Plasma Sprayed Manganese-Cobalt Spinel Coatings: Process Sensitivity on Phase, Electrical and Protective Performance

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Abstract

Manganese cobalt spinel ($\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$, 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

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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.

Key words: Interconnect protection; Cr-poisoning; Manganese cobalt spinel; Electrical conductivity; Plasma spray

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 °C to 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 the most

commonly used coating material being $\text{La}(\text{Sr})\text{MnO}_3$ (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, $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ (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, $\sim 60 \text{ S cm}^{-1}$ at 800°C ,¹⁸⁻²⁰ good electrochemical performance,¹⁹ reasonable thermal expansion compatibility with ferrous alloys (CTE: $11\text{--}13 \times 10^{-6} \text{ K}^{-1}$),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 research²²⁻²⁸ has been conducted as well as applications²⁹⁻³⁰ 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, $\text{Mn}^{3+}/\text{Mn}^{4+}$ or $\text{Co}^{2+}/\text{Co}^{\text{III}}$, 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 conductivity²⁰ 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, $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$ 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 hours 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 H₂ 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, ATI441HPTM) 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 ($\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$, 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 Ltée., St. Bruno, QC, Canada). The diagnostic results were represented in a particle temperature and velocity (T - v) first order process map as shown in Figure 1.³⁷ A F4 MB-XL gun with a 8mm 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 particle injection was used to produce particles at high velocities with minimal thermal exposure. This is designated as the condition E in the particle T - v map. The particle temperature distributions of all of conditions

obtained from the DPV2000 sensor show higher range than the melting temperature of MCO (1650–1700 °C), indicating that the majority of the particles underwent melting during the spray process.

2.2 Coating Characterization

As-sprayed A-E coatings on stainless steel were cross-sectioned, mounted in epoxy molds and then polished to examine microstructure and element ratio of coatings by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX) (LEO 1550-EDAX Detector). Also, image analysis was attempted with low magnification SEM images (x500) from 10 different locations of each coating to calculate porosity of coatings by using threshold binary images applying Otsu formula in ImageJ 1.48v software (National Institutes of Health, USA). In order to establish the proper post-annealing temperature, thermo-gravimetric analysis (TGA)/differential scanning calorimetry (DSC) (STA 449C Jupiter for TGA/DSC, NETZSCH, LLC, Burlington, MA, USA) were used. Figure 2 shows typical TGA/DSC curves of D coating. In the TGA curve, weight gaining starts at 352 °C, corresponding to temperature sharp exothermic peak is emerged in the DSC curve which indicates oxygen recovery. Subsequently, TGA suggests further oxidation as observed by the increasing weight while broad exothermic peak is observed in the DSC (after the peak corresponding to oxygen recovery) which corresponds to the metastable amorphous phase relaxation at relatively low T of phase transition starting point ~ 620 °C (confirmed by temperature dependent XRD, discussed in detail in the later sections).³⁸ After the phase transition, DSC shows a sign change from exothermic to endothermic as well as the slope of weight gain is also decreased in TGA at 700 °C where oxygen vacancy generation and oxygen recovery processes start competing. Based on the

TGA/DSC analysis, post-annealing process was carried out at 700 °C to maximize oxidation state of MCO coatings. Dilatometry was employed to obtain the temperature dependent coefficient of thermal expansion (CTE) of the coatings (DIL402C, NETZSCH, LLC, Burlington, MA, USA). Freestanding samples were carefully prepared for CTE measurement with size of sample length about 1'' and thickness about 1 mm. CTE was measured with two thermal cycles from two different sample batches by applying 15 cN of push load, and the results are averaged and plotted. Ambient XRD measurements of as-sprayed and annealed coatings (at 700 °C for 2 h) were done with Phillips x-ray diffractometer (CuK α radiation, 40 kV and 30 mA). Temperature dependent phase composition of MCO coatings was investigated by D8 Discover powder diffractometer equipped with 1D detector (Bruker AXS, 40 kV and 30 mA, CoK α source) and heat chamber (MRI, Germany) with Platinum heating filament. Phase identification was done in X'Pert HighScorePlus software and Rietveld analysis in TOPAS 4.2; PDF-2 and ICSD databases were used. Rietveld refinement was performed with structural information taken from references 39–41 and it should be noted that measurements were done on the as-sprayed surface with corresponding penetration depth of several micrometers. Magnetic hysteresis loops of MCO powder, as-sprayed and annealed coatings (at 700 °C for 2 h) were obtained using vibrating sample magnetometer (VSM) (Model 880, Digital Measurement Systems, Microsense, LLC. Lowell, MA, USA) in order to understand electrical conduction mechanism of the coatings. Temperature dependent electrical conductivity (σ) of the geometry confined MCO coatings (A through E) was measured by four-point probe method. Four probe contacts were carefully prepared to ensure ohmic contacts are established (measurements at multiple span lengths were used to ensure no contact resistance was present). Samples were thermally cycled from room temperature to 800 °C then isothermally held for 24 hours and cooled down to room T while

