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Publisher's version / Version de l'éditeur:
https://doi.org/10.1149/1.3429008
ECS Transactions, 26, 1, pp. 357-362, 2010-06-15

ECS Transactions, 26 (1) 357-362 (2010)
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Dense Protective Coatings for SOFC Interconnect Deposited by Spray Pyrolysis

Yongsong Xie, Wei Qu, Baisheng Yao, Nima Shaigan, and Lars Rose
Institute for Fuel Cell Innovation, National Research Council Canada
4250 Wesbrook Mall, Vancouver, BC, V6T 1W5, Canada

Spray pyrolysis deposition is a cost-effective process to deposit films of a wide variety of materials, especially solid oxides. In this study, spray pyrolysis deposition was used to deposit 2-3 μm thick $Mn_{1.5}Co_{1.5}O_4$ spinel and Ta_2O_5-doped CeO_2 on a ferritic stainless steel as protective coatings on SOFC interconnect. The coated samples were exposed to air at 1000°C to study the diffusion and oxidation behaviours. Characterization results indicated that the coatings are dense, have good adhesion to the substrate, and are stable and effective to prevent Cr outward diffusion at the high temperature.

Introduction

Chromia-forming stainless steels, in particular ferritic stainless steels, are considered to be promising candidate materials for interconnect and metallic support in solid oxide fuel cells (SOFCs) because of their low cost, good coefficient of thermal expansion (CTE) matching with cell materials and excellent electrical and thermal conductivity [1]. However, the area specific resistance (ASR) of the steels continuously increases during SOFC operation, particularly at the cathode side, due to the growth of oxides at the interface between cathode and steel. In addition, chromium evaporation and diffusion from Fe-Cr steels to SOFC cathodes are observed. The migrated Cr degrades the electrochemical performance of the cathode. Coatings of $(Mn,Co)_3O_4$ spinels on chromia-forming steels have been demonstrated to effectively reduce the oxygen inward and Cr outward diffusion while maintaining a sufficient high-temperature electronic conductivity [2-4]. The studies on $(Mn,Co)_3O_4$ coatings also discovered that the composition of the coating and the method of deposition are equally critical. For an effective protection, fully dense coatings or coatings without open porosity are required. The best coatings were produced by the direct formation of a dense and adherent coating on the substrate.

In anodic conditions, a CeO_2 layer applied by radio-frequency (RF) magnetron-sputtering was the most effective protective coating among several candidate coatings [5]. The performance of the CeO_2 layer can be further improved by increasing the electronic conductivity and decreasing the oxygen ion conductivity, which can be achieved by doping CeO_2 with pentavalent cations. Such a doping can increase the Ce^{3+} defects that increase electronic conductivity and decrease the density of oxygen vacancies that are available for ionic conduction [6,7].

Spray pyrolysis deposition is a versatile process to deposit films of a wide variety of materials, especially solid oxides. This technique involves atomizing a solution, which contains soluble salts of the constituent atoms of the desired compound, into discrete droplets and spraying the droplets onto a heated substrate (usually between 300 and 700°C). The sprayed droplets reaching the hot substrate surface undergo pyrolytic

decomposition and form a chemical compound. The chemical reactants are selected such that the products other than the desired compound are volatile at the temperature of deposition thus escape in the vapor phase. The substrate provides the thermal energy for the thermal decomposition and subsequent sintering of the constituent species giving rise to a coherent film. Unlike closed vapour deposition methods, spray pyrolysis deposition does not require high quality targets and/or substrates nor does it require vacuum at any stage, which is a great advantage if the technique is to be scaled up for industrial applications. Spray pyrolysis deposition offers an extremely easy way to dope films with virtually any element in any proportion by merely adding it in some form to the precursor solution. Films from very porous to very dense can be deposited on various substrates when using different spray parameters. The main advantages of spray pyrolysis deposition include the simplicity of the apparatus, the low cost of the process and the ease of scalability to a large scale. National Research Council Canada's Institute for Fuel Cell Innovation (NRC-IFCI) has been developing spray pyrolysis technique for the cost-effective fabrication of fuel cells since 2004. Processes for depositing various films for SOFC applications, including dense and thin electrolyte deposited on porous anode [8], have been developed. In this study, dense $(Mn,Co)_3O_4$ and Ta_2O_5-doped CeO_2 coatings were deposited on a Fe-Cr substrate by spray pyrolysis as potential protective layers for SOFC applications.

