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Plasma sprayed manganese–cobalt spinel coatings: Process sensitivity on phase, electrical and protective performance

Su Jung Han [a,*], Zdenek Pala [b], Sanjay Sampath [a]

[a] Department of Materials Science and Engineering, Center for Thermal Spray Research, Stony Brook University, Stony Brook, NY, 11794-2275, USA
[b] Institute of Plasma Physics, ASCR, Za Slovankou 3, 182 00, Prague 8, Czech Republic

HIGHLIGHTS

- MCO is coated via plasma spray with five *T-v* conditions to protect interconnect.
- Correlation of process-microstructure-phase-properties of MCO coatings is examined.
- *T*-dependent XRD is used to track phase change of trapped metastable rock salt phase.
- Optimization of process is critical to achieve both density and stoichiometry.

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ABSTRACT

Manganese cobalt spinel ($Mn_{1.5}Co_{1.5}O_4$, MCO) coatings are prepared by the air plasma spray (APS) process to examine their efficacy in serving as protective coatings from Cr-poisoning of the cathode side in intermediate temperature-solid oxide fuel cells (IT-SOFCs). These complex oxides are susceptible to process induced stoichiometric and phase changes which affect their functional performance. To critically examine these effects, MCO coatings are produced with deliberate modifications to the spray process parameters to explore relationship among process conditions, microstructure and functional properties. The resultant interplay among particle thermal and kinetic energies are captured through process maps, which serve to characterize the parametric effects on properties. The results show significant changes to the chemistry and phase composition of the deposited material resulting from preferential evaporation of oxygen. Post deposition annealing recovers oxygen in the coatings and allows partial recovery of the spinel phase, which is confirmed through thermo-gravimetric analysis (TGA)/differential scanning calorimetry (DSC), X-ray Diffraction (XRD), and magnetic hysteresis measurements. In addition, coatings with high density after sintering show excellent electrical conductivity of 40 S cm^{-1} at 800 °C while simultaneously providing requisite protection characteristics against Cr-poisoning. This study provides a framework for optimal evaluation of MCO coatings in intermediate temperature SOFCs.

1. Introduction

In order to cope with the depletion of fossil fuels, there are significant worldwide efforts at developing efficient power generation. Solid oxide fuel cells (SOFCs) are highly efficient electrical power generation alternatives that use natural gas which is reformed into hydrogen in situ as their fuel with air which provides oxygen for the electrochemical reaction [1]. SOFCs are multicomponent, multilayer systems comprising of cathode, anode, electrolyte, and interconnect, with specific material and microstructure attributes to meet a system level function. Typically, cells operate in the temperature range of 600–1000 °C depending on the material configurations. Cells operating at the higher end of the temperature spectrum typically use ceramic based electrical interconnects. A key benefit of intermediate temperature fuel cells that operate in the temperature range of 600–800 °C is the ability to replace ceramic interconnects with less expensive metallic alloys [2]. Typically, ferritic or stainless steels are used as the interconnect layer but these chromia containing systems can form oxide deposits at triple phase boundaries and degrade cell performance [3–5]. Thus, protective oxide coatings that are simultaneously electrically conductive are sought to address this degradation issue with

* Corresponding author.
E-mail addresses: sujung.han@stonybrook.edu, jrefiner@gmail.com (S.J. Han).

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the most commonly used coating material being $La(Sr)MnO_3$ (LSM) perovskites [6–10]. However, LSM coatings can be difficult to apply and can be expensive due in part to the cost of the rare-earth lanthanum component.

For more than a decade now, $Mn_xCo_{3-x}O_4$ (MCO) spinels have been considered as rare-earth alternative conductive oxides to impart protection to metallic interconnects [11–17]. They offer excellent electrical conductivity at typical cell operation temperature, ~60 S cm^{-1} at 800 °C [18–20], good electrochemical performance [19], reasonable thermal expansion compatibility with ferrous alloys (CTE: 11–13 × 10^{-6} K^{-1}) [18], and chemical stability with other cell components. Following the initial discovery of interesting structural and magnetic properties of MCO in 1958 by Wickham and Croft [21], significant scientific research [22–28] has been conducted as well as applications [29,30] of the material have been contemplated. In order to elucidate their electrical conduction mechanism, several researchers have tried to investigate their cation distribution in terms of Mn/Co ratio using X-ray fluorescence spectra [31], neutron diffraction [32], and electronic structure calculation [33]. Structural studies found Mn ions preferentially occupy B site (octahedral site) and cubic spinel phase structure starts to distort above 55% occupancy of Mn^{3+} [22]. Electrical conduction takes place by hopping electrons between adjacent different oxidation state cations in the octahedral site, Mn^{3+}/Mn^{4+} or Co^{2+}/Co^{III}, because their atomic distances are the shortest [23,32]. The electrical conductivity of bulk $MnCo_2O_4$ is reported to be 60 S cm^{-1} at 800 °C while that of bulk $CoMn_2O_4$ has only shown 6.4 S cm^{-1}; almost 10 times difference of electrical conductivity [20] is due to the availability of additional Co in the unit cell that has shorter electron hopping distance in the octahedral sites than Mn-Mn.

