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Fabrication of (Mn,Co)$_3$O$_4$ Surface Coatings onto Alloy Substrates

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Abstract

Ferritic stainless steels are promising candidates for IT-SOFC interconnect applications due to their low cost and resistance to oxidation at SOFC operating temperatures. However, several challenges remain, including long term electrical conductivity and surface stability under interconnect exposure conditions and chromia scale evaporation. One means of extending interconnect lifetime and improving performance is to apply a protective coating, such as $(Mn,Co)_3O_4$ spinel, to the cathode side of the interconnect. These coatings have proven effective in reducing scale growth kinetics and Cr volatility. This report describes several procedures developed at PNNL for fabricating $(Mn,Co)_3O_4$ spinel coatings onto ferritic stainless steels.

Introduction

In recent years, progress in materials and fabrication techniques have allowed for a reduction in SOFC operating temperatures to a range (e.g., 650-800ºC) in which commonly used oxidation-resistant alloys, such as ferritic stainless steels, can be considered as replacement materials for the traditional ceramic interconnect materials used in high temperature (900-1,000ºC) SOFC stacks. Compared to doped lanthanum chromites, ferritic stainless steels offer advantages such as improved manufacturability, higher thermal conductivity, and lower material and fabrication costs. However, to demonstrate satisfactory durability and performance as interconnects, the selected alloys must satisfy a set of stringent material requirements, including:

- Excellent surface stability during simultaneous exposure to both cathodic (air) and anodic (fuel gas) atmospheres at elevated temperatures.
- Strong scale adhesion to the metal substrate and low Cr volatility from the scale to avoid potential cell poisoning.
- Good thermal expansion matching to other stack components (particularly for stacks using a rigid seal design).
- High electrical conductivity through both the bulk material and *in situ* formed oxide scales.
- Chemical compatibility with other materials in contact with the interconnect, such as seals, contacts and cell materials.
- Satisfactory mechanical reliability and durability at the device's operating temperatures.
- Ease of manufacture.

In the past, conventional high-temperature oxidation-resistant alloys were developed for a range of applications that required excellent surface and/or structural stability, but not high scale electrical conductivity, which is important for SOFC interconnect applications. Recently, however, several ferritic stainless steels, including Crofer22APU (ThyssenKrupp) and ZMG232 (Hitachi), have been specifically developed for the interconnect application. Overall, these alloys demonstrate improved performance over traditional compositions, but several challenges remain, including long term electrical conductivity and surface stability under interconnect exposure conditions, chromia scale evaporation, and compatibility with the adjacent stack components, such as electrical contact layers and seals.

One means of extending interconnect lifetime and improving performance during exposure to air (oxidant) is to apply a protective coating, such as $(Mn,Co)_3O_4$ spinel, to the cathode side of the interconnect.[1-4] In addition to investigating the properties of a number of compositions in the $(Mn,Co)_3O_4$ spinel family, PNNL has also developed techniques for fabricating spinel coatings which have proven effective in reducing scale growth kinetics and Cr volatility when applied onto ferritic stainless steels.[3,4] This document, which contains specific details regarding PNNL's slurry-based coating process, is intended to a) assist SECA participants in preparing and evaluating the performance of these coatings, and b) provide a basis from which SECA participants can tailor formulations and application procedures to meet the specific requirements of their SOFC development activities.

Fabrication Procedure
A simplified process schematic of the coating process is shown in Figure 1. Most of the coatings at PNNL are prepared using $Mn_{1.5}Co_{1.5}O_4$ powder which is attrition milled to a particle size distribution similar to that shown in Figure 2. The coating process begins with the preparation of a slurry with a viscosity that is appropriate for the chosen application method, such as painting, screen-printing, dip-coating, or spraying. Screen-printing has been found to be convenient for coating of flat parts, but other methods may be better suited for coating of shaped parts. After application of the slurry, the coated substrate is dried and then heat-treated in a reducing environment to decompose the spinel powder into a mixture of MnO and Co (see Figure 3, taken from Reference 3). During subsequent heat treatment in air, reaction-assisted sintering (during which the MnO and Co react to re-form the spinel phase) produces the final coating on the substrate (see Figure 4, taken from Reference 3). Specific details for several application methods are described below:

1. Painting or Screen-Printing
    a. Prepare a slurry by mixing the spinel powder with a binder system (e.g., Ferro B-75717) using a three-roll mill. A typical weight ratio of powder to binder is 1.0 : 0.6.
    b. Coat the alloy part with slurry. Alloy parts are typically cleaned by degreasing in acetone in an ultrasonic bath followed by washing with 2-propanol. This can be accomplished by painting with a brush or, for flat parts, by screen-printing, which allows for better control of the coating thickness. At PNNL, 165 mesh screens with 2 mil emulsion thickness are typically used to obtain coatings ~10-15 microns thick. The coated sample should be dried in air at ~100°C for 1-2 hours.
    c. Heat the coated sample under reducing conditions at 800°C for at least 2 hours; at PNNL, coatings are typically reduced for 4 hours. A 5°C/min heating and cooling rate is commonly used. The typical reducing gas is dilute hydrogen (2.75%H_2+in Ar) with ~3%H_2O (added by flowing the gas through a water bubbler at room temperature).
    d. Heat the coated sample in air at 800°C for 4 hours to complete the coating fabrication.

2. Dip Coating
    a. Prepare a slurry by mixing the spinel powder, Ferro B-75717 binder, and 2-propanol. A typical weight ratio for the mixture is spinel : B-75717 : 2-propanol = 1.0 : 0.6: 1.0-1.5.
    b. Dip-coat the alloy part. At PNNL, the slurry is typically shaken for ~1 hour to assure homogeneity prior to dipping. Figure 5 shows a typical relationship between part

withdrawal rate and normalized coating mass after drying. After dip-coating, the coated part is typically dried at 80°C in a vacuum oven for ten minutes.
c. Perform the reducing and oxidizing heat treatments described in Steps 1c and 1d above.

3. Spray Coating
   a. Prepare a slurry by mixing the spinel powder with B-75717 binder and carbitol or 2-propanol. A typical weight ratio for a carbitol-based slurry is spinel : B-75717 : carbitol = 1.0 : 0.3-0.6 : 0.6-1.0. A typical weight ratio for a 2-propanol-based slurry is spinel : B-75717 : 2-propanol = 1.0 : 0.6 : 0.75-1.0. If carbitol is used as the solvent, overnight stirring is recommended. All slurries are typically shaken for at least 1 hour before spray-coating.
   b. Spray-coat the alloy part. At PNNL, spraying is performed using an air brush (Model 100-LGF, Badger Air Brush Co.) with a diaphragm compressor (Model 80-2, Badger Air Brush Co.). The distance between the nozzle and the substrate is kept at ~6 cm. The coating mass (and therefore thickness) is controlled by adjusting the spray-duration time; typical results are shown in Figure 6. Coated parts are typically dried overnight at room temperature, and then dried at 120°C in a vacuum oven for 8 hrs.
   c. Perform the reducing and oxidizing heat treatments described in Steps 1c and 1d above.

Conclusion

(Mn,Co)$_3$O$_4$ spinel coatings prepared according to procedures developed at PNNL have proven effective in reducing scale growth kinetics and Cr volatility when applied onto ferritic stainless steels. It should be noted that PNNL's experimental validation of the coating formulations and application processes was primarily conducted on small specimens (e.g., 1.2 cm x 2.5 cm). Investigations into the process consistency and reproducibility for larger sample sizes and various shapes (e.g., with integrated gas distribution and flow channels, manifolds, etc.) would be required to understand and optimize the coating thickness uniformity, microstructural consistency, and adherence.

References:

1. Y. Larring and T. Norby, J. Electrochem., Soc., 147, 3251 (2000).

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3. Z.G. Yang, G.G. Xia, S.P. Simner, and J.W. Stevenson, "Thermal Growth and Performance of Manganese Cobaltite Spinel Protection Layers on Ferritic Stainless Steel SOFC Interconnects," J. Electrochem. Soc, 152, A1896 (2005).