measuring electrical resistance. The details of the measurements are published in our earlier paper on LSM coatings.¹⁰ The coatings on FS substrate were heat treated at 800 °C for 600 hours in atmospheric condition to grow oxide scale. Each heat treated sample was cross-sectioned, mounted in epoxy and examined for the size of grown oxide scale by SEM/EDX (LEO 1550-EDAX Detector).

3. Results & Discussion

Microstructure and EDX spectra of the MCO feedstock powder and cross-sectioned as-sprayed coatings B and E are shown in Figure 3. Feedstock particles show agglomerated and sintered structure with narrow size distribution but they contain unevenly brighter surface regimes (See the box in Fig. 3(a)). In order to examine chemical composition of the bright regime, the electron beam is focused on the circled area in Fig. 3(b) and the EDX detector indicates Co dominant metallic phase in the bright regime. The bright regime is also seen in cross-sectioned coating microstructures. Figure 3(d) and (g) are 10k magnified images of coating B and E. Their chemical compositions of the coating matrices and bright regimes are compared. Figure 3(e) and (h) represent chemical composition of matrix regimes of coating B and E, respectively, that indicate that both coatings contain Mn-Co-O composition. However, EDX spectra of bright regimes (Fig. 3(f) and (i)) show similar patterns to that of feedstock powder (Fig. 3(c)) with less noticeable oxygen peak. Thus, the brighter regime in the coatings is the reduced cobalt dominant metallic phase originating from the feedstock powder. Cross-sectional microstructures at 3k magnification of coatings A-E are represented in corresponding locations to their respective particle thermal and kinetic energies identified in the T - v map as shown in Figure 4. Also, the average porosity of coatings calculated by image analysis is displayed.

Coatings deposited at high particle temperatures and medium velocity plasma condition (such as coating C) show the highest density compared to those sprayed at lower temperature such as coatings B and D, which exhibit relatively porous microstructures. In addition, microstructural microcracking was apparent in the coatings that were sprayed at lower particle velocity conditions. This microcracking is attributed to the large quenching stresses associated with the rapid solidification of the depositing particles. Because particles are exposed to the high thermal energy (with longer in-flight thermal exposure) the resultant splats are subjected to larger tensile quenching stresses and thus greater propensity for cracking.⁴² Coating E, on the other hand, had high porosity (~10 %), preferentially showing void structure, originating from the unmolten character of the particles at this high velocity plasma condition. Even with sufficiently high particle temperature, the high velocity did not allow adequate residential time for the particle in the plasma plume, which resulted in limited melting of depositing particles.

XRD of as-sprayed and annealed coatings A-E with feedstock powder are shown in Figure 5(a) and (b), respectively. The patterns of MCO feedstock powder displayed a combination of cubic MnCo_2O_4 (space group $Fd-3m$) and tetragonal Mn_2CoO_4 (space group $I41/amdS$) spinel phases with 2:1 weight ratio as refined by quantitative Rietveld method. The broad diffraction profiles mirror the small crystallite sizes, i.e. coherently scattered domains which belong to the lower tens of nanometers size range. The coexistence of cubic and tetragonal phases, with stoichiometry range of $x = 1.3$ to 1.9 in $\text{Co}_{3-x}\text{Mn}_x\text{O}_4$, and their broad diffraction profiles are in accordance with literature findings⁴³, confirming the appropriate phase content in the feedstock. XRD patterns of as-sprayed coatings A-E deviate from that of the feedstock. The intensities of spinel reflections are reduced and broadened, and additional reflections corresponding to CoO rock salt phase (space group $Fm-3m$) are apparent. MnO phase, although a rock salt phase

similar to CoO, is not observed in any of the sprayed coatings. This can be attributed to the significant larger lattice parameter of MnO compared to that of CoO. More discussion on the preferential phase evolution of CoO is carried out in the next section. The reflections of rock salt phase are most intense for coating A and the least for coating E. This is mirrored in the results of quantitative Rietveld refinement presented in Figure 5(c) where the rock salt phase forms about 80 wt% of coating A and coating C being closer to A, while its presence in coating E is less than 60 wt% with coating D being closer to E. Hence, conditions that processed with the shorter dwell times (high ν condition) and that used helium generates less amount of rock salt phase, on the other hand, high T and low ν conditions lead to higher content of rock salt.

