Self-Healing of Precoated AISI 441 for Solid Oxide Fuel Cell Interconnects

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Sandvik Materials Technology develops nanocoatings for SOFC stainless steel interconnects. The self-healing properties of cerium cobalt coated AISI441 (EN 1.4509) have been studied. A partially coated sample was oxidized in air at 800°C for a total of 504 hours. Prior to oxidation a focused ion beam (FIB) was used to mill a trench on the uncoated surface to be used as a reference point relative the coated border. A second FIB trench, made after oxidation, revealed that the oxide formed on the uncoated part adjacent to the coated area contained both cobalt and cerium. Cerium was detected with EDS in the surface oxide of the uncoated area as far as 10 µm away from the coated edge, cobalt had diffused even further. These findings are encouraging since they suggests that cracks introduced in the coating during stamping and/or forming, which are usually in the 1-3 µm range, are likely to self- heal (i.e. become enclosed by the forming Co, Mn, Cr-spinel) upon oxidation.

Introduction

Metallic interconnects used in solid oxide fuel cells (SOFC) must be able to operate at high temperatures (700-850 °C) and in an oxidizing atmosphere. Steel manufacturers have developed special alloys in order to meet requirements such as; slow scale growth, high surface conductivity and low chromium evaporation rates. A major drawback with these alloys is the inherently high cost as compared to regular off-the-shelf ferritic grades, e.g AISI 441 (EN 1.4509). In an uncoated condition the special alloy may outperform the cheaper standard steels but still they suffer from rather high chromium evaporation rates [1] which may poison the cathode of the fuel cell. One common way to reduce the chromium evaporation is to coat the interconnect steel with a cap layer, usually a spinel type oxide [2]. Since these coating are rather thick and brittle they must be applied after that the flow patterns have been imprinted on the interconnect. This means the each interconnect has to be coated individually in a batch process.

Another way of achieving a chromium blocking cap layer is to coat the steel with a thin metallic coating which is then let to oxidize into a spinel structure. At AB Sandvik Materials Technology a roll-to-roll PVD coating technique is used to coat steel substrates with a thin layer (< 1 µm) of cobalt. Good results are seen for both special alloys, e.g. Sanergy HT and Crofer 22 APU, and for standard steels as the AISI 441. When the cobalt coating combines with manganese that diffuses out from the bulk steel a cobalt-manganese-spinel will form on the surface of the interconnect. This spinel effectively reduces chromium evaporation from the surface [3] and it also possesses relatively good

electronic conduction. Even better performance is achieved when small amounts of reactive elements, e.g. cerium, are deposited as a seed layer underneath the cobalt coating [4]. The cerium layer helps to slow down the rate of chromia formation, the cobalt coating is still needed for the chromium blocking outer spinel [5]. The thin coating does not spall off during forming operations and therefore the steel can be delivered in a pre-coated condition. This means that no batch coating of individual plates is required.

During forming operations of the pre-coated steel the cobalt coating is bound to crack when the substrate material is stretched. An earlier study has shown that thin cracks (sub micrometer) in the coating will become enclosed due to the instant volume expansion that follows when the metallic cobalt becomes oxidized [6]. In this manuscript, longer oxidation exposures are used to see what effect this has on the cracked areas.

Experimental Procedures

Material

Sheets of cold rolled commercial grade ferritic stainless steel AISI 441 (EN 1.4509) were used in the present study. The nominal chemical composition of the steel was (wt%): 18 Cr, 0.11 Ti, 0.47 Nb, 0.28 Mn, 0.54 Si, 0.012 C, Ni 0.13. The thickness of the sheets was 0.2 mm. The samples were coated with 600 nm cobalt and 30 nm cerium (cerium closest to the steel) on one side of the sheet. Both coatings were deposited in a PVD batch coater. Before coating, the substrates were cleaned in an alkali detergent at 60°C for 10 min. After the alkaline cleaning the substrates were rinsed in hot tap water, deionized water and finally in ethanol.