4. Z.G. Yang, G.G. Xia, and J.W. Stevenson, "Mn$_{1.5}$Co$_{1.5}$O$_4$ Spinel Protection Layers on Ferritic Stainless Steels for SOFC Interconnect Applications," Electrochem. and Solid-State Letters, 8, A168 (2005).

Acronyms
IT-SOFC: Intermediate temperature Solid Oxide Fuel Cell
PNNL: Pacific Northwest National Laboratory
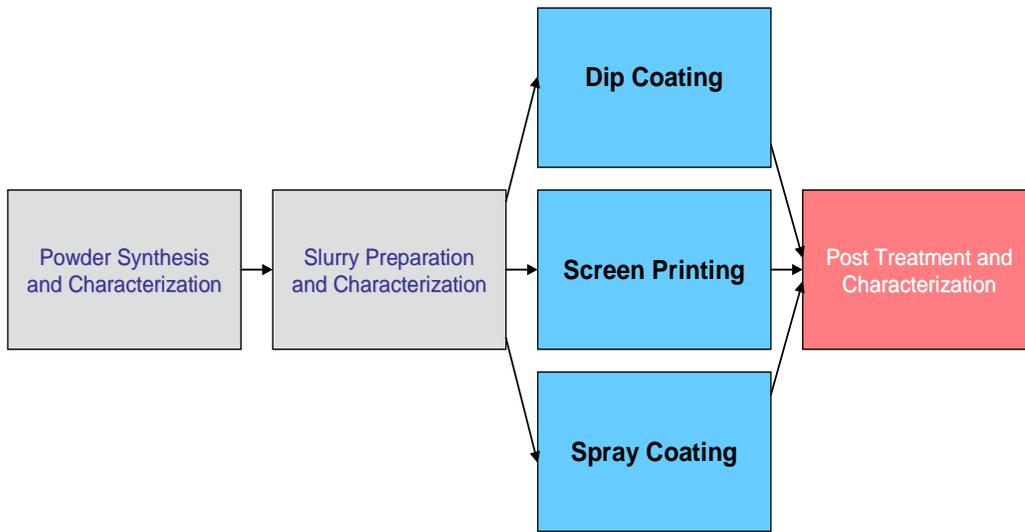SECA: Solid-State Energy Conversion Alliance
SOFC: Solid Oxide Fuel Cell

Figure 1. Schematic diagram of spinel coating fabrication process.
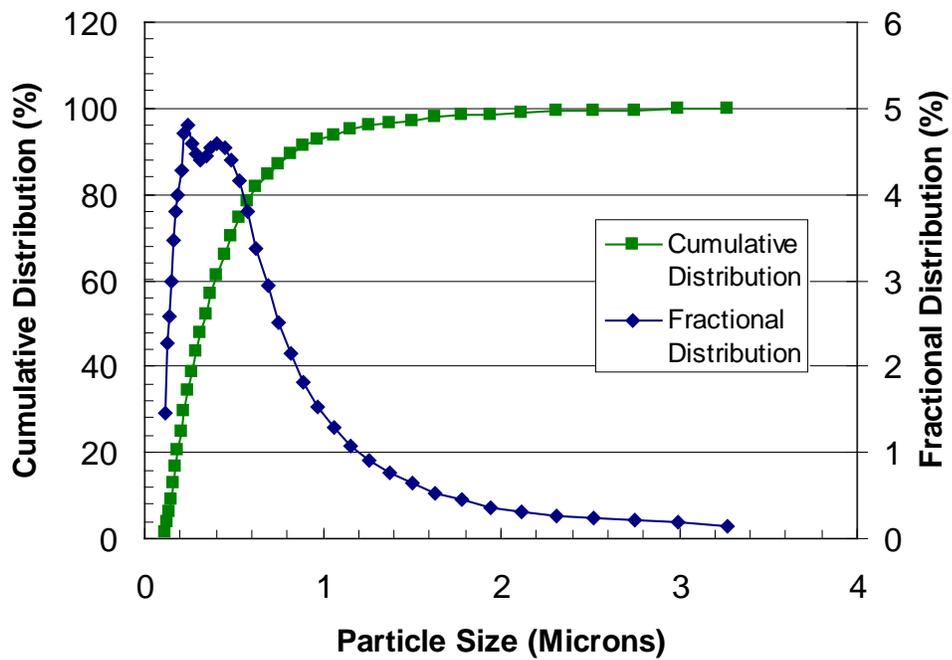