Room temperature XRD is re-examined with post annealed MCO coatings at 700 °C for 2 hours. Indeed, the annealed coatings exhibit more pronounced spinel reflections (as seen e.g. in XRD pattern of annealed coating A), but the CoO phase still remains trapped, especially in high T and low ν conditions (high thermal energy exposure of coatings A and C). This phase recovery indicates metastable rock salt phase located in between liquid and spinel phases in the Mn-Co-O phase diagram²²⁻²³ is trapped in the as-sprayed coating by rapid quenching spray process of $\sim 10^6$ K s⁻¹ rate.⁴⁴ Aiming at detecting differences between the annealed coatings, Rietveld refinement was performed with the same structural information as for as-sprayed coatings and the results of the phase quantitative presence in the irradiated volumes are summarized in Figure 5(d). Ensuring that the lattice parameters had not deviated from the viable range, their refined values were checked and are presented in Table 2. All the refined lattice parameters are within the range seen in ICSD database except for those of CoO that are larger in comparison to the $a = 4.230$ to 4.273 Å range; for comparison MnO phase has lattice parameters ranging from 4.408 to 4.538 Å. As shown for the rock salt phase in Table 2, the difference between as-sprayed and annealed

state is virtually nonexistent. Larger dimensions of CoO lattice indicate that a form of substitution occurs and/or interstitials are present. In fact, the substitution of Co ions by Mn ions leads in general to unit cell expansion⁴⁵⁻⁴⁶ and the rock salt is most probably disordered (Co, Mn)O. Unfortunately, the poor peak-to-background ratio and broadened reflections do not facilitate refinement of the site occupancy factor (SOF) for this phase. Moreover, the annealed coatings can be grouped into two batches according to values in Table 2; the coatings A-C having larger CoO and CoMn₂O₄ lattices on one side and coatings D-E produced at high velocities with smaller CoO and CoMn₂O₄ lattices on the other. As for the quantitative presence of rock salt in the annealed coatings, it follows the trend seen in the as-sprayed coatings with coatings A and C having the largest amount of rock salt phase in comparison with coatings D and E with less than 20 wt%. The transformation from rock salt phase follows the common wisdom⁴⁷ that the CoO converts to spinel structure if heated to 600-700 °C.

In order to gain more information about the phase recovery process from the metastable rock salt phase to the stable spinel phase, as-sprayed coatings (A-E) were crushed into powder and temperature dependent XRD was carried out. The powder XRD patterns were taken at the following temperatures: 25, 500, 530, etc with a 30 °C increment in temperature up to 800°C with a dwell time of 10 minutes at each temperature, and upon slow cooling, patterns were also taken at 500 °C and at 25 °C. The transition temperature from rock salt phase to spinel with tetragonal structure is about 620 °C as seen specifically for coating A in Figure 5(e). Nevertheless the transition took place at virtually the same temperature level for all A-E coatings. Rietveld refinements of the XRD patterns taken at 800 °C showed that the spinel formed over 80 wt.% of the irradiated volumes (we excluded the regions corresponding to diffraction of PtRh

heating filament during evaluation) for all coatings and the amount of spinel barely changed after cooling to room temperature.

