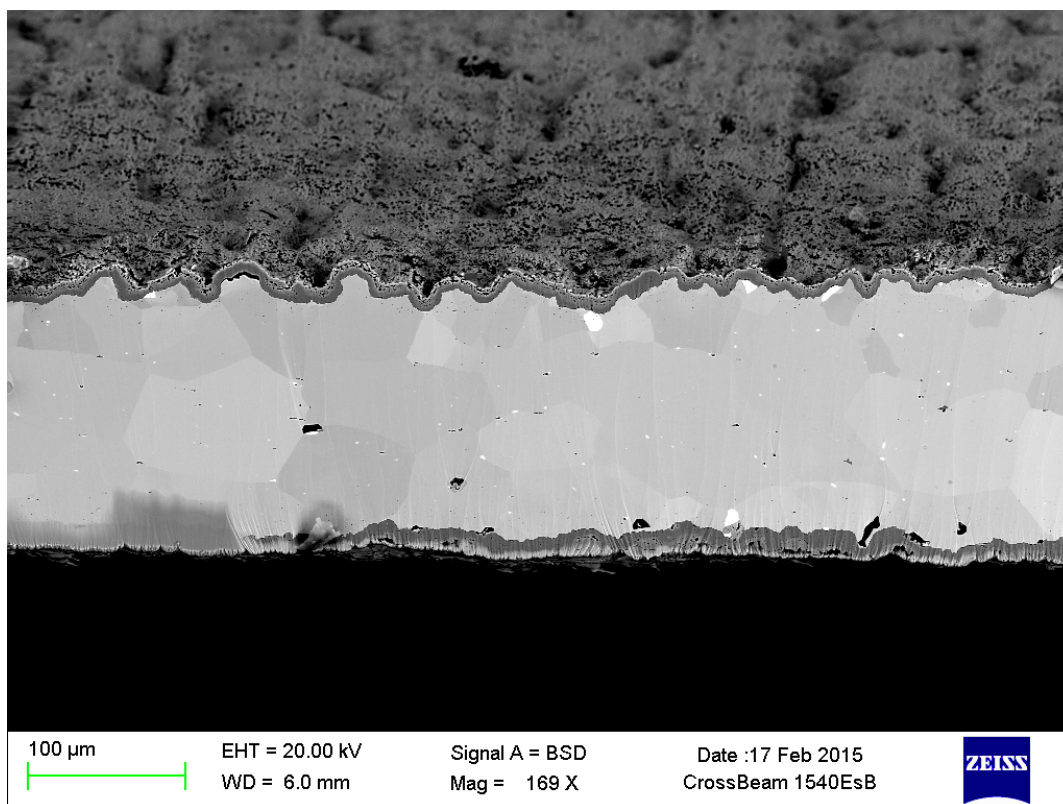| 100 µm | EHT = 20.00 kV | Signal A = BSD | Date :17 Feb 2015 | ZEISS |
| | WD = 6.0 mm | Mag = 169 X | CrossBeam 1540EsB | |

Figure 4. SEM micrograph of the CeCrCeCo-coated sample after 20,160 hours of cyclic oxidation at 800°C in ambient air. The artifacts at the bottom part of the sample is due to sample preparation.