Figure 2. Typical particle size analysis for spinel powder used in slurry preparation.
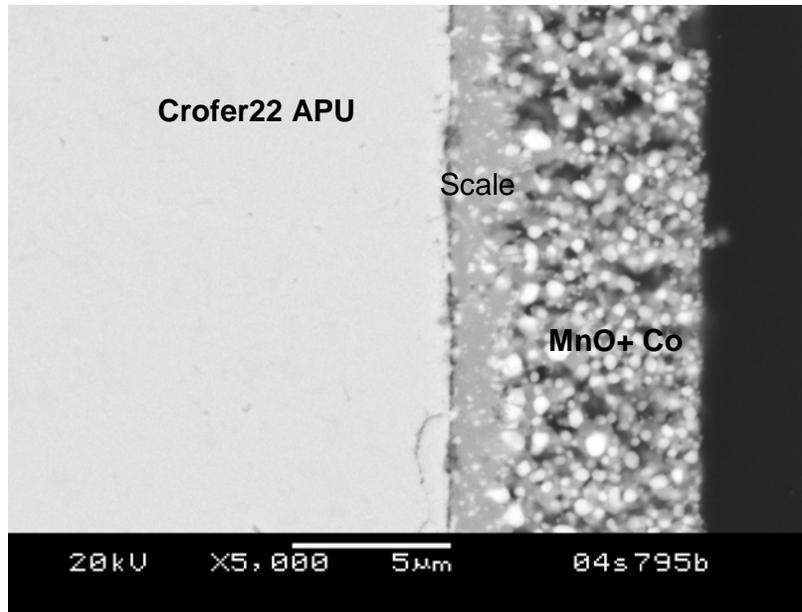
Figure 3. SEM micrograph of cross-section of spinel coating on Crofer22APU after heat-treatment at 800°C for 24 hours in 2.75%H$_2$/bal. Ar (Reference 3).
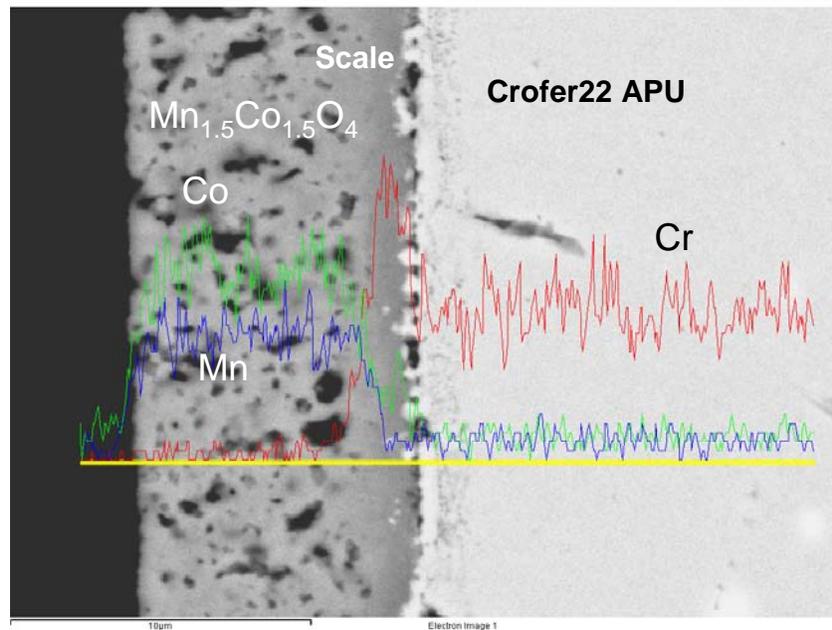

