



CeO₂-doped (Co,Mn)₃O₄ coatings for protecting solid oxide fuel cell interconnect alloys



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ABSTRACT

Reactive element-doped (Co,Mn)₃O₄ spinel is considered as the most promising coating system to protect ferritic alloys for solid oxide fuel cell interconnect application. In this paper, a CeO₂-doped (Co,Mn)₃O₄ coating was synthesized on a Crofer 22 APU alloy substrate via electrolytic codeposition of a composite layer consisting of a Co matrix and embedded Mn₃O₄/CeO₂ particles, followed by thermal conversion of the deposited layer in air at elevated temperatures. After oxidation at 800 °C in air for 250 h, no Cr penetration was detected in both the CeO₂-doped and CeO₂-free spinel coatings. However, CeO₂ doping significantly reduced the Cr₂O₃ scale growth at the coating/substrate interface. An area specific resistance of 8 mΩ·cm² at 800 °C was achieved for the CeO₂-doped coating sample, which was much lower than that of the CeO₂-free coating sample (13 mΩ·cm²) or the bare substrate (24 mΩ·cm²) at the same temperature. CeO₂ doping in the spinel coating also improved the performance stability of the anode-supported cell in contact with the alloy interconnect.

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1. Introduction

(Co,Mn)₃O₄-base spinel coatings are widely perceived as the best coating system for protecting ferritic interconnect alloys (e.g. Crofer 22 APU) used in intermediate-temperature solid oxide fuel cell (SOFC) stacks, due to its high electrical conductivity, low Cr volatility, and adequate match in coefficient of thermal expansion (CTE) with adjacent cell components [1,2]. Several techniques have been investigated for applying the (Co,Mn)₃O₄ coating on the ferritic alloys, including: (1) screen printing of a spinel powder or an oxide powder mixture, followed by a treatment in a reducing environment and then a re-oxidization treatment [3,4]; (2) spray pyrolysis [5]; (3) thermal spray [6,7]; (4) physical vapor deposition (e.g. sputtering) [8]; and (5) sequential electroplating of Co/Mn multilayers, electrodeposition of a Co–Mn alloy layer, or electro-codeposition of a Co–Mn₃O₄ composite layer, followed by thermal conversion [9–11]. Among them, electroplating-based technique is quite attractive, based on the consideration of processing cost, coating quality, and ability to coat the complex-shaped interconnect. Furthermore, thermal conversion of the deposited layer to the spinel coating may also be accomplished in situ during the stack startup

sintering step. Overall, this processing route offers a potentially low-cost approach for application of the (Co,Mn)₃O₄ spinel coatings onto SOFC interconnects with complex geometries and 3-D features.

Even though the (Co,Mn)₃O₄ coatings are capable of blocking Cr evaporation/migration from the ferritic interconnect alloy to the cathode, it still allows oxygen transport to the coating/alloy interface, which can cause continuous Cr₂O₃ scale growth and subsequent electrical resistance increase during long-term thermal exposure of the interconnect [2–4,12,13]. Recently, it has been reported that CeO₂, La₂O₃, or Y₂O₃ doping in the spinel coating can reduce the oxide scale growth rate and improve the scale adhesion [14–17], via the so-called “reactive element effect” [18,19]. However, the processing techniques used for such reactive element doping are either too expensive or not directly applicable to corrugated SOFC interconnects. Due to the nature of the electrolytic codeposition, various dopants can be readily incorporated into the spinel coating, by adding the relevant metal or metal oxide particles into the plating solution and codepositing these particles into the composite layer. Upon thermal exposure in air, the composite layer can be converted to a spinel layer containing the desired dopant(s).

In this paper, the electrolytic codeposition was explored for the synthesis of both the CeO₂-free and CeO₂-doped (Co,Mn)₃O₄ coatings. Furthermore, the microstructural feature and the performance of these coatings were characterized and the effectiveness of CeO₂ doping in improving the spinel coating performance was critically assessed.

