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Application of composite coatings as protection/contacting layers for metallic *high-chromium-content* SOFC interconnect material

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Abstract

Oxidation of the surface of metallic chromium oxide forming metallic interconnect (MIC) can cause up to one third of the total SOFC stack degradation during the long-time operation at elevated (750 - 850 °C) temperatures. The application of protective coatings is the most effective method not only for reduction of the growth of oxide scales but also for prevention of evaporation of Cr-containing species from MIC and of the poisoning of the air electrode. Two approaches to form the protective layers on the surface of CFY interconnect material with high chromium content (~ 94 %) have been tested. The CuNiMn-spinel (CNM) coatings were deposited using the wet powder spraying (WPS) of the slurries. As an alternative approach physical vapour deposition (PVD) method was used to apply thin metallic films on the surface of MIC and to form the protection layer by in-situ oxidation under the stack relevant conditions. The experiments were carried out at first using the model samples of different geometries to evaluate the properties and efficiency of the coatings. Composite pastes with addition of perovskite powders were also tested, because the CNM layers densify at SOFC operating conditions and shrinkage during long-term operation can cause the decrease of the contact area between the components and accelerate the degradation of the stack performance. The experiments have shown that the perovskite additive can efficiently reduce the shrinkage compared to the pure CNM material and match it well to the shrinkage of other stack components. Moreover, the perovskite additive do not deteriorate the electrical properties of the composite since the perovskites have electrical conductivity comparable to CNM. The PVD coatings were tested in combination with CNM containing contacting layers applied by screen printing to reduce the chromium release rate. The experiments have shown a good compatibility and mechanical stability between the contacting layer and PVD protective coating during operation and thermal cycling. The materials and composites have been characterized by scanning electron microscopy (SEM/EDX), optical dilatometry and electrical conductivity measurements. Finally, the most promising material combinations obtained for model samples were transferred to SOFC stacks MK35x and evaluated under real operation condition.

Introduction

Degradation of the stack performance during the long-term operation is the main challenge in the development and application of the solid oxide fuel cells. The oxidation of the interconnect material accompanied by the growth of the oxide scale (i) and the Cr-evaporation (ii) from the metallic interconnect are considered to be the main factors influencing the degradation of the stack operating at high temperatures (above 800 °C). The growth of the oxide scale takes place at the interconnect surface even in the reducing ambience of the anode gas [1] since the small quantities of oxygen or moisture (H₂O, OH⁻) can be enough to form the oxide scale on the MIC surface. There are different approaches to create the reliable protective layers on the surface of interconnects to prevent or reduce their oxidation. The perovskite layers applied by atmospheric (APS) or high-velocity oxygen fuel (HVOF) spraying are used for a long time [2, 3] as the relative reliable protective coatings at the cathode side of SOFC interconnects. The perovskite layers applied by these methods are dense and stable. However they have often the layered structure with various micro-cracks typically generated during the spraying process [4], facilitating the penetration of oxygen to the metallic surface of interconnect. Apart from, the dense perovskite layer hinder the interlayer diffusion of elements, what can result in formation of high ohmic overlays (like Cr₂O₃, SiO₂) accelerating dramatically the stack performance degradation. The spinel materials are good alternatives to the perovskite protective coatings [5]. First of all, they can be densified at the SOFC stack operating temperatures allowing relatively easy interdiffusion of the elements (Cr, Mn, Co, Ni: depending on interconnect and spinel compositions) from interconnect, which is important for metal interconnect materials with high chromium contents (like CFY). Such a feature of spinel materials leads to the doping of the spinel protective layer or even to formation of the solid solution having good electric conductivity at the stack operating temperatures. Due to their good sinterability and reactivity the spinel protective layers can be suitable for application by relatively low-price deposition methods: wet powder spraying (WPS), screen printing, roll-coating. One of the promising ways to form the protective layers on interconnect surface is the vacuum deposition (PVD, CVD) of thin metallic films with well defined stoichiometry followed by their in-situ oxidation during the stack sealing and initialization.

A chromium-based alloy CFY containing 5 % iron by weight as well as the traces of yttrium was used as metallic interconnect (MIC) material. Physical properties of the CFY alloy make it ideal for use in high-temperature fuel cells, however a very high content of chromium sets down the special requirements to the properties and to the quality of protective layers. Two types of coatings were tested in our experiments: CuNiMn-spinel (CNM) pastes were deposited using the wet powder spraying (WPS) and physical vapour deposition (PVD) method was used to sequentially apply thin metallic films on the MIC surface and to form the protective layer by in-situ oxidation under the stack relevant conditions.

