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Low temperature deposition of dense $MnCo_2O_4$ protective coatings for steel interconnects of Solid Oxide Cells

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Abstract

In this work manganese cobalt spinel ($MnCo_2O_4$) coatings were deposited on steel substrates by spray pyrolysis at 390 °C. This is at much lower temperatures than previously reported (typically in excess of 900 °C). It was possible to produce coatings with well controlled thickness (2-5-10 µm). The as-deposited coatings were evaluated for their microstructural changes and electrical conductivity up to 800 °C. Results confirm the formation of a single phase spinel with high density and electrical conductivity. Based on the obtained results, it might be concluded that spray pyrolysis is a very promising method to develop protective coatings for steel substrates at low temperatures overcoming limitations of many other methods.

Introduction

State of the art protective ceramic coatings for the steel interconnects of Solid Oxide Cells are based on the $Mn_{3-x}Co_xO_4$ spinel [1–3]. This material offers high electrical conductivity, good thermal expansion coefficient match to typical stack components and good protection against Cr evaporation and poisoning of the oxygen electrodes. Though the material is used for many years, development of cost effective and simple fabrication routes is still of scientific interest. For protection against chromium evaporation, the coatings should form a dense structure, thus many research works focused on sintering and densification of the coatings. Typically, the coating is at first deposited as a powder and then it is subsequently heat treated. Two-step sintering seems to be the most common method [4]. Firstly the spinel is reduced to metallic Co and MnO, and then it is reoxidized in air. This procedure offers high density, but requires long processing and the reduction step, complicating the manufacture of coated interconnects. Other methods for low temperature sintering of MnCo and other similar spinels are reasearched [5,6].

Spray pyrolysis is a solution based deposition method, that offers the possibility to produce ceramic layers at relatively low temperatures [7–10]. Process can be also considered cost effective as it directly uses metal nitrates and deposits them without prior powder formation [11]. It can be also used to fabricate complex powders [12–14]. In comparison to typical methods used for preparation of spinel coatings (electrophoretic deposition, screen printing, slurry spraying etc), dense coatings can possibly be deposited at much lower temperature, with easier processing and much higher density without the need for high temperature sintering [15,16].

Previously, our group has produced and analyzed thin $(Mn,Co)_3O_4$ layers on sapphire substrates. It was shown that spray pyrolysis offers facile fabrication of doped materials with tailored electrical conductivity and thermal expansion coefficient [17].

As was previously reported, spray pyrolysis can typically be used for thin functional layers preparation. In the case of yttria stabilized zirconia (YSZ) and cerium gadolinium oxide (CGO), it was shown that a thickness limit for a single deposition exists. Only ~500 nm can be deposited in a single process. If thicker layers are desired, sequential deposition with intermediate heat treatment is required. In this work we were able to deposit up to 10 µm thick coatings in a single deposition process, which can be considered an important step towards a practical use of the method.

The importance of the present work is connected to the low temperature (390 °C) fabrication of dense spinel coatings on steel substrates by spray pyrolysis. Deposited coatings at this temperature form a desired spinel phase with high density and high electrical conductivity.

Experimental

Thin and dense $(Mn,Co)_3O