Forming Trials

A cerium cobalt coated steel sheet was cut to 240×240 mm^2. The sample was lubricated before the forming experiments in order to reduce the friction between the steel sheet and the forming tool, i.e. the punch. The forming experiment was performed 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.

Surface Diffusion

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 1. This trench could then be used as a reference point during oxidation trials.

Exposure

The samples were oxidized, hanging by a platinum thread, in a muffle furnace at 800°C. The furnace had no circulation and ambient air was used. Before exposure the coated samples were cleaned in acetone and ethanol.
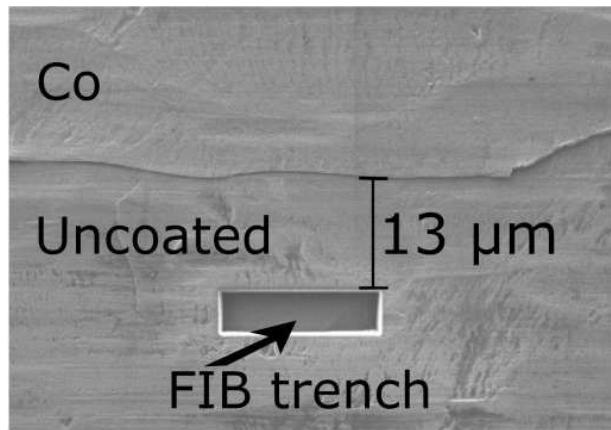
Figure 1. A FIB trench was milled as a reference point close to the edge.

Results and Discussion

<u>Forming Trials</u>

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 2 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 2, 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
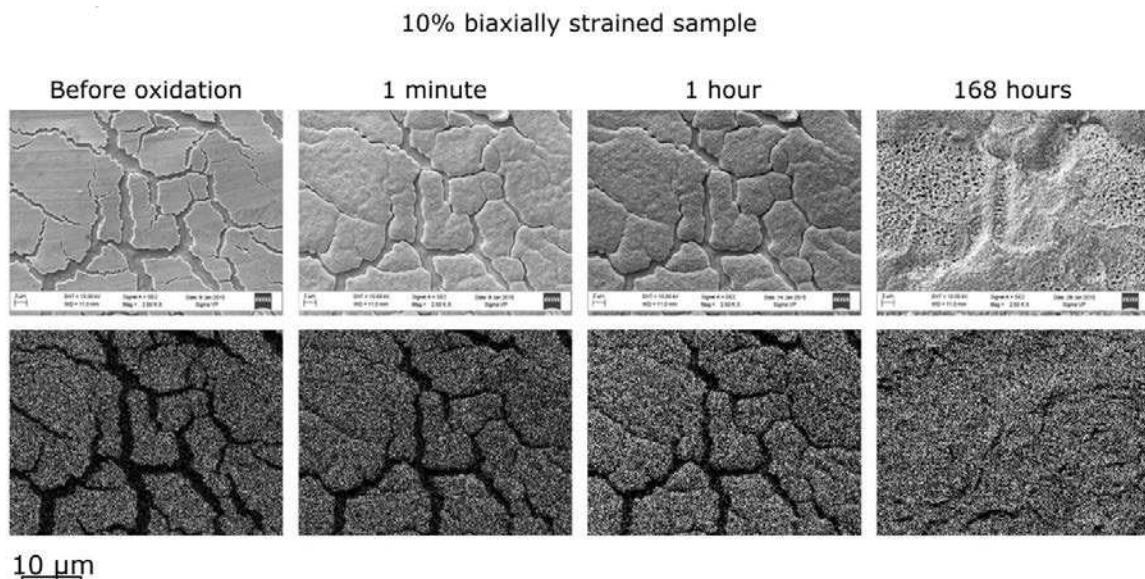

Figure 2. SEM images of strained and oxidized (800°C) samples (top); EDS cobalt maps from corresponding areas (bottom).

(~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.