1. Experimental

A modified spray gun TR 80 LCD of the company REKA was used to apply the CNM spinel slurries (pastes) by the wet powder spraying (WPS). An advantage of this gun is the possibility to vary the temperature of the sprayed medium (from room temperature up to 100 °C and even higher), which allows the flexibility in setting the slurry viscosity and, correspondingly, effective control of the uniformity of the layers deposited on interconnects with structured surface. Physical vapour deposition (PVD) method was used as a second deposition technique to apply the thin metallic films on the surface of MIC. The coatings

were deposited by unbalanced magnetron sputtering from three pure metallic targets Co, Mn and a rare earth (RE) metal. The samples were mounted on a substrate holder, introduced into a vacuum system, pumped to a base pressure $< 2 \cdot 10^{-5}$ mbar and subjected to a plasma treatment to remove some native oxide scales and to activate their surface, enhancing the adhesion of the metallic coating. The metallic coating was deposited adjusting the power to the Co and Mn targets to achieve a Co:Mn ratio of 50:50. The overall coating thickness of as-deposited metals was approximately 4 μm . The formation of protective layer was carried out by in-situ heat treatment of the sample or interconnect under the stack relevant conditions to achieve a uniform transformation of the metallic layer into a metallic oxide (RE-CoMn-Oxide). To evaluate the properties and efficiency of the coatings, the coating materials were tested initially using the model samples of high chromium material CFY. The chromium evaporation tests were carried out at the Chalmers University using the denuder technique described in [6]. The structured symmetrically joined samples with area of $20 \times 20 \text{ mm}^2$ cut from the interconnects were prepared for the time dependent measurements of electrical resistance. The contact ribs in symmetric samples were applied in all the cases by the screen printing of the CNM-pastes. The resistance measurements (ASR) were carried out with two thermal cycles in the stagnant air ambience at the stack relevant temperatures. The samples were cut and polished for the cross-section analysis using SEM imaging and EDX analysis.

2. Results and discussions

Influence of protective coatings on Cr-evaporation from the CFY interconnect material

The efficiency of different types of protective coatings for the CFY MIC material was firstly tested in chromium evaporation experiments at temperature 850 °C under humidified (3 % H_2O) air gas flow. The possibility of the time resolved measurements with the denuder technique gives information about the rate of chromium evaporation from the material as a function of time. Figure 1 shows the Cr vaporization versus exposure time for the uncoated, the PVD RE-CoMn-coated, and the CNM paste-coated CFY interconnect material.

The uncoated CFY material does evaporate significantly more chromium compared to the coated samples: the Cr vaporization rates for both the RE-CoMn PVD- and CNM WPS-coated coupons were more than one order of magnitude lower than the rate for the uncoated material. The difference between the RE-CoMn PVD- and CNM WPS-coated samples was not so pronounced as in the case of uncoated material (only 10 – 15 % difference). However, it should be noted that the thickness of the PVD layer was about three times smaller after formation of oxide scale in comparison with the CNM ones.

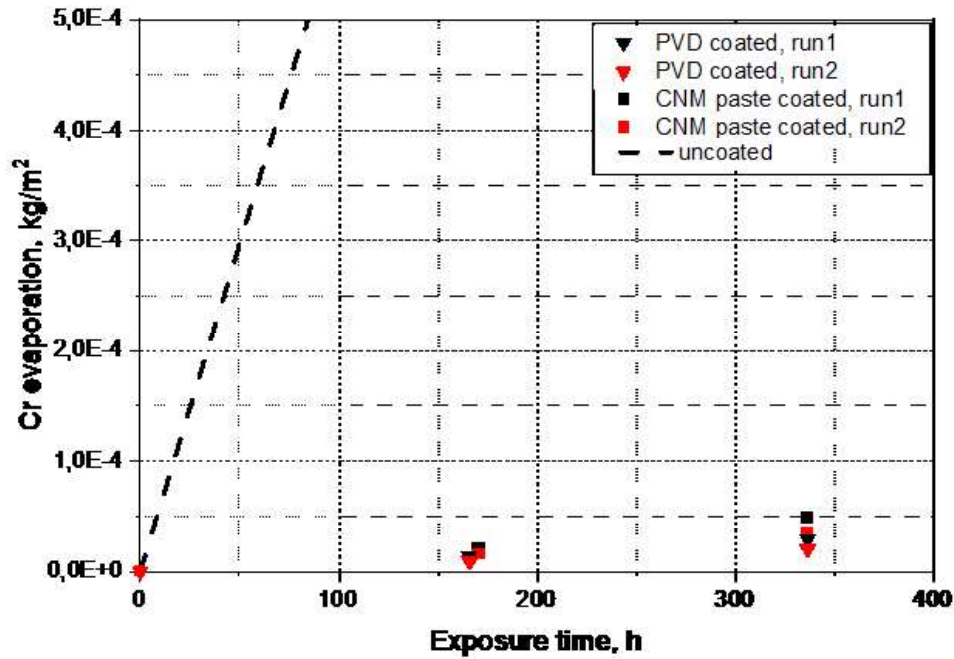


Fig. 1. Cr-evaporation as a function of exposure time for PVD-coated (triangles), CNM paste-coated (squares) and uncoated (dashed line) CFY samples in air containing 3% H₂O with a flow rate of 6000 sml/min (two runs for each type of samples).