Magnetic hysteresis of the feedstock powder and the as-sprayed and annealed coatings are measured from -1 Tesla to $+1$ Tesla using a VSM instrument in order to understand electrical conduction mechanism of plasma sprayed MCO coatings. Saturation magnetization (M_s) values are decided by extrapolation from the top and bottom plateaus to y-axis (See Figure 6(a)) and are then averaged. The extrapolated M_s values of as-sprayed and annealed MCO coatings are plotted (Figure 6(b)) with respect to the product of average particle temperature (T) and dwell time (τ), which numerically represents the exposure to thermal energy during the process. Comparing the M_s values of MCO coatings deposited under different processing conditions is an indication of the oxidation state of Mn and Co in the coatings. Firstly, the powder contains a mixture of $MnCo_2O_4$ and Mn_2CoO_4 with a 2:1 ratio which is confirmed by XRD Rietveld analysis. It is known that manganese preferentially occupies the octahedral site, thus Co^{2+} occupies tetrahedral sites and the rest of Mn^{3+}/Co^{III} and two of Mn^{3+} occupy octahedral sites for $MnCo_2O_4$ and Mn_2CoO_4 , respectively. Since the coatings electrically conduct via the hopping of adjacent cations in octahedral sites, their formula can be written as $Co^{2+}[Co^{2+}_xCo^{III}_{1-x}Mn^{3+}_{1-x}Mn^{4+}_x]O_4$ and $Co^{2+}[Mn^{3+}_{2-y}Mn^{4+}_y]O_4$.²⁵⁻²⁶ The $Co^{2+}(d7)$ in tetrahedral sites has a high spin state with higher t_{2g} orbital energy than that of e_g orbital, and hence comprises of 3 unpaired electrons in each tetrahedral site. However, d -orbitals in octahedral sites split in opposite ways to tetrahedral due to the difference of bonding position with oxygen atoms, thus e_g shows a higher energy level. Trivalent $Mn^{3+}(d4)$ with high spin has 4 unpaired electrons while $Co^{III}(d6)$ with low spin has none. Thus, $Co^{2+}Mn^{3+}Co^{III}O_4$ has 7 unpaired electrons and $Co^{2+}Mn^{3+}Mn^{3+}O_4$ has 11 unpaired electrons, respectively. Hence, there is an average of 8.3 unpaired electrons per molecule in the

feedstock powder and the extrapolated M_s value of feedstock powder shows 0.615 emu g^{-1} . However, M_s of as-sprayed coatings A-C shows lower magnetization than that of feedstock powder, while those of coatings D and E show higher magnetization. This categorized magnetic signal appears to be closely related to the lattice parameters of (Co, Mn)O and CoMn_2O_4 . During the deposition of coatings A-C the particles were exposed to high thermal energy and consequentially large thermal gradients within the plasma plume. Moreover the increased hydrogen flow rates and the reduced particle dwell time arising from the nature of the processing condition resulted in coatings undergoing oxygen loss in-flight. The ensuing rapid quenching of the particles resulted in the formation of metastable (Co, Mn)O phases with larger lattice parameter which indicates the disordered rock salt phase. Since coatings A-C mostly contains antiferromagnetic rock salt phases (Co, Mn)O and minimal amounts of non-stoichiometric MCO (due to process induced oxygen losses) the total number of unpaired electrons in these coatings is reduced.

However, the actual number of unpaired electrons per molecule is increased to 11.7 if we assume that non-stoichiometric MCO has only the lowest oxidation state of Mn^{2+} and Co^{2+} with broken *d*-orbitals degeneracy which can be attributed to lower orbital splitting energies due to the loss of oxygen. Coatings D and E that were processed with high velocity (less thermal exposure) plasma process using helium instead of hydrogen (only E) show increased magnetism even though they also contain antiferromagnetic (Co, Mn)O phases. However, none of the annealed coatings shows magnetic hysteresis even though their spinel phase is recovered from metastable (Co, Mn)O phases (see Figure 5(b, d)). It still remains unclear as to why their magnetic property changed. It is likely that ferrimagnetic ordering might have taken place during the heat treatment

associated with antiferromagnetic exchange between tetrahedral Co^{2+} and octahedral Mn^{4+} cations.²⁶