Surface Diffusion

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 in the experimental procedure 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 3. 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 [4]. In this sample the lower oxide scale was 1-1.5 µm thick on both the coated and the uncoated area. The upper oxide was 1-1.5 µm on the uncoated part but about double that on the coated side. In between the two layers was seen a pearl like streak of bright particles. The size of these particles was in
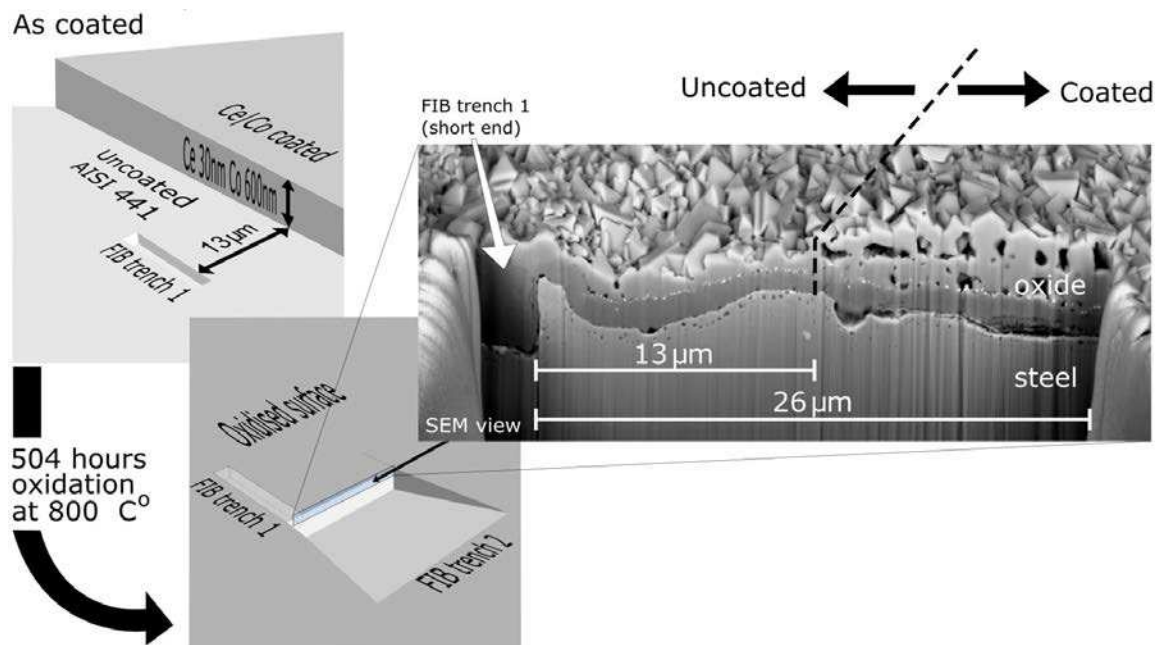

Figure 3. The AISI 441 sample was masked before being coated with 30 nm cerium and 600 nm cobalt, respectively. With the mask removed a sharp border between coated and uncoated surface was created. After oxidation at 800°C the formed oxide of the uncoated part was examined. Cerium rich particles were detected in the scale as far as 10 µm away from the coated area.

the 100 nm range and they stretched from the coated part roughly 10 µm into the uncoated area of the sample. A buckling of the steel surface, which created a wavy appearance, could be seen. This deformation can be attributed to plastic deformation of the steel due to strains imposed on the steel surface by the growing oxide.