Electrical Resistance

The influence of different protective coatings on performance of the CFY MIC material was also tested using the time dependent measurements of resistance of symmetrically joined samples within two thermal cycles at the SOFC stack relevant operating conditions via 4-probe method. The the area specific resistance (ASR) values can be then evaluated from resistance using the simple equations:

$$R = \frac{U}{I}; ASR_{sample} = R \cdot A,$$

and, taking into account the symmetrical cell assembly: $ASR = \frac{R \cdot A}{2},$

R – resistance, U – voltage; I – current; A – contact area.

The diagram of the change of resistance of the CFY samples with the RE-CoMn PVD and CNM WPS coatings within two thermal cycles is presented in Figure 2.

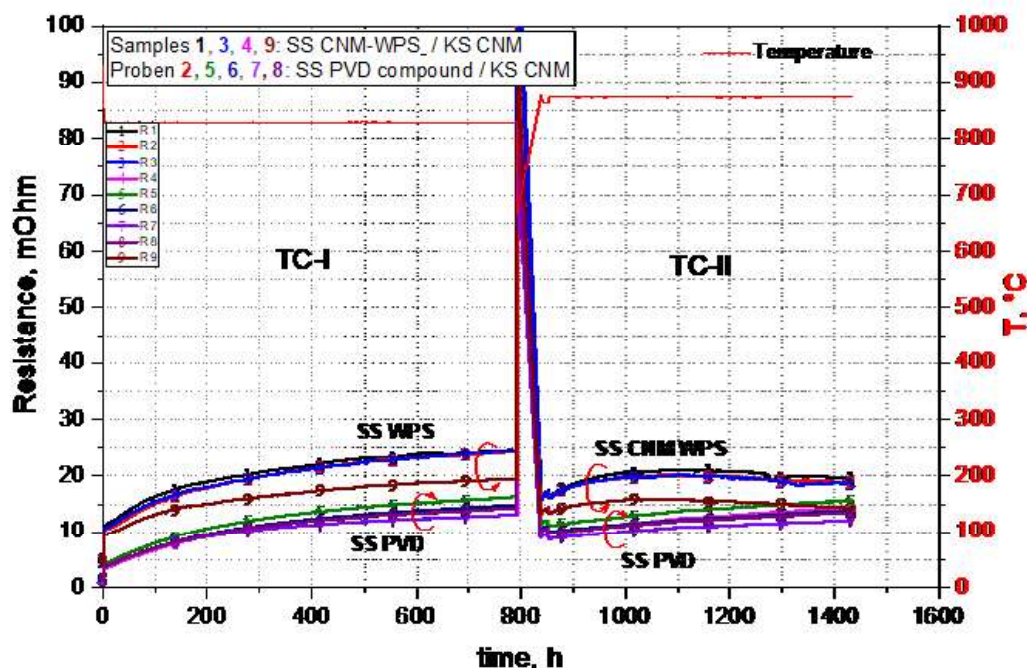


Fig. 2. Time dependent development of resistance of symmetric model samples coated with RE-based PVD- and CNM spinel WPS-layers (SS) within two thermal cycles and contacted with CNM paste (KS). TC-I: $T \sim 840^{\circ}\text{C}$; TC-II: $T \sim 875^{\circ}\text{C}$.