Temperature dependent electrical conductivities (σ) of MCO coatings were measured from room temperature to 800 °C and the results are plotted using $\ln(\sigma T)$ vs. T^{-1} form. The electrical conduction mechanisms is known to be small polaron hopping between the adjacent metals occupied in octahedral sites which is governed by the Arrhenius equation (Figure 7).³² From room T up to ~130 °C (0.0033 – 0.0025 range of T^{-1} (K^{-1})), electrical conductivity gradually increases but the conductivities of coatings A-D show discontinuities in the temperature range from 130 °C to 160 °C (0.0025 – 0.0023 range of T^{-1} (K^{-1})) as indicated by arrow in Figure 7. This unusual conductivity discontinuity is also seen in coating E but at a different T range of 93-101 °C (~0.0027 in T^{-1} (K^{-1})). Above 160 °C (101 °C for E coating), conductivity continues to increase with raising temperature. However, the slope is slightly higher than which was observed between room temperature to 130 °C which is indicative of the change in activation energy (E_a) of coatings post the unusual fluctuation. This large fluctuation (~10 times) in electrical conductivity might be attributed to cubic-tetragonal phase transition at this temperature range. In order to prove the hypothesis that the fluctuation is associated from phase transition, temperature dependent XRD has been re-employed and measured from 130 to 200 °C with 10 degree intervals and analyzed for each phases' quantity via Rietveld analysis. Initially, the quantity of more conductive cubic MnCo_2O_4 phase decreases while the content of less conductive tetragonal Mn_2CoO_4 phase increases with increasing temperature from 130 to 170 °C. Then, the amount of cubic spinel phase increases while tetragonal spinel phase decreases from 170 to 200 °C. The results of phases' quantity analysis are shown in Table 3. During further increasing T (350-450 °C), the conductivity curves show some kinks at the temperature that TGA indicated the

initiation of oxygen recovery. Furthermore, rapid rises of conductivity at around 600 °C are observed where the phase transition from metastable rock salt phases to spinels occurs. Beyond this up to a temperature of 800 °C, electrical conductivities continue to increase with different slopes (E_a). Electrical conductivity has also been measured during isothermal exposure at 800 °C for 24 hours (time dependent conductivity curves are not shown). During the isothermal exposure, conductivity further increased through the recovery of spinel phases as shown in the inset of Figure 7 after 24 hours exposure. Coatings A and C show lower electrical conductivity despite their dense microstructures, which is attributed to the presence of more metastable rock salt phases resulting from higher plasma energy exposure and H₂ content at these conditions (XRD results in Figure 5). Coatings sprayed at parameters incorporating lower hydrogen content (B and D) as well as those deposited using He containing plasma (E) show higher electrical conductivity (up to 40 S cm⁻¹ for E coating) due to more appropriate phase retention with smaller lattice parameters of conductive phases, MnCo₂O₄ and Mn₂CoO₄, which provide shorter electron hopping distances. This value is about 67 % of bulk MCO. Continued measurements of conductivity during the cooling cycle show a linear behavior (only shown for coating E). Activation energies (E_a) of coatings A-E are calculated from the cooling curves using Arrhenius equation with data summarized in Table 4. The lowest E_a is 0.40 eV corresponding to that of coating E while coating C shows the highest E_a of 0.64 eV. The result points to the importance of stoichiometry and phase retention over coating density on electrical performance.

Oxide scales of these MCO coatings (A-E) on ferritic steel were grown by subjecting them to a thermal excursion of 800 °C for 20 and 600 hours in a tube furnace. Subsequently oxide scale growth and their cross-sectional images are investigated by SEM along with chemical analysis via EDX (Figure 8). Since the atomic profile of EDX only shows one specific location

of the sample, averaged values from multiple location measurements along with their standard deviation following exposures of 20 hours and 600 hours are also presented in Figure 8(d) and (h), respectively. While the **microstructures** of coatings C-E heat treated for 600 hours **appear** similar, possibly due to the effects of sintering, coatings A and B showed signs of significant crack formation. Denser coatings obtained from higher process temperature and velocity show sluggish oxide scale growth. Oxide **scales** of coatings C and E after heat treatment for 600 hours **are** only about 1 μm . However, low velocity processed **coatings** A and B show about 50 μm thick grown oxide **scales** with large variability. This could possibly be due to the easy pathway available for the diffusion of volatile Cr species through the microcracks present in these coatings. The growth of oxide scales was found to vary between coatings A and E. The oxide scale in coating A exhibited a growth rate of 0.8 $\mu\text{m h}^{-1}$ for the initial 20 hours and then slowed down to 0.06 $\mu\text{m h}^{-1}$ for the next 580 hours, which was still about 45 times faster than the growth rate observed in coating E. This thick grown oxide scale between FS substrate and MCO coating causes crack propagation within the MCO coating in either the vertical or perpendicular directions as shown in Figures 8(e) and (f). This leads to the catastrophic failure of the protective layer as result of delamination of the coating. These results point to the need for adequate density in sprayed MCO coatings to impart resistance to failure arising from the growth of oxide scales.