SEM EDS analysis was used to analyze the different parts of the oxide scale. Despite the limited lateral resolution of this technique it was possible to get some valuable information from the oxide scale. It could be concluded that the bright particles were rich in cerium and that the upper oxide contained cobalt in the coated as well as the uncoated part. Elemental maps recorded with SEM EDS from the uncoated side are shown in Figure 4.
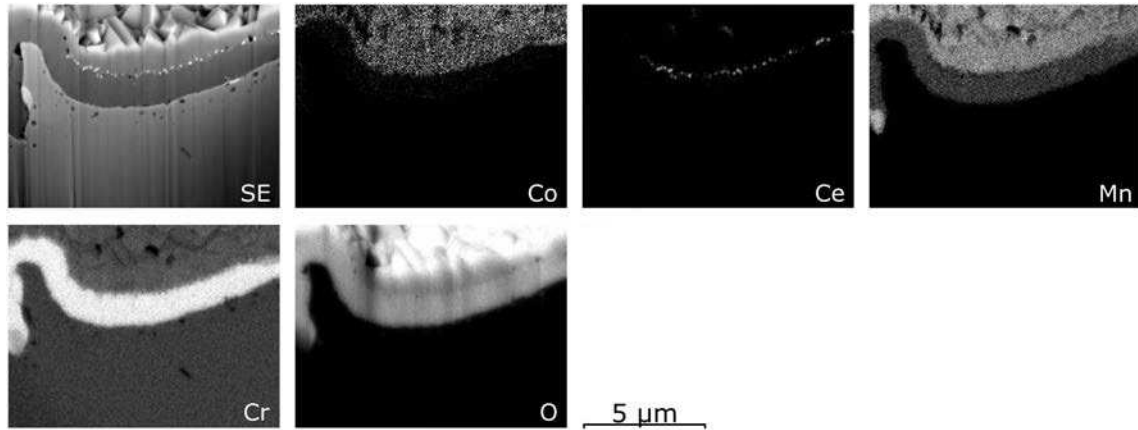

Figure 4. SEM EDS elemental maps recorded from the uncoated part of FIB trench 2.

From the results in Figure 3 it is evident that the diffusion of cobalt extends beyond the first FIB trench. In Figure 5 the extent of the Co diffusion is revealed with an EDS line scan of a larger part of the sample showing that a cobalt signal is detectable up to 70 µm into the uncoated region. Certainly, the amount of cobalt wears off as we move away from the border out towards the uncoated region. In Figure 6 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. The surface diffusion experiment described in this section 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 3 given enough exposure time and temperature is supplied.