Figure 4. SEM micrograph of cross-section of spinel coating on Crofer22APU after heat-treatment at 800°C in air for 100 hours (Reference 3).
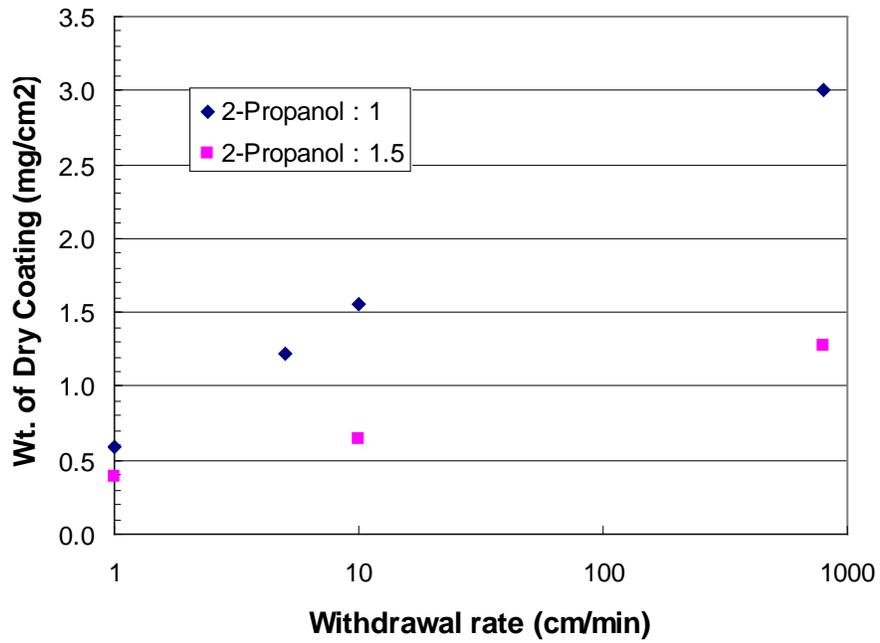
Figure 5. Normalized dry weight of dip-coated spinel coating as a function of withdrawal speed from slurry.
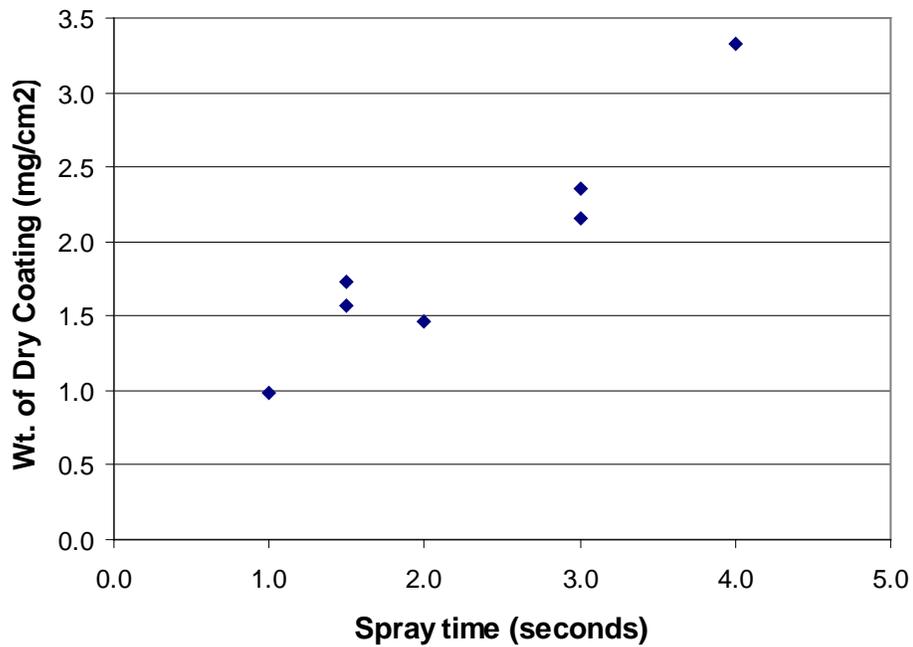

Figure 6. Normalized dry weight of sprayed spinel coating as a function of spray duration time. Slurry recipe (weight basis) was spinel powder : B-75717 : 2-propanol = 1.0 : 0.6 : 1.0.