Deposition of Coatings

The precursor solutions used for depositing $(Mn,Co)_3O_4$ and Ta_2O_5-doped CeO_2 coatings were prepared according to the stoichiometries of $Mn_{1.5}Co_{1.5}O_4$ and $(CeO_2)_{0.96}(Ta_2O_5)_{0.04}$ by dissolving nitrate and isopropoxide precursors in organic solvents. The Fe-Cr substrate was dense ZMG232L from Hitachi Metals Ltd. which has a composition of Cr 22.04%, Mn 0.48%, Ni 0.33%, Zr 0.20%, La 0.08%, C 0.02% and Fe balance [9]. Fig. 1 schematically shows the set-up of the self-built apparatus used in this study. The apparatus utilized a twin-fluid, parallel flow nozzle for the atomization and spray of the precursor solution supplied by a syringe pump. A sufficiently high force applied to the solution at the outlet of the nozzle by a compressed air caused the disintegration of the solution into micron-sized droplets and the spray of the droplets onto the substrate heated to around 600°C. The spray nozzle was moving back and forth along two perpendicular directions during the deposition process. The process is scalable for high volume manufacturing in which a moving table and an array of nozzles can be used to achieve continuous, large area deposition.

The as-deposited $Mn_{1.5}Co_{1.5}O_4$ and $(CeO_2)_{0.96}(Ta_2O_5)_{0.04}$ coatings were 2-3μm thick. Fig. 2 shows the SEM images of the top surfaces of the coatings. The coatings were dense but there were some shallow micro-cracks on the top of the doped ceria coating. A coating was gradually built up during the deposition by the repeated movement of the spray nozzle. Due to the repetitive nature of the process, when shallow micro-cracks form on the top of a coating during a spray run, the next run would fill the cracks. Therefore, such shallow micro-cracks were not a problem for obtaining dense coatings. X-ray diffraction (XRD) patterns and energy dispersive X-ray spectra (EDS) indicated that the two coatings had the intended microstructures and compositions.

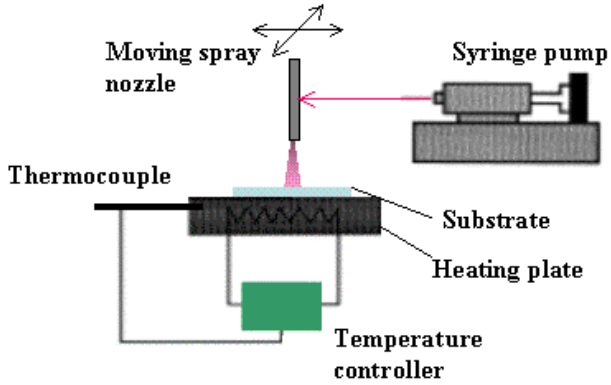
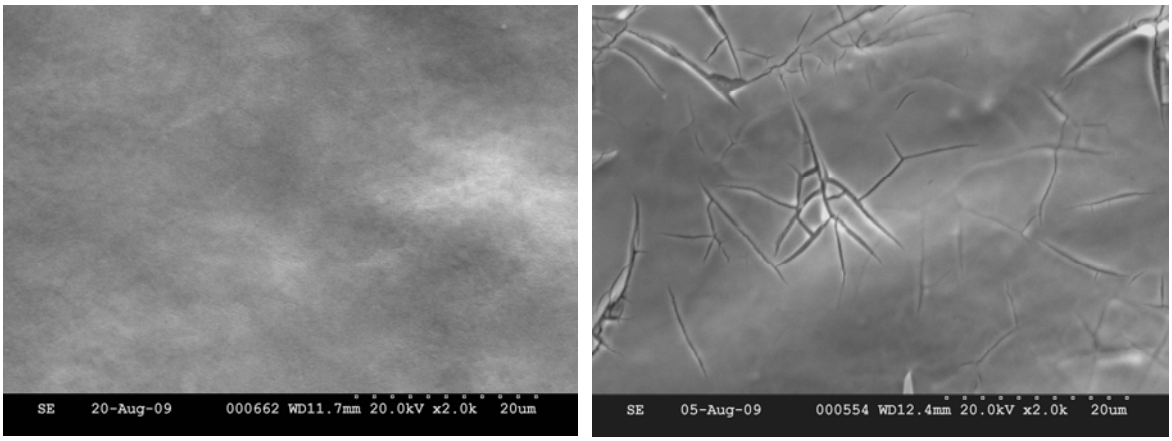


