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Mikkelsen, Lars; Neufeld, Kai; Hendriksen, Peter Vang

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Interface Resistance Between FeCr Interconnects and $\text{La}_{0.85}\text{Sr}_{0.15}\text{Mn}_{1.1}\text{O}_3$

L. Mikkelsen, K. Neufeld, and P. V. Hendriksen

Fuel Cells and Solid State Chemistry Division, Risø National Laboratory for Sustainable Energy, Technical University of Denmark – DTU, DK-4000 Roskilde, Denmark

The long term oxidation behaviour and the electrical interface resistance between FeCr interconnects and $\text{La}_{0.85}\text{Sr}_{0.15}\text{Mn}_{1.1}\text{O}_3$ plates was studied by a DC four-point method in air at 750°C for 10000 h. The tested FeCr alloys were: Crofer 22 APU, Sanergy HT, Plansee IT10, Plansee IT11, and Plansee IT14. The alloys were slurry sprayed with a dual layer coating consisting of an inner Co_3O_4 layer and an outer layer consisting of $\text{La}_{0.85}\text{Sr}_{0.15}\text{Mn}_{1.1}\text{O}_3$ with some Co_3O_4 added. The microstructure and composition of the oxide scales formed at the interfaces were investigated using SEM/EDX analysis. Low degradation rates of less than 1 $\text{m}\Omega\text{cm}^2/1000$ h were measured on all interfaces. The microstructure analysis showed that a duplex Cr_2O_3 - $(\text{Mn},\text{Co},\text{Cr})_3\text{O}_4$ oxide scale with a thickness of 3-5 μm had evolved on the alloys.

Introduction

Interconnects are positioned adjacent to the cathode in SOFC stacks, so the interface resistance between alloys and cathode materials is an important parameter for SOFC applications. Oxidations tests of slurry coated FeCr interconnects have previously been performed at 900°C in air for up to 4000 h (1). This accelerated oxidation, where temperature was increased relative to normal SOFC operation temperature was performed to simulate multiyear oxidation behaviour at lower temperatures.

The objective of the present work was to investigate the long term oxidation behaviour of the alloys and measure the interface resistance between the interconnects and $\text{La}_{0.85}\text{Sr}_{0.15}\text{Mn}_{1.1}\text{O}_3$ during oxidation in air closer to the expected operation temperature of the technology at 750°C. The effect of the minor alloying additions in the alloys on the electrical performance as well as the oxidation behaviour is investigated and comparisons are made to oxidation tests performed at 900°C.

Experimental

Two commercially available alloys Crofer 22 APU (Thyssen Group VDM GmbH) and Sanergy HT (AB Sandvik Materials Technology) and three test alloys from Plansee were examined in the present work. The nominal composition of the alloys as given by the suppliers is shown in Table I. Samples with thicknesses of; Sanergy HT: 0,2 mm; Crofer 22 APU: 0,3 mm; Plansee IT10, IT11, IT14: 2 mm; were cut in pieces of 2×4 cm^2 and grinded with 1200 grid SiC paper and finally washed with acetone and alcohol using an ultra-sonic bath. The samples were coated on both sides (applied by wet-spraying)

with a two-layer coating consisting of an inner layer of Co_3O_4 and an outer layer of $\text{La}_{0,85}\text{Sr}_{0,15}\text{Mn}_{1,1}\text{O}_3$ (LSM15) containing a small amount of Co_3O_4 . Each coating layer had a thickness of $\sim 15 \mu\text{m}$. A $2 \times 2 \text{ cm}^2$ mask was used for the spraying in accordance with the dimensions of the auxiliary LSM15 plate (see below). The samples were positioned between unsintered LSM plates ($2 \times 2 \text{ cm}^2$) giving a nominal contact area of 4 cm^2 between the foils and the LSM plates. Platinum wires were spot-welded to the alloy sheets for voltage probing. Platinum voltage probes were also applied on either side of the LSM plates completing the sandwich. A schematic illustration of the experimental setup is shown in Figure 1. The electrical interface resistance between the steel samples and LSM plates was measured by a DC four-point method. Each sample resulted in two measurements of the interface resistance. The values shown below are an average of the two measurements. Details of the experimental setup are given in (2).

Table I. Nominal composition of the investigated alloys (in wt.%). A “+” indicates that the element is present in the alloy, but the quantity is unknown to the authors.