Numerous techniques have been investigated to apply the MCO protective coating layer onto metallic substrates such as screen printing [11–13], slurry-spraying [14], electroplating [15], electrophoretic deposition [16], and air plasma spraying [17], etc. Among them, plasma spray is a promising method, offering scalability and cost effective manufacturing for SOFC applications. Plasma spray is a directed melt-spray-deposition process in which powdered feedstock is injected into high temperature thermal plasma and propelled towards a prepared substrate with high velocity. The coating is built up by successive impingement and rapid solidification of the impacting droplets (splats). Thermal sprayed metallic and ceramic coatings find wide ranging applications from aero- and land-based gas turbines, engineering machinery, biomedical implants, and reclamation. The process allows significant material versatility and application flexibility as wide ranging alloys and oxides can be deposited on to numerous substrate and component types. The inherent scalability of the process, along with the ability to apply coatings at near ambient substrate temperatures, has allowed plasma spray to be a highly competitive and cost effective materials manufacturing technology. However, upon rapid quenching, the particles contain structural disorder (metastable phases) and produce architectural defects such as pores, cracks, and interfaces within the coating. Compositional changes of the particles via decomposition or preferential species volatilization from the thermal and chemical gradient interactions experienced during flight are also included in the deposit [34,35]. These factors, together with process-induced residual stresses can affect electrical properties and functional performance. Thus, understanding the process-property-performance interplay for thermal sprayed MCO coatings is an important endeavor towards development of reliable protective and simultaneously functional coatings.

In this study, $Mn_{1.5}Co_{1.5}O_4$ coatings were deposited using plasma spray under atmospheric conditions onto ferritic steel interconnect substrates. Five different process conditions were used to provide deliberate strategic excursions in terms of thermal and kinetic energies of the in-flight particles. Such excursions allow assessment of thermal decomposition, structural changes and coating density effects. Particle characteristics are measured through in-flight temperature and velocity measurements and mapped to visualize the resultant effects and process correlations. Cross-sectional microstructures and temperature dependent phase transformations are studied to assess deposit characteristics and structure/phase states. In addition, thermal analysis measurements are used to understand the thermo-physical and thermo-chemical changes. The electrical and magnetic properties of the coatings are measured to assess the electrical performance with elucidating electrical conduction mechanisms of the sprayed materials for various process conditions. Finally, oxide scale growth studies were conducted by subjecting the different coatings at 800 °C for 600 h to evaluate performance as a protective layer for SOFCs. The results from this study not only provide a pathway for optimizing multifunctional properties of MCO coatings for large scale application via thermal spray, but also provide scientific insights into the behavior of such complex oxides that undergo rapid thermal exposure and the resultant coating metastabilities on functional performance.

2. Experimental

2.1. Coating preparation and particle diagnostics

MCO coatings were produced by air plasma spray (APS) with five different spray conditions (A–E), which were obtained through strategic variations to plasma H_2 content, overall gas mass flow rate, applied power and spray hardware configurations. The coatings were prepared with thickness of ~70 µm on 18% chromium (Cr) containing ferritic steel (FS) substrate (1'' diameter, 0.133 '' thickness, ATI441HP™) for oxide scale growth test. Electrical conductivity samples were deposited through a bar-shaped mask (0.196 '' W × 1'' L) on yttria stabilized zirconia (YSZ) coated 316 Stainless steel (SS) in order to confine coating geometry of the conductive coating deposit within the surface area of the insulating YSZ layer. In order to measure the intrinsic electrical conductivity of the coatings, thickness of 200 µm scales was chosen as it minimizes any post deposition surface preparation for direct property measurement. It has been shown in past study the electrical property of thermal spray metals is not sensitive to the coating thickness [36]. The feedstock materials used in all coatings were YSZ (9024, −75 + 10 µm, Saint-Gobain Coating Solutions Thermal Spray Powders, Northampton, MA, USA) and MCO ($Mn_{1.5}Co_{1.5}O_4$, Metco 6820, −45 + 15 µm, Oerlikon Metco, Westbury, NY, USA). Stoichiometry was selected based on the commercial availability of sprayable sized powders. A statistical design-of-experiment methodology was utilized to vary process conditions to achieve a range of thermal and kinetic energies exposure and the details of the processing parameters are shown in Table 1. All the coatings were prepared on preheated substrate with raster speed and stand-off distance of the plasma torch set to 500 mm s^{-1} and 100 mm, respectively. In-flight particle temperature and velocity of each condition was monitored by the particle diagnostic sensors DPV2000 and AccuraSpray-G3 (both from Tecnar Automation Lté., St. Bruno, QC, Canada). The diagnostic results were represented in a particle temperature and velocity (*T-v*) first order process map as shown in Fig. 1 [37]. A F4 MB-XL gun with a 8 mm nozzle was used for coatings A–C located on the low velocity regime with varying temperature. By switching nozzle size from 8 mm to 6 mm for condition D, particle velocity was increased with concomitant reduction in particle temperature due to reduced dwell time of particles in the plume. A Praxair TAFA SG100 plasma torch with a 4.5 mm nozzle and internal