Fig. 1: Schematic drawing of the spray pyrolysi apparatus.



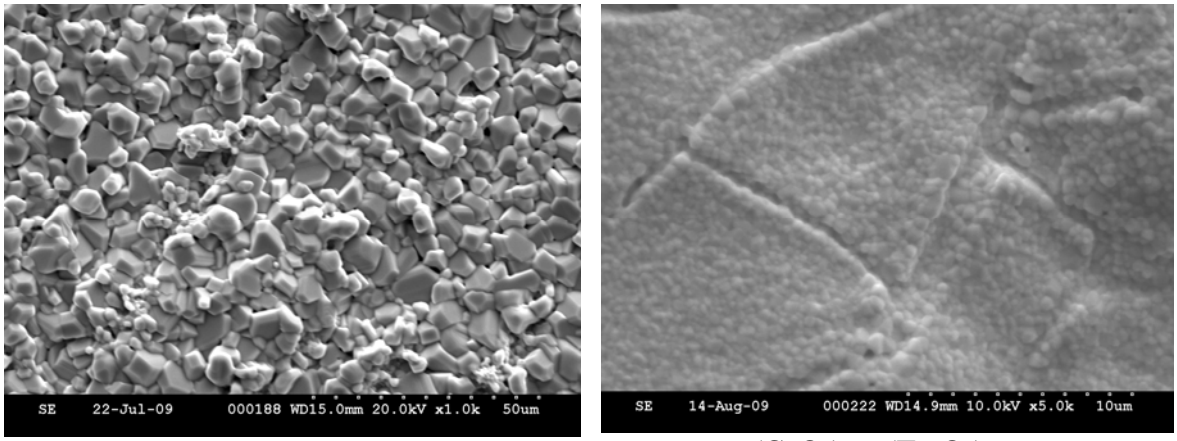
$Mn_{1.5}Co_{1.5}O_4$ $(CeO_2)_{0.96}(Ta_2O_5)_{0.04}$

Fig. 2: SEM micrographs of the top surfaces of as-deposited coatings.

High Temperature Diffusion and Oxidation Characterization

According to a study carried out by the supplier of ZMG232L, the structures of the oxide layers formed on ZMG232L were similar after oxidations at 750°C and at 1000°C [9]. Since the thickness of oxide scale achieved by oxidation at 750°C was too thin to study, The oxidation and diffusion behavior of the coated samples were studied at 1000°C in still air. The samples were put into a pre-heated furnace for 168 hours, and then air-cooled to room temperature.