Both types of coatings have shown the similar behaviors during the first thermal cycle of measurements: (i) an increased parabolic gain of resistance at initial phase of the experiment (150 – 200 h) followed by (ii) slow nearly linear further increase of resistance. The parabolic behavior of the resistance dependence is typical for the metallic interconnect materials and is determined by oxidation processes at the MIC surface. At the beginning of the process, the coatings are not dense enough and cannot prevent the penetration of oxygen to the surface of interconnect. Oxidation of the MIC is accompanied in both cases by the intensive initial formation of the oxide scale at the metal surface due to reaction of chromium with penetrating oxygen. Apart from, the oxidation of deposited metallic films takes place in the samples prepared by the PVD techniques contributing to acceleration of the oxide scale formation. In the samples prepared by WPS from the CNM spinel paste the formation of the dense protection layer takes place gradually due to the sintering of the powder particles of CNM material. After formation of the densified protective layers, the growth of the oxide scale at the MIC surface goes more slowly (stage ii). The samples with the PVD coating have the lower starting resistance due to the smaller total thickness of the layer as compared to CNM WPS layer even after complete oxidation of deposited metallic components. The surprising behavior of the samples with the CNM spinel coating was observed during the second thermal cycle of the resistance measurements. This cycle was carried out at temperature of 875°C that is about 25 – 30 $^{\circ}\text{C}$ higher than the standard stack operation temperature and was aimed to simulate conditions of accelerated stack degradation. The parabolic-like course of the resistance dependence at the beginning of the second cycle was similar to one in the first cycle. However the negative value of resistance change was observed in these samples after nearly 200 h of measurements. Such a behavior of the samples we can attribute to high reactivity of the spinel materials at increased temperatures. At the beginning of the second thermal cycle, the change of composition of the adjacent to interconnect protection layer on the basis of CNM spinel takes place due to enhanced diffusion of chromium atoms to interconnect surface and owing to increase of the thickness of the chromium oxide scale.

Chromium oxide have much higher resistivity than the pure CNM material [5, 7]. Therefore the resistance of the CNM-coated samples increases at the beginning of the second cycle. After saturation of the surface layer with chromium oxide, the further oxidation of MIC is hindered. The high temperature process is further governed by diffusion of chromium into the CNM coating resulting in the mutual doping or even in formation of solid solution on basis chromium containing species and CNM, which have the higher electrical conductivity as compared to pristine compounds [5]. Additionally, the sintering CNM is accelerated due to increased temperature. This leads to reduction of the total layer thickness, to improvement of the contact area and to negative tendency of the resistance dependency during the second thermal cycle.

The dramatic influence of amount of chromium oxide on conductivity of the CNM coatings was proved by measurements of resistance of the CNM samples with different content of admixed chromium oxide powder. Three powder compositions with ratios CNM:Cr₂O₃ as high as 90:10, 75:25 and 50:50 (mol. %) were prepared by thorough mixing of corresponding powders and compared with pure CNM material. The standard screen printing pastes were manufactured from these compositions, printed as the rectangular samples onto 8YSZ substrates and sintered at temperature 1100 °C for 50 hours. The temperature dependence of resistance of the samples was measured via 4-probe method in temperature range between room temperature and 950 °C. Figure 3 shows the temperature dependence of resistance of the samples with different content of chromium oxide.

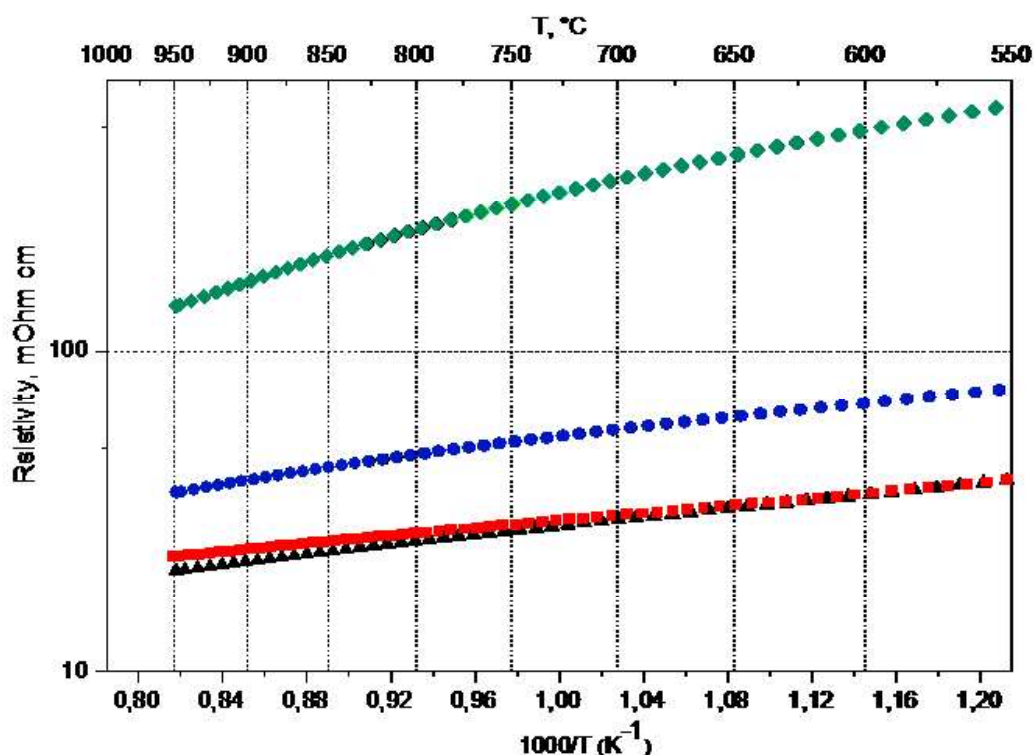


Fig. 3. Temperature dependence of resistance of sintered paste samples containing different ratios of CNM spinel compound and Cr₂O₃ (■ - pure CNM material; ▲ - CNM:Cr₂O₃=90:10; ● - CNM:Cr₂O₃=75:25; ◆ - CNM:Cr₂O₃=50:50).