From micrographs in Figures 5 and 6 it is also evident that the surface morphology is different where the CeCo coated samples display facetted spinel crystallites, whereas the CeCrCeCo samples appear to have some minor porosity and no obvious facetted crystallites in similar size as in the CeCo samples. Further studies are under way to discern if there is any impact of the crystallite size, the esthetics aside, on the properties. In Figure 5 the chromia layer is roughly 10 micron thick for the CeCo sample compared to 3-4 microns for the CeCrCeCo sample. The area specific resistance is dependent on the chromia scale and thus the CeCrCeCo coatings thinner oxide should be more beneficial for extended exposure times.
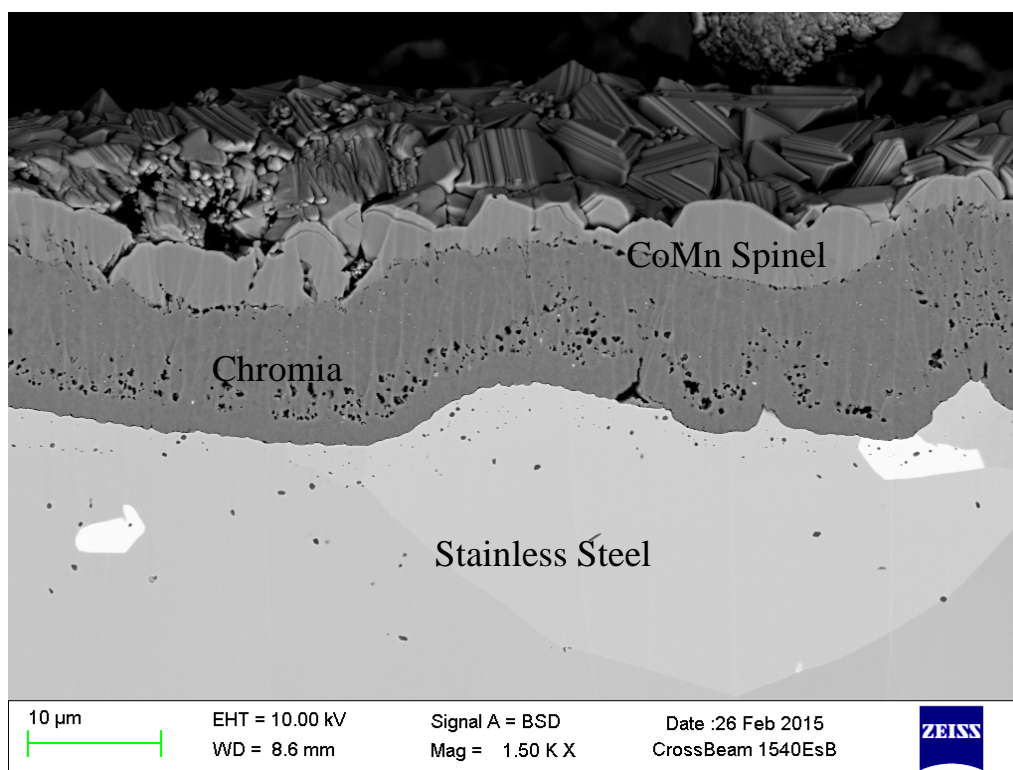
Figure 5. SEM micrograph of the CeCo-coated sample after 20,160 hours of cyclic oxidation at 800°C in ambient air.
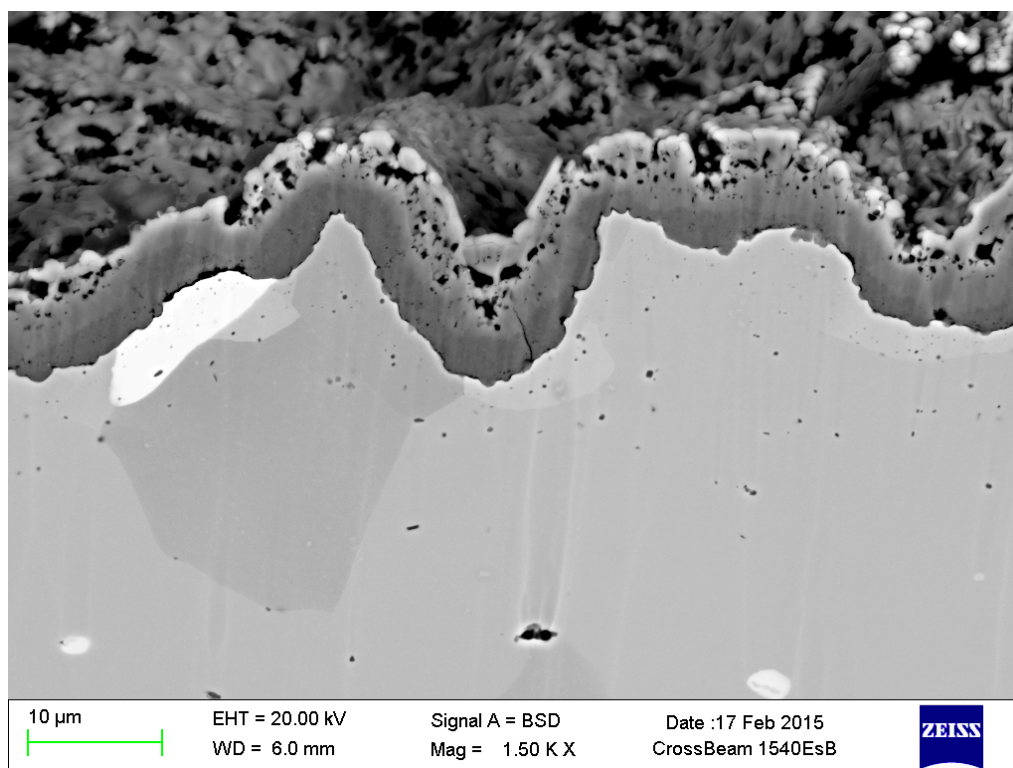

Figure 6. SEM micrograph of the CeCrCeCo-coated sample after 20,160 hours of cyclic oxidation at 800°C in ambient air.

Conclusions

In this work we have shown that pre-coated AISI 441 show very promising results for SOFC interconnectors at 800°C. We have studied and compared state of the art CeCo coating with a new four layered coating that shows slightly higher cumulative chromium volatilization, similar ASR values and reduced mass gain in the cyclic oxidation experiments. The SEM micrographs showed that the CeCrCeCo coating has a 3-4 micron thick chromia layer compared to 10 microns for the state of the art CeCo coating, after 20,160 hours of exposure. From these studies it shows that focusing solely on one parameter e.g. cyclic oxidation will not give the full understanding on interconnector behavior. Also, long exposure times have to be performed to understand the evolution of the oxide scale its properties. Extrapolation from short exposure times do not render a full picture of what is going on.

The comparison of data from cyclic oxidation in the muffle furnace and the tube furnace with flowing controlled atmosphere showed that the mass gains in the muffle furnace are generally higher. Still for comparison and with this in mind the muffle furnace is a good tool for screening of large batches and achieving better statistics.

Acknowledgments

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