Finally, coefficient of thermal expansion (CTE) of coatings was measured to assess mechanical stability with **the** other cell components (**dL L_o⁻¹** and CTE curves of coating D are displayed in Supplementary Materials 1). The percent change in length, **dL L_o⁻¹** curve shows linear thermal elongation up to 800 °C but a constant CTE of $11.0 \times 10^{-6} \text{ K}^{-1}$ was observed only up to 700 °C **and** a sudden drop in CTE was observed **above 700 °C**. This is likely related to the

metastable rock salt **phases** transition to stable **spinels**. These findings suggest that the coatings investigated in the current study could be reliably utilized at temperatures below 700 °C.

4. Conclusion

In this paper, MCO coatings were deposited by APS to examine the effect of process induced thermal excursions on the phase, microstructure and electrical properties. The process dependence on the efficacy of the coating to provide requisite protection to SOFC metallic interconnect from chromia scale is also investigated. MCO coatings were subjected to deliberate thermal excursions within the plasma spray process through modifications to process parameters including hydrogen content in the plasma gas, arc current, and total gas flow. Torch hardware configurations were also varied to provide a wide window of particle thermal and kinetic energies. The resultant process map was used to benchmark coating attributes such as density and phase **contents**. Particles exposed to high thermal energy and high kinetic energies result in coatings with dense microstructures while those produced at low temperatures and velocities produce coatings with significant porosity. In almost all cases, the as-deposited coatings contain two different stoichiometric spinel phases, Mn_2CoO_4 and MnCo_2O_4 , with a trapped metastable rock salt **phases** with (Co, Mn)O chemical formula. This result is not surprising and is attributed to the rapid quenching ($\sim 10^6 \text{ K s}^{-1}$) occurring during the plasma spray process. Post deposition annealing allowed recovery of spinel **phases** from the metastable rock salt structure as confirmed via *T*-dependent XRD measurement with a transition *T* of 620 °C. However, substantial differences in initial and post-anneal phase **contents** resulted from different process conditions. Coatings that retained a higher fraction of the desirable spinel phases (e.g. coating E produced at high kinetic energies, **less** thermal exposures) showed excellent electrical conductivity of up to

40 S cm^{-1} at 800 °C. Correspondingly, coatings with high density achieved through a combination of high thermal and kinetic energies (e.g. coating C) show excellent oxidation protection of the underlying metallic interconnect. The results point to both efficacy of plasma sprayed functional oxides in SOFC applications as well as the need for fundamental understanding of the interplay among process conditions, phase evolution, microstructure and properties to ensure requisite performance.

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Table 1. Plasma Spray Parameters for deposition of YSZ and MCO coatings. Temperature and velocity of particles are measured via Accuraspray particle diagnostics sensor. ^aHelium is used as secondary gas instead of hydrogen in this particle torch-parameter configuration.

Condition- Torch Hardware	Feed Rate (g min ⁻¹)	Ar Flow (L min ⁻¹)	H ₂ Flow (L min ⁻¹)	Current (A)	Power (kW)	Mean Particle Velocity (m s ⁻¹)	Mean Particle Temperature (°C)
YSZ-F4 8mm Nozzle	30	47.5	6	550	35.5	173	2840
A-F4 8mm Nozzle	30	35.0	10	650	42.9	127	2281
B- F4 8mm Nozzle	30	60.0	3	400	23.5	154	2087
C- F4 8mm Nozzle	30	60.0	6	700	47.3	212	2318
D- F4 6mm Nozzle	30	60.0	3	550	29.7	345	2251
E-SG100	17	90.0	35 ^a	590	39.4	580	2360

Table 2. Refined lattice parameters of phases present in annealed A-E coatings; specifically for (Co,Mn)O the refined lattice parameters for as-sprayed coatings are given in parentheses.