Name	Fe	Cr	Mn	Si	Mo	Nb	Ti	Minor
Plansee IT10	Bal.	26	+				+	Y_2O_3
Plansee IT11	Bal.	26			+		+	Y_2O_3
Plansee IT14	Bal.	26	+		+		+	Y_2O_3
Sanergy HT	Bal.	21,9	< 0,5	< 0,3	1	0,75	+	
Crofer 22 APU	Bal.	22,9	0,5	0,02			0,06	

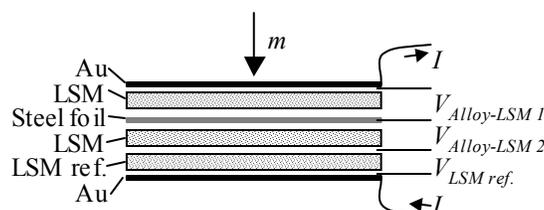


Figure 1. Schematic illustration of the experimental setup used for electrical characterization of alloy-LSM interface.

The temperature was initially increased to 870°C ensuring complete removal of organic components from the sample and contacting of the components. After 4 hours at 870°C the temperature was decreased to 750°C , where it was held for $\sim 10000 \text{ h}$ (400 days). The test was terminated with thermal cycles between 750°C and $\sim 100^\circ\text{C}$. The cooling and heating rate during thermal cycling was 100°C/h . The microstructure of polished cross sections were subsequently analysed in a scanning electron microscope (FEG-SEM, Zeiss Supra-35) equipped with an energy-dispersive x-ray spectrometer (EDX, Noran).

Results and Discussion

Electrical Degradation

The measured ASR-values are shown in Figure 2. The ASR-values include a contribution from the auxiliary LSM plate corresponding to $7\text{-}8 \text{ m}\Omega\text{cm}^2$. The interface resistance increases for all the alloys during the initial $100\text{-}800 \text{ h}$ of annealing, until the ASR-values start to decrease slowly. The ASR-values are a result of a complex interplay between the scale growth, increased electrical contacting between the coated interconnects and the LSM plates as a result of sintering, and a gradual change of

composition of the oxide scale as a result of diffusion of cations from the alloy and reaction between the oxide scale and the coating. The initial increasing ASR-values indicate that a fast growth of the oxide scale dominates the ASR-values initially. After the increasing interface resistances, the ASR-values start to decrease. This is probably a result of a slower oxide growth combined with a gradual change of the composition of the oxide scale and a better electrical contact. The ASR-values of Sanergy HT and Crofer 22 APU increase after approx. 5000 h, probably as a result of a higher growth rate for these alloys. The ASR-values of the Plansee alloys are almost constant with time after 2000 h, probably as a result of a very slow oxide growth rate of the oxide scale at the interface.

Low degradation rates were observed for all the interfaces. Thermal cycles were performed after 10000 h of testing without a degradation of the ASR-values. This shows that the differences in TEC-values do not lead to delamination between the different layers. The interface resistances were strongly temperature dependent, showing an Arrhenius type temperature dependency with an activation energy of 0,5-0,6 eV.

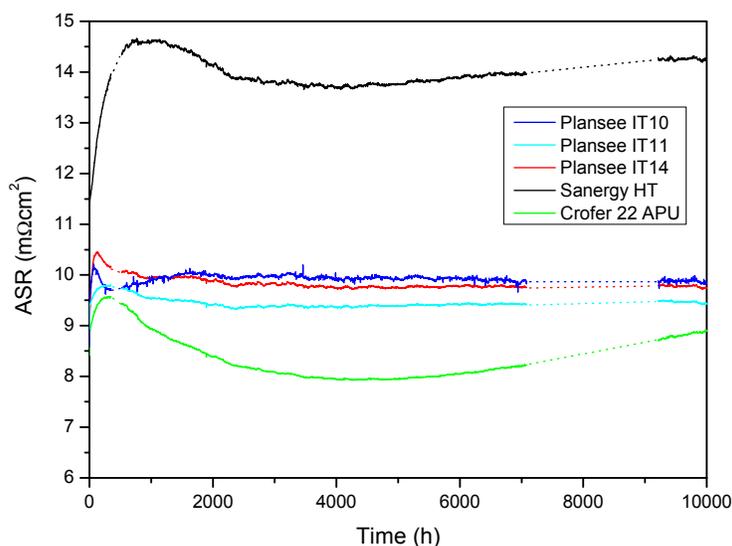


Figure 2. ASR-values of the interfaces measured in air at 750°C. Data acquisition failed for two periods of time as indicated in the plot.