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2. Experimental

2.1. Substrate and coating preparation

Crofer 22 APU coupons of 15 mm × 15 mm × 1 mm with a chemical composition of Fe–22Cr–0.45Mn–0.06La–0.1Si–0.12Al–0.08Ti (in wt.%) were used as the substrate for electrolytic codeposition. Test samples were cleaned ultrasonically in water and acetone for 5 min each. After grinding to 400-grit finish, the samples were then etched in a 10% HCl solution for 10 min to improve the adhesion of the deposited layer. After cleansing, the sample was placed vertically between two pure Co anodes which were spaced around 20 mm apart for electroplating. The aqueous plating electrolyte consisted of 300 g/L CoSO₄·7H₂O, 50 g/L CoCl₂·6H₂O, 15 g/L boric acid (as a pH buffer) and 0.3 g/L sodium n-dodecyl sulfate (as a wetting agent). For synthesis of the Co + Mn₃O₄ composite layer, 150 g/L Mn₃O₄ powder (with an average particle size of ~2 μm, from Aldrich) was added to the solution. Additional CeO₂ powder (10 g/L, with an average particle size of ~0.5 μm) was further added for synthesis of the Co + Mn₃O₄ + CeO₂ composite layer. The plating bath was kept at room temperature and a pH value of around 4, and was agitated continuously by an impeller near the bottom of the container at a speed of 450 rpm. Electroplating was conducted at a current density of 22 mA/cm² for 5 min. After deposition, the samples were cleaned, and subsequently they were thermally exposed in static air at 600 °C for 6 h and then at 800 °C for 4 h to convert the composite layer into the spinel coating. The use of the two-stage thermal conversion procedure was to ensure the formation of a well-adhering spinel coating with a minimum amount of defects in it. The samples were weighed before and after the thermal conversion treatment and the corresponding specific mass gains were calculated.

2.2. Oxidation and electrical resistance testing

After thermal conversion, some of the coated samples were isothermally oxidized in air at 800 °C for 250 h. They were weighed before and after oxidation and the specific mass gains after oxidation were obtained. Bare Crofer 22 APU substrate samples were also included in the evaluation for comparison.

Electrical resistance of the oxidized samples was measured using the 2-probe 4-point method at 800 °C in air. Two of the oxidized surfaces were first covered with Pt paste over an area of 0.5 cm². Two Pt meshes with two Pt leads attached to each of them were then placed on top of the Pt paste for current collection and voltage measurement. A constant current (*I*) of 10 mA from a power source was applied to the samples, and the corresponding voltage drop (*V*) was measured using a digital multimeter. A widely accepted parameter for quantifying the electrical resistance of the oxide scales, area specific resistance (ASR), was reported here. The resistance (*R*) was calculated according to Ohm's law, $R = V/2I$. The factor of 2 is used to take into account the consideration that the resistance is contributed by the oxide scales formed on both surfaces of the sample. The ASR was then determined as *R* multiplied by the area covered by Pt (i.e. 0.5 cm²).

The samples after electro-codeposition, thermal conversion, and isothermal oxidation were characterized by scanning electron microscopy (FEI Quanta 200 FEG) attached with energy dispersive spectroscopy (SEM-EDS). The crystal structures of the coatings were determined by X-ray diffraction (XRD; Rigaku Ultima IV) using Cu Kα radiation.

2.3. In-cell testing

In order to understand how the CeO₂-free and CeO₂-doped spinel coatings behave in the realistic SOFC environment with simultaneous oxidation and electric current flow, channeled Crofer 22 APU interconnects were coated and tested in direct contact with the cathode of single cells. The anode-supported anode/electrolyte bilayer with a diameter of 27 mm was purchased from NexTech Materials. In this bilayer, the

anode support was a mixture of Ni and yttria-stabilized zirconia (YSZ), while the electrolyte was YSZ. To form a complete single cell, a cathode consisting of a 15-μm La_{0.8}Sr_{0.2}MnO₃ (LSM)–YSZ inner layer and a 50-μm LSM outer layer was screen printed onto the electrolyte side of the bilayer, followed by calcination at 1250 °C for 2 h. The diameter and active area of the LSM cathode were 18 mm and 2.5 cm², respectively.