It can be seen that the presence of small amounts of chromium oxide in the spinel layer do not deteriorate sufficiently the electrical conductivity of the material, which can be attributed to formation of the doped CNM spinel or of solid solution with chromium oxide. However the resistance of the composition increases remarkably with the increase of the Cr₂O₃ content in the samples. The resistance of the sample containing 50 % of high

resistive chromium oxide is one order of magnitude higher compared to the resistance of material with low content of Cr_2O_3 .

Microstructure of coatings

Microstructure of the coatings was analyzed after two cycles of measurements (total time about 1600 h) at the stack relevant conditions. The SEM images of polished cross-sections of the samples are presented in the Figure 4.

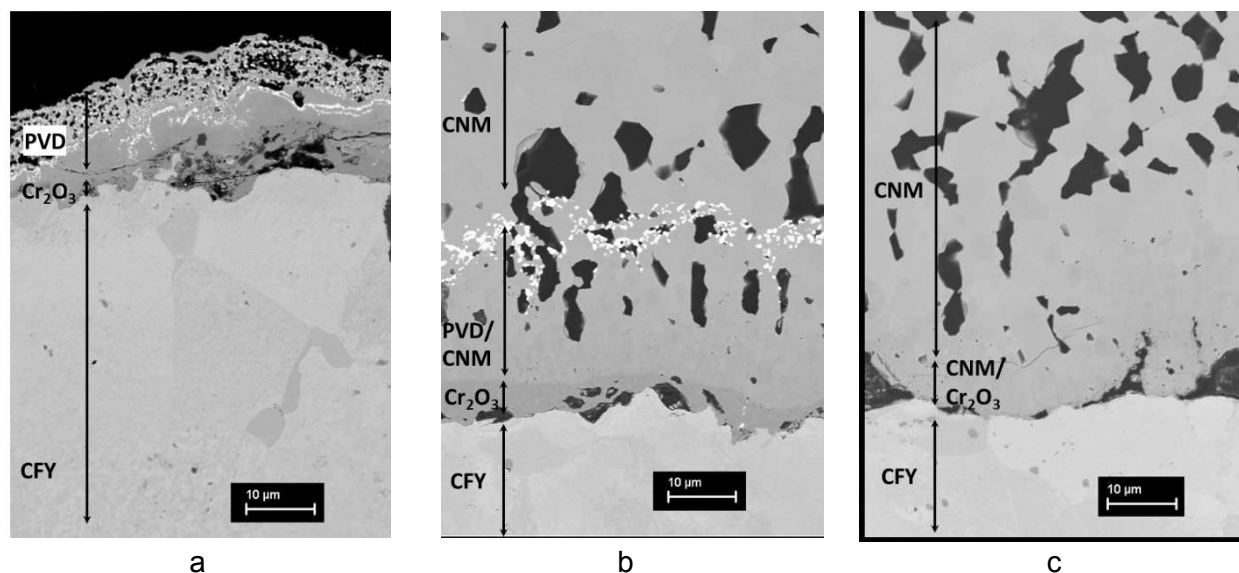


Fig. 4. SEM images of polished cross-sections of the layers formed from PVD-deposited RE-CoMn thin films (a), PVD-deposited films in contact with CNM paste (b), and WPS-deposited CNM paste (c).