Figure 3 show the top surfaces of the coated samples after the high temperature exposure. Both coatings showed complete adherence to the substrate, and no spallation or cracking was observed. This is attributed to a good oxide scale adherence and CTE match between the coatings and substrate as well as a good structural stability of the coatings. The grains of the two coatings have grown from the original nanometer size (as deposited oxide coatings by spray pyrolysis typically have grain sizes less than 20 nm [8]) to micron size and sub-micron size, respectively. The shallow micro-cracks on the top of the doped ceria coating have healed after the high temperature exposure.



$Mn_{1.5}Co_{1.5}O_4$ $(CeO_2)_{0.96}(Ta_2O_5)_{0.04}$

Fig. 3: SEM micrographs of the top surfaces of the coated samples after exposure in air at 1000°C for 168 hours

The micrographs and EDS elemental maps/spectra of polished cross-sections of the samples after the high temperature oxidation are shown in Figs. 4 and 5 (because the peaks of some elements overlap, elemental maps are not shown for the doped ceria sample). The coatings were well bonded to the Fe-Cr substrate via thin chromium oxide sub-layers . The Cr map and peak indicate that Cr did not diffuse into either of the coatings. The Mn and Co maps and the Ce and Ta peaks show that these elements in the coatings barely diffused into the oxide sub-layers, which implies that the coatings were stable at high temperature. The fact that the thin oxide scales formed between the protective layers and the Fe-Cr substrate during the high temperature oxidation indicates that the thin coatings could not completely block the oxygen inward migration.

Summary

Thin and dense $Mn_{1.5}Co_{1.5}O_4$ and $(CeO_2)_{0.96}(Ta_2O_5)_{0.04}$ were deposited by spray pyrolysis on Fe-Cr substrates as protective coatings. At 1000°C in air, the deposited coatings were stable and were effective barriers to Cr outward diffusion. Further studies will include the characterization of the electrical conductivity of the coatings, and the optimization of the coating thickness to ensure sufficient blocking of oxygen inward migration while maintaining the ASR of the coated steels at acceptable values.