Coating	(Co,Mn)O	Co ₂ MnO ₄	CoMn ₂ O ₄	
	a ± Δa (Å)	a ± Δa (Å)	a ± Δa (Å)	c ± Δc (Å)
A (ann.)	4.336 (4.332) ± 0.001	8.167 ± 0.004	5.756 ± 0.003	9.195 ± 0.007
B (ann.)	4.306 (4.306) ± 0.001	8.144 ± 0.004	5.750 ± 0.003	9.157 ± 0.006
C (ann.)	4.328 (4.321) ± 0.001	8.162 ± 0.004	5.755 ± 0.003	9.175 ± 0.006
D (ann.)	4.296 (4.304) ± 0.001	8.167 ± 0.003	5.734 ± 0.003	9.159 ± 0.005
E (ann.)	4.296 (4.296) ± 0.002	8.182 ± 0.003	5.736 ± 0.003	9.162 ± 0.005

Table 3. Phases' quantity and lattice parameter of (Co,Mn)O changes of D condition MCO coating by analyzing temperature dependent XRD results from 130 to 200 °C via Rietveld Analysis.

T (°C)	Phases' Quantities (%)			Lattice Parameter of (Co,Mn)O, a (Å)
	(Co,Mn)O	CoMn ₂ O ₄	Co ₂ MnO ₄	
130	48.75	8.75	42.49	4.285931
140	47.55	8.04	44.4	4.286651
150	47.71	10.14	42.15	4.286649
160	45.38	10.17	44.46	4.288496
170	47.24	11.22	39.54	4.288941
180	45.05	6.77	48.18	4.291645
190	48.42	8.76	42.82	4.291482
200	48.37	9.91	41.72	4.292028

Table 4. Estimated activation energy (E_a) values of A through E coatings via calculating slope of cooling down curves in Arrhenius plot (Figure 8).

	A	B	C	D	E
E_a (eV)	0.53	0.47	0.64	0.54	0.40

Figure(s)

Figure 1. Han *et al.*

Figure 2. Han *et al.*

Figure 3. Han *et al.*

Figure 4. Han *et al.*

Figure 5. Han *et al.*

Figure 6. Han *et al.*

Figure 7. Han *et al.*

Figure 8. Han *et al.*

Figure Captions

Figure 1. First-order T - v process map of MCO coatings with torch hardware information.

Figure 2. TGA/DSC curves of D coating.

Figure 3. (a) Microstructure of feedstock MCO powder with 3.00k magnification. (b) Magnified image ($\times 30.00k$) of the box in fig. 3(a). (c) EDX spectrum at the marked bright regime in fig. 3(b). (d) and (g) Cross sectional microstructure with 10.00k magnification of B and E coatings, respectively. (e) and (h) EDX spectra at the matrix regimes in fig. 3(d) and (g), respectively. (f) and (i) EDX spectra at the bright regimes in figure 3(d) and (g), respectively.

Figure 4. Cross-sectional SEM images with 3.00k magnification of as-sprayed MCO coatings on 1st order process map locations. Porosity (%) of coatings calculated by image analysis is displayed in the images.

Figure 5. XRD patterns ($CuK\alpha$) of as-sprayed (a) and annealed (b) MCO coatings and feedstock powder. Quantities of phases in the as-sprayed (c) coatings and after annealing at 700 °C for 2 hours (d) as determined by Rietveld refinement of XRD patterns. (e) Temperature dependent XRD patterns ($CoK\alpha$) of A coating. The transition temperature is at ~ 620 °C (the 2 intensive reflections at 46 and 54 °2 θ over the whole temperature range are from PtRh heating filament). The gray arrows are placed above the reflections of distorted tetragonal spinel.

Figure 6. (a) Magnetic hysteresis curves of as-sprayed and annealed MCO coatings (A and E conditions) and feedstock powder. (b) Extrapolated saturated magnetizations (M_s) vs. product of process dwell time (τ) and temperature (T) of MCO feedstock powder and freestanding as-sprayed and annealed A through E coatings.

Figure 7. Temperature dependent electrical conductivity of A-E coatings up to 800 °C. Arrows indicate cubic-tetragonal and CoO-Spinel phase transition points, respectively. Cooling down curve is only provided for E condition due to the overlay with heating curves. Inset: Electrical conductivity of bulk and A-E MCO coatings at 800 °C.

Figure 8. EDX line profiles (a)-(c) and 1.00k (A) or 2.00k (B and E) magnified SEM images (e)-(g) of A, B, and E MCO coatings on ferritic steel substrate after 600 hours oxidation at 800 °C. (EDX profiles and SEM images of C and D coatings are not shown since they are similar to E.) The all of scale bars in the SEM pictures represent 50 μm . Average oxide scales are provided by bar graphs after 20 h (d) and 600 h (h) heat treatments at 800 °C.