The oxidation process of thin metallic RE-CoMn thin films deposited by PVD is accompanied by the exchange of Co and Mn between the layers at 850°C and should, ideally, result in formation of the uniform interlayer at the surface of the metallic interconnect. In fact, it can be seen, that the RE-CoMn PVD deposit forms the multicomponent structure. Moreover, this structure is dense only at the interface to MIC whereas the surface of the newly formed layer is pretty porous (Fig. 4a). Apart from, the oxidized RE-metal forms an additional interlayer which is very thin and is not continuous. On the other hand, the formation of the dense protective layer from the CNM spinel particles applied by WPS technique takes place during high temperature treatment of the deposited paste/slurry (Fig. 4c). Due to good sinterability of the CuNiMn spinel compound at temperatures below 900 °C, the formed layer possess only the closed porosity, is uniform and has a good adhesion to interconnect surface. It can be seen from the SEM images of cross-sections in Figure 4, that the layer formed from the PVD deposited metal films in combination with CNM contact paste (Fig. 4b) has the dense uniform microstructure at the interface to interconnect. The RE-based interlayer probably provides an additional barrier against the chromium diffusion into the coating hindering its diffusion to CNM and evaporation of chromium volatile components at operating temperatures of the SOFC stack. The efficiency of such approach is illustrated by the chromium distribution analysis presented in Figure 5. Chromium concentration was lower in the structure formed from the PVD + CNM combination as compared to solely CNM WPS layer at equal distances to interconnect surface. The sharp drop of Cr concentration is remarkable between the points 2 and 3 in the layer combination RE-CoMn PVD + CNM as compared to slow decrease one in the samples with only CNM-WPS layer, confirming the higher efficiency of PVD + CNM-paste combination.

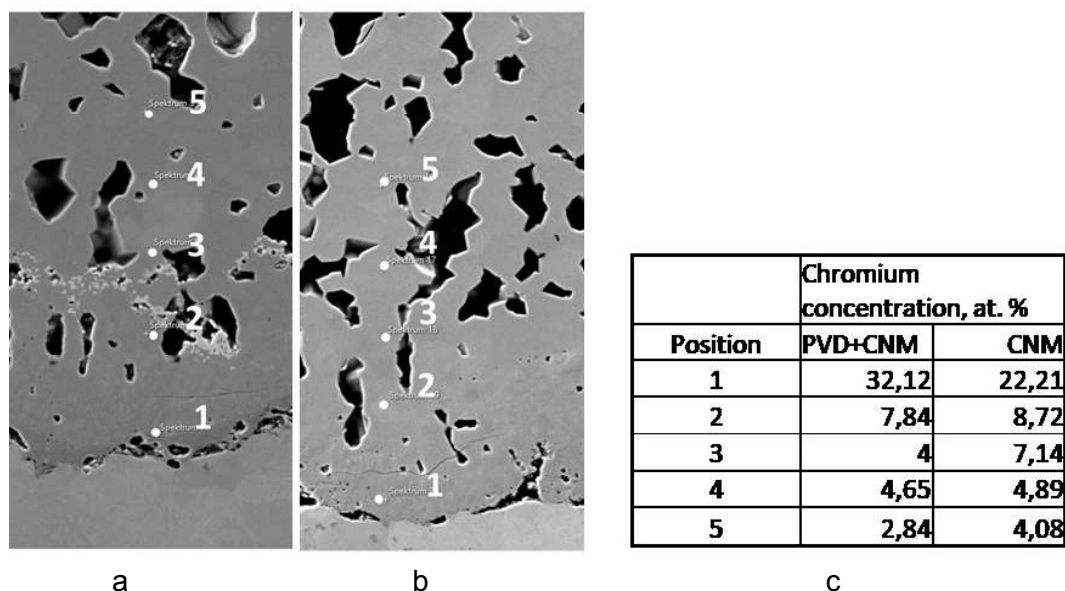


Fig. 5. Cross-sections of layers formed from PVD deposited RE-CoMn films + CNM paste (a) and only from WPS CNM paste (b), and chromium distribution in these layers (c).

The similar microstructure resulting from this material combination was also observed in the real SOFC stack post-test analysis of cross-sections of the interconnects after operation for 3000 h (Fig. 6).