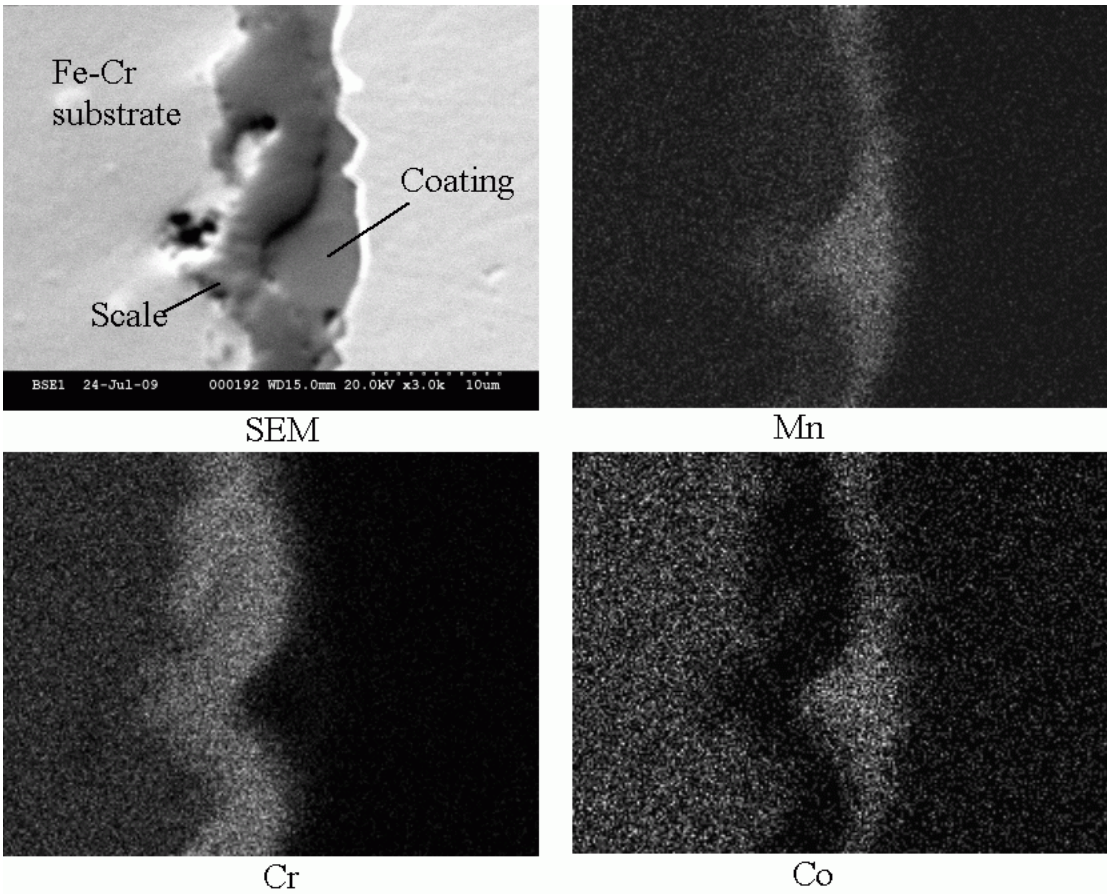


Fig. 4: SEM image and EDS elemental mapping of a polished cross-section of $Mn_{1.5}Co_{1.5}O_4$ coated ZMG232L after exposure in air at 1000°C for 168 hours.

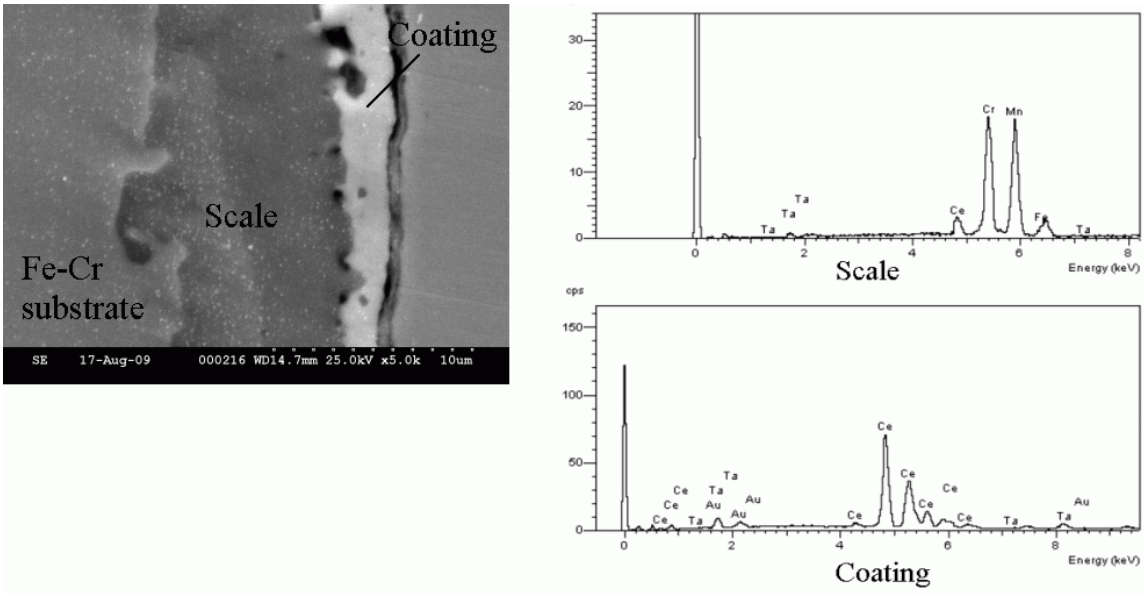


Fig. 5: SEM image and EDS spectrum of a polished cross-section of $(CeO_2)_{0.96}(Ta_2O_5)_{0.04}$ coated ZMG232L after exposure in air at 1000°C for 168 hours.

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