Microstructure

A cross section of Plansee IT10 is shown in Figure 3. An oxide scale with a thickness of 4-5 μm has grown on the alloy. Linescan analysis across the oxide scale as well as the cobalt oxide coating is shown in Figure 4. The oxide scale was identified as an inner approx. 1 μm thick layer of Cr_2O_3 and an outer spinel layer. The two phases can also be distinguished by the contrast difference. The dark particles in the alloy matrix were identified as titanium oxide resulting from internal oxidation. Titanium was also identified in the Cr_2O_3 layer. The linescan analysis shows that the composition of the spinel layer changes from a chromium rich spinel to a cobalt and manganese rich spinel. The composition of the inner coating layer is almost constant containing a small amount of chromium. The compositions of the spinel phase in the oxide scale and in the inner coating are summarized in Table II for all samples.

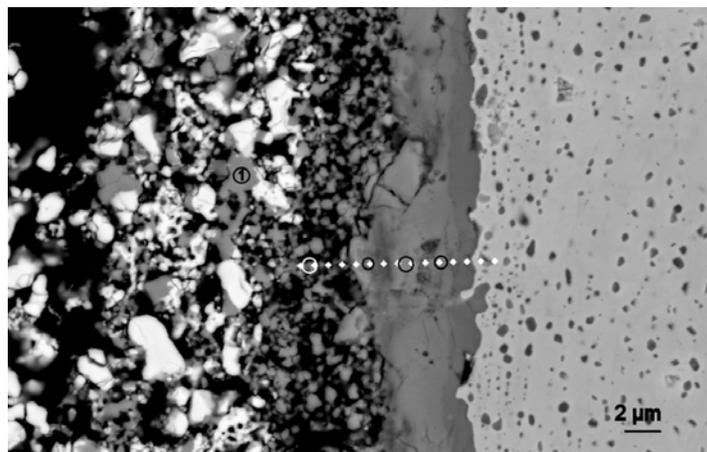


Figure 3. SEM micrograph of cross section of the Plansee IT10-coating interface. The EDX linescan and points where composition analysis was carried out are indicated.

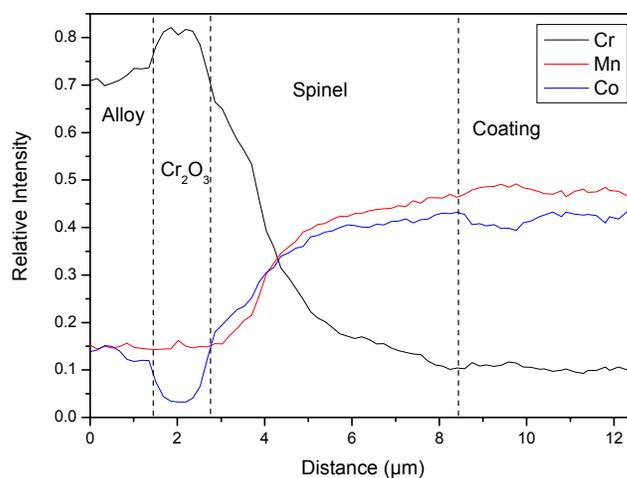


Figure 4. EDX linescan analysis across the Plansee IT10-coating interface. See Figure 3 for position of the scan.

Table II. Composition (in at.%) of cations in the spinel in the oxide scale and in the coating of the samples measured by EDX analysis.

	Co	Mn	Cr	Fe
Plansee IT10-inner spinel	43	19	38	
Plansee IT10-middle spinel	52	35	12	
Plansee IT10-outer spinel	52	41	6	
Plansee IT10-coating	52	44	3	
Plansee IT11-middle spinel	54	32	14	
Plansee IT11-coating	58	39	3	
Plansee IT14-middle spinel	49	38	6	7
Plansee IT14-coating	52	41	4	3
Sanergy HT-inner spinel	37	9	54	
Sanergy HT-middle spinel	52	33	15	
Sanergy HT-outer spinel	57	40	3	
Sanergy HT-coating	57	40	3	
Crofer 22 APU-inner spinel	32	8	60	
Crofer 22 APU-middle spinel	46	36	18	
Crofer 22 APU-outer spinel	49	46	5	
Crofer 22 APU-coating	49	48	3	

Dark particles were observed in the LSM15-based coating. EDX point analysis (see Table III) shows that the particles are (Mn,Co,Cr)-spinel containing approx. 3 at.% Cr. Dark particles were observed on all samples and no difference of the Cr-content was observed between the different samples. Furthermore, the chromium content did not vary systematically as a function of distance from the coating-oxide scale interface. The dark particles were evenly distributed in the LSM15 layer.

Table III. Composition (in at.%) of elements in the samples measured by EDX analysis. The points are indicated in the micrographs.

Point	Fe	Nb	Mo	Co	Mn	Cr
1				56	41	3
2	61		4			35
3	6			51	37	6
4	16			43	31	10
5	61,5		3,5			35
6	46	42				12

A cross section of Plansee IT11 is shown in **Figure 5**. An oxide scale with a thickness of 2-3 μm has grown on the alloy although areas exist where the oxide scale is thicker (4-5 μm) as shown in **Figure 5**. EDX analysis of the sample is shown in Table II and Table III. The coating contains a small amount of iron. The presence of iron does not increase the ASR-values measured over the interface (see Figure 2), since iron containing spinels in general have a high electrical conductivity (3). The presence of iron indicates, however, local failure of the oxide scale during oxidation. These failures of the oxide scale accelerate the growth of the oxide and may lead to catastrophic oxidation for longer oxidation times than 10000 h. It is also observed that the oxide scale is not adherent to the alloy over the whole alloy-oxide interface. A slightly smaller amount of manganese is present in the oxide scale and coating compared to Plansee IT10. Plansee IT11 does not contain manganese, so the manganese diffuses from the LSM15 coating layer instead. The comparison between the two alloys shows that a significant part of the manganese present in the inner coating layer and in the oxide scale originates from the coating. The thinner oxide scale grown on the Plansee IT11 is, however, a result of the lack of manganese in the alloy.

White particles are observed within the alloy matrix. These particles are probably Sigma phases. The formation of Sigma phases has previously been observed in similar alloys (4). The Sigma phase is relatively chromium rich. The formation of Sigma phases probably alters the mechanical properties of the alloy, since the Sigma phases is known to be brittle.

A cross section of Plansee IT14 is shown in **Figure 6**. Results from the EDX analysis of the cross section are shown in Table II and Table III. The microstructure of the cross section is similar to the microstructure of Plansee IT11. A higher content of manganese is present in the oxide scale, which is a result of the presence of manganese in Plansee IT14. The Sigma phase is also present in this sample. Iron is also present in the oxide scale in this case.

A cross section of Sanergy HT is shown in **Figure 7**. An oxide scale of approx. 5 μm has grown on the alloy. The linescan EDX analysis shows that the oxide scale consists of an inner Cr_2O_3 layer and an outer spinel layer. The thickness of the Cr_2O_3 layer is approx. 2 μm . The two layers can be distinguished by the contrast difference in the micrograph.

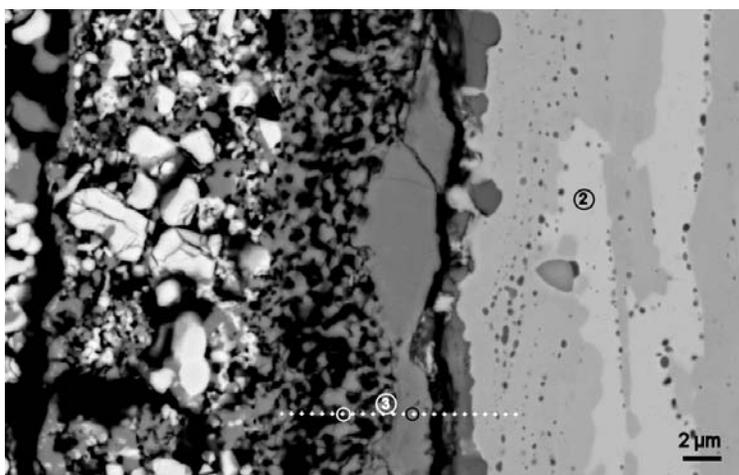


Figure 5. SEM micrograph of cross section of the Plansee IT11-coating interface.

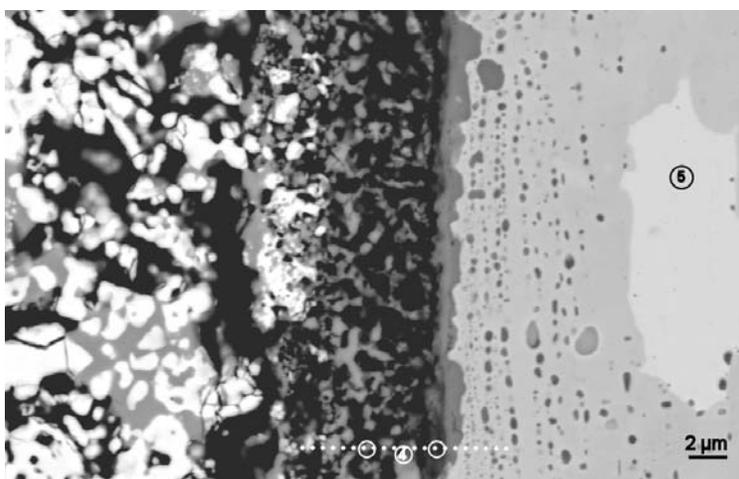


Figure 6. SEM micrograph of cross section of the Plansee IT14-coating interface.

The inner layer was identified as pure Cr_2O_3 . The content of chromium in the spinel is higher for Sanergy than observed for the Plansee alloys, albeit the Cr content in the outer spinel layer and in the Co_3O_4 coating is low. The chromium content of the spinel at the air-oxide scale interface is interesting, since Cr-species evaporates from the oxide scale during operation resulting in the so-called Cr-poisoning of the SOFC cathode. Thus, the results indicate that the oxide grown on Sanergy HT inhibits Cr-poisoning in a similar way as the Plansee alloys. The oxide scale appears to be well adherent on most of the interface and iron was not detected in the oxide scale. Titanium oxide is identified in the alloy matrix resulting from internal oxidation. White particles are observed in the alloy matrix. The particles are probably Laves phases. The formation of Laves phases have previously been shown to result in high creep strength and increased oxidation resistance of alloys (5).

A cross section of Crofer 22 APU is shown in **Figure 8**. An oxide scale of approx. 5 μm has grown on the oxide scale. The oxide scale is similar to the oxide scale grown on Sanergy HT although the Cr_2O_3 layer grown on Crofer 22 APU is thinner. The content of chromium in the spinel grown on Crofer 22 APU is comparable to Sanergy HT (both have higher Cr-content than the spinel layer grown on the Plansee alloys).

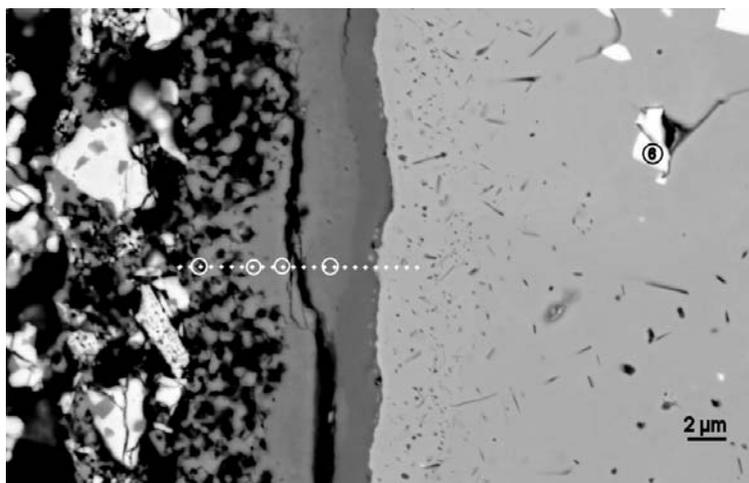


Figure 7. SEM micrograph of cross section of the Sanergy HT-coating interface.

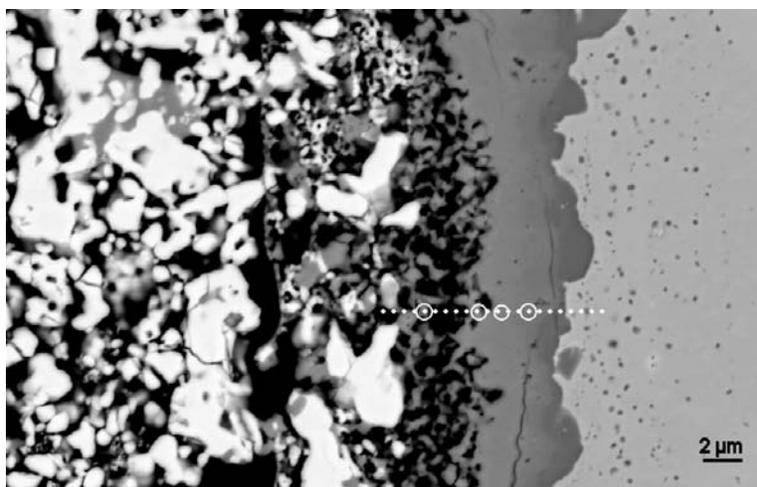


Figure 8. SEM micrograph of cross section of the Crofer 22 APU-coating interface.

Microstructure and Electrical Tests

The dual layer coating resulted in formation of dual layer oxide scales on the all the samples. The inner Co_3O_4 coating resulted in spinel oxide scales containing a large amount of cobalt. Furthermore, manganese supplied from the LSM15 coating and the alloy resulted in spinel oxide scales (and inner coating) containing large amount of manganese.

The contact resistance measurements showed that all the interfaces had ASR-values of less than $10 \text{ m}\Omega\text{cm}^2$ (after subtract of the auxiliary LSM plate) after 10000 h oxidation at 750°C in air. The measured ASR-values must be a result of the formed oxide scale at the interface. The electrical conductivity is approx. 5 S/cm for MnCoCrO_4 at 750°C in air (6). The conductivity is too high to account for the observed ASR-values, so the interface resistance must be governed by Cr_2O_3 instead. It was found that Sanergy HT formed the thickest layer of Cr_2O_3 . This explains that this alloy also exhibited the largest ASR-values. The evolution of the ASR over time indicates that the largest part of the Cr_2O_3 is formed during the initial oxidation. The ASR-values of the Plansee alloys are almost constant after an initial period.

750°C vs. 900°C

Oxidation tests of Crofer 22 APU coated with the same two-layer coatings have previously been performed at 900°C in air for a period of up to 4000 h (1). An accelerated test temperature of 900°C was chosen to simulate long term (40000-50000 h) oxidation behaviour at 750°C. The thickness of the oxide scale formed after 10000 h at 750°C in this study corresponds to the thickness of the oxide scale grown after approx. 1000 h at 900°C. The relative thicknesses of the Cr₂O₃ and spinel layers are also comparable at the two temperatures. The composition of the formed spinel is however different; the composition in the outer part of the spinel formed at 750°C is approx. Mn_{1,35}Co_{1,5}Cr_{0,15}O₄, while the composition in the outer part of the spinel formed at 900°C was approx. Mn_{0,9}Co_{1,7}Cr_{0,4}O₄. Spinel particles surrounding the LSM15 particles in the outer coating layer were also present at the sample oxidized at 900°C. The content of chromium was 10 at.% in these particles, while it was 3 at.% for the sample oxidized at 750°C. The results show that the outward chromium diffusion is relatively high at 900°C compared to 750°C compared to diffusion of the other cations. The difference is probably a result of a higher activation energy for diffusion of chromium compared to the diffusion of manganese and cobalt. The differences show that accelerated tests should be performed with great care.

The thicknesses of the oxide scales grown on the interconnects were 3-5 µm after 10000 h of aging at 750°C. This corresponds to an oxide scale of 6-10 µm after 40000 h assuming a parabolic oxidation rate. The low degradation rates measured combined with the slow grow rate of the oxide scale is promising for the lifetime durability of slurry coated interconnects in SOFC stacks.

Conclusion

The long term oxidation behaviour and the electrical interface resistance between coated Crofer 22 APU, Sanergy HT, Plansee IT10, Plansee IT11, Plansee IT14 and La_{0,85}Sr_{0,15}Mn_{1,1}O₃ plates were studied by a DC four-point method in air at 750°C for 10000 h. The formation of a dual layer Cr₂O₃-(Mn,Co,Cr)₃O₄ on all the alloys resulted in low interface resistances for all the samples. The interface resistances were governed by the growth of the Cr₂O₃ layer. The low degradation rates measured combined with the slow grow rate of the oxide scale during the 10000 h long term test is promising for the lifetime durability of slurry coated interconnects in SOFC stacks.

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