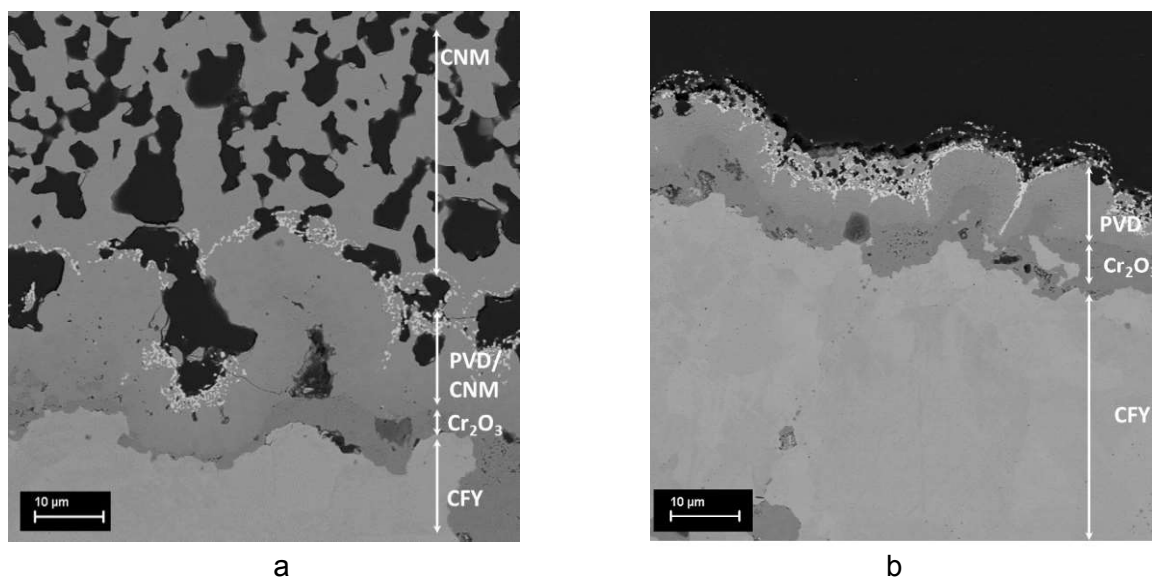


Fig. 6. SEM images of polished cross-sections of interconnect samples with RE-CoMn-PVD coating cut from the real stack after operation for 3000 h at different positions: a) PVD-deposited films in contact with CNM rib; b) air flow channel with PVD coating only.

The porosity of the composite layer in the stack (Fig. 6a) is higher than in the model samples (Fig. 4b) because of almost twice longer holding time at high temperature (3000 h and 1600 h correspondingly) and therefore longer sintering time of the CNM material.

Influence of perovskite addition on high temperature behavior of CNM spinel material

Due to the good reactivity of its constituents, the spinel materials, based on combinations of Mn, Co, Fe, Ni, Cu components, show an enhanced sinterability at operation temperatures of SOFC stacks, facilitating the possibility of formation of reliable contacting between different components of the stack. At the same time, the sufficient shrinkage of the material can occur during a long operation times of the SOFC stack at elevated temperatures. This causes in turn the reduction of the contact area between the stack components up to full contact loss due to mechanical disruption, especially during the thermal cycling because of difference of the thermomechanical properties of the stack components: interconnect, protective/contact layer, sealing glass, electrolyte. In this case, the formation of the composite layers consisting of mixtures between the spinel and perovskite materials can be used as an effective countermeasure. Figure 7 demonstrates the temperature dependence of the shrinkage of the material composed from mixture of CuNiMn-spinel and LSM-based perovskite (50:50 by weight) in comparison to the samples made from the pure CNM-spinel. The holding of the samples at temperature of 950 °C (~100 °C higher than the stack operating temperature) was applied to simulate the accelerated degradation conditions.

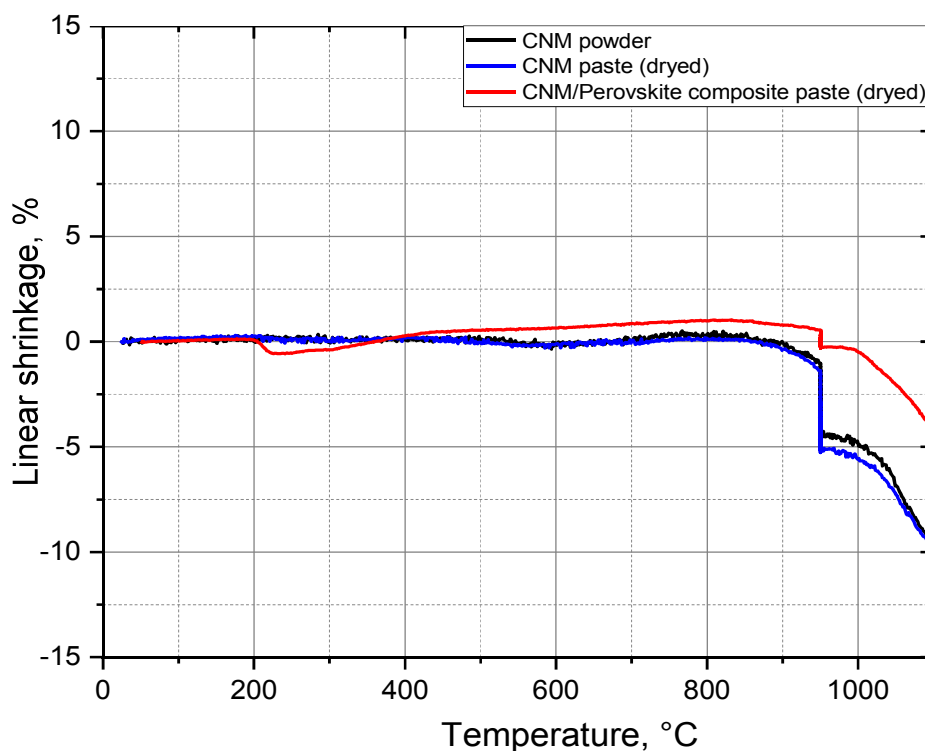


Fig. 7. Comparison of linear shrinkage of pure CNM spinel material and of composite CNM + LSM based perovskite.