Since the design of the channeled interconnect and the overall cell testing procedures/parameters have been reported in our previous paper [20], only some specific details are given below. The bare and electroplated interconnects were given the standard thermal conversion treatment, prior to being loaded for cell testing. The anode was fitted with an 18-mm diameter Ni mesh, Ni paste, and Pt lead wires for current collection. For the baseline testing, no alloy interconnect was attached to the cell, and the LSM cathode-side current collection was achieved with Ag mesh/paste, which is widely employed in single cell testing. No contact mesh was applied on the cathode side for the cell testing with the bare or coated alloy interconnect. Instead, prior to the testing, the interconnect side facing the cathode was brushed with a thin layer of Pt paste to improve electrical contact and strain tolerance with the cathode. Note that rather than the typical perovskite contact materials such as La_{0.8}Sr_{0.2}Co_{0.5}Mn_{0.5}O₃ (LSCM) [21,22], Pt was utilized as it is more inert and does not react with other cell components/species. The power density of the cell was determined as a function of the test time at a constant cell voltage of 0.7 V. During the test, the flow rates of the fuel (H₂ + 3%H₂O) on the anode side and the air on the cathode side were maintained at 50 and 500 mL/min, respectively.

3. Results and discussion

3.1. Microstructures before and after thermal conversion

Fig. 1(a) and (b) show the coating surface morphology and cross-sectional view for the Co + Mn₃O₄ + CeO₂ composite-coated samples in the as-deposited condition, respectively. The typical morphology of electroplated Co, with the addition of adsorbed Mn₃O₄ and CeO₂ particles, was observed, as indicated by the arrows in Fig. 1(a). The CeO₂ particles in Fig. 1(a) were smaller and appeared slightly brighter than the Mn₃O₄ particles. During electro-codeposition, the Mn₃O₄ and CeO₂ particles became partially adsorbed and then completely embedded by the growing Co layer. From Fig. 1(b), the amount of the Mn₃O₄ and CeO₂ particles in the deposited layer was quite significant. Also, since most of the CeO₂ particles were located near the Mn₃O₄ particles, it is difficult to distinguish one from another. EDS analysis of the surface of the as-deposited samples indicated a significant Mn content of 15–20 at.% and a reasonable amount of Ce of 1–2 at.%. The as-deposited coating was about 4-μm thick, and was free of spallation or cracks, Fig. 1(b). In addition, the Mn₃O₄ particles were relatively evenly dispersed in the layer. The surface morphology and cross-sectional view of the Co + Mn₃O₄ composite coating without CeO₂ have been reported earlier [11].

Thermal conversion of the as-deposited Co + Mn₃O₄ and Co + Mn₃O₄ + CeO₂ composite layers in static air at 600 °C for 6 h and 800 °C for 4 h led to the formation of the (Co,Mn)₃O₄-based coatings, as confirmed by the XRD analysis. The specific mass gains after the initial conversion treatment for the bare and coated samples are listed in Table 1. For the bare Crofer 22 APU alloy, the mass gain was small, about 0.02 mg/cm², as a result of the initial oxidation. For the two coated samples, the mass gains were drastically higher, i.e. 0.51 and 0.48 mg/cm² for the CeO₂-free and CeO₂-doped (Co,Mn)₃O₄ coatings, respectively. Obviously, the incorporation of oxygen into the coatings during thermal conversion significantly increased the weight of the coated samples. During thermal conversion in air, the Co matrix was oxidized into the Co oxide, which interacted concurrently with the Mn₃O₄ particles to form the (Co,Mn)₃O₄ spinel via solid-state interdiffusion and reaction, as shown in Fig. 2. The small difference in mass gain after

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