Conclusions

We have studied and compared how stretching the coated 441 stainless steel in the deep drawing cup test or in a tensile test rig generates cracks and that these cracks readily self-heal over time at 800°C. We have also shown by placing FIB milling trenches nearby a border of coated and uncoated steel surface that the self-healing extends larger distances than previously have been shown. Furthermore, that even if cracks form or delaminated flakes of the coating are in the size of 25 µm range, the coating would self-heal. The results also suggest that even larger cracks could self-heal given enough time
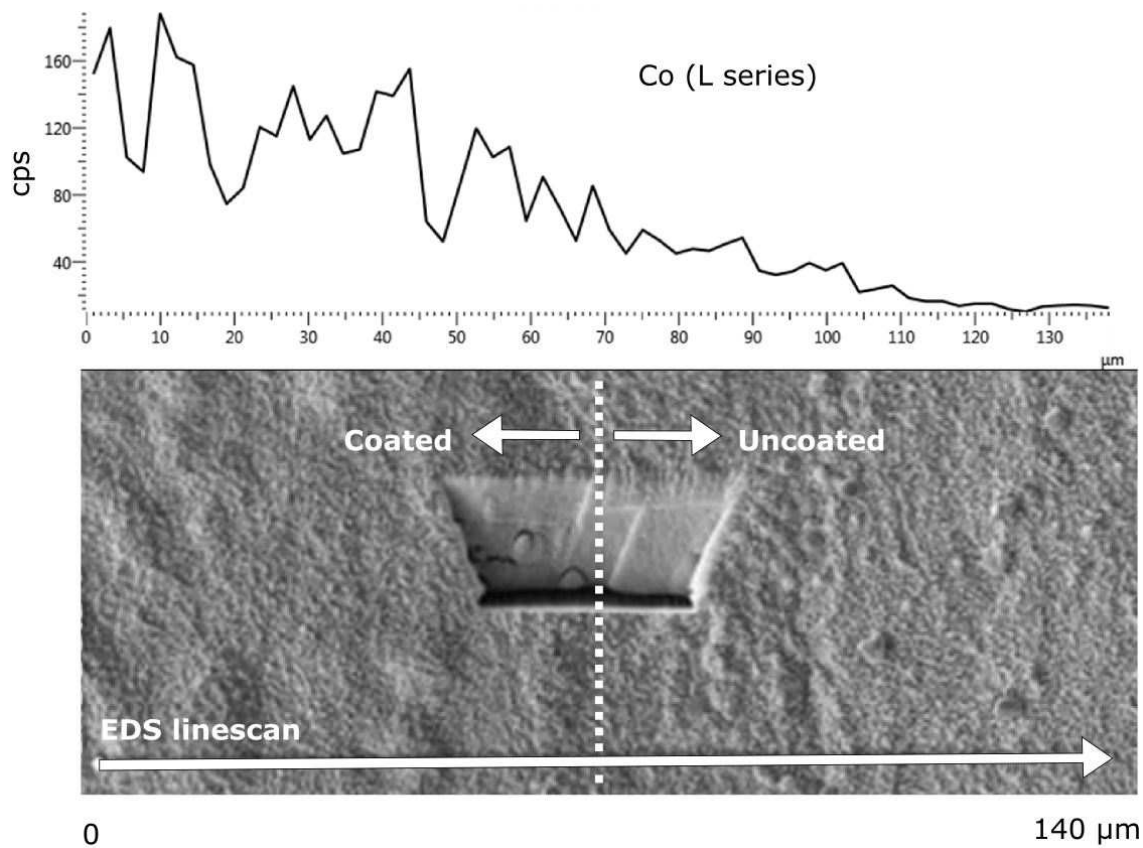
Figure 5. EDS linescan performed over wide part of the sample after 504 hours of exposure at 800°C (bottom part of the image), starting in the coated part (left) and ending up roughly 70 µm into the uncoated region. The corresponding cobalt signal is shown in the graph above.
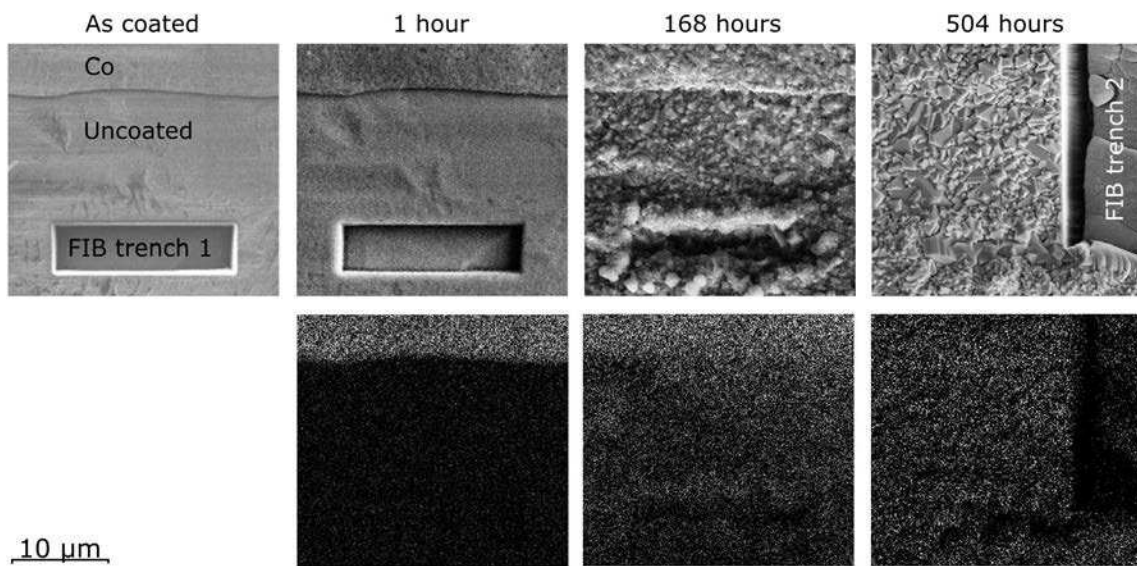

Figure 6. Top row shows SEM images of the investigated area before and after 1 hour, 168 hours and 504 hours of oxidation at 800 °C. The bottom row shows cobalt EDS maps of the oxidized samples.

and temperature. 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.

Acknowledgments

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