Perovskites have the higher sintering temperature (> 1100 °C) [8] and cannot be dense sintered at SOFC stack operating temperatures (~850 to 950 °C). The CNM material acts in this case as the sintering aid for the mixed composition CNM + LSM based perovskite providing the good joining of particles in the composite layer and for almost no change of electrical properties as compared to the pure CNM material (Fig. 8). At the same time the perovskite particles form the backbone matrix preventing excessive sintering and the shrinkage of the combination protection/contacting layer.

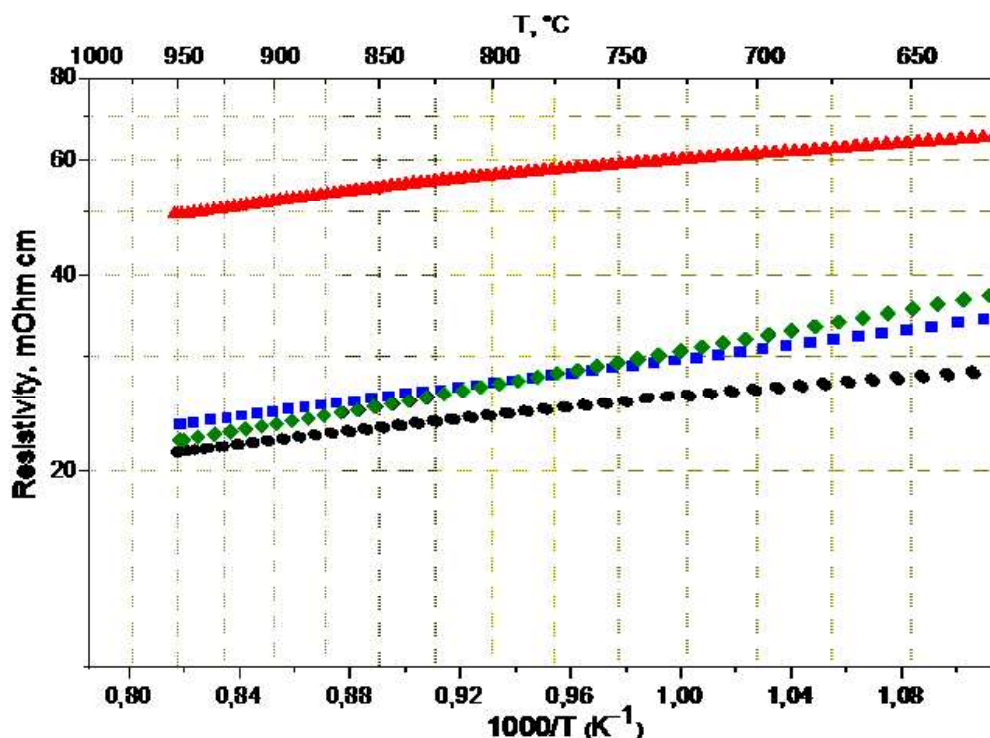


Fig. 8. Resistivity of sintered at 950 °C composite CNM:LSM = 75:25 (mol.%) (◆) in comparison with resistivity of samples sintered from pure CNM (■), LSM (▲), and perovskite cathode (●) sintered at 1350 °C.

Conclusions

Effective chromium retention coatings could be prepared on the surface of the *high-chromium-content* CFY interconnect material by different techniques: the CuNiMn-spinel coatings were deposited using the wet powder spraying (WPS) method; thin metal Co, Mn, and RE (RE-CoMn) films were applied by physical vapour deposition (PVD) followed by in-situ oxidation at SOFC stack operation conditions. Both types of coatings have shown comparable efficiency to reduce the release of chromium volatile components from CFY interconnect material. The Cr vaporization rates for both the RE-CoMn PVD- and CNM paste-coated material were more than one order of magnitude lower than the Cr vaporization rate of the uncoated material. The combination of both techniques results in formation of the coating/contacting composite layer with enhanced chromium retention and improved electrical properties. The composite layers formed on the basis of perovskite and CNM spinel powder mixtures can be used to improve the long-term thermomechanical and electrical performance of the coating and contacting layers. Testing of these materials combinations is now in progress in the SOFC stacks.

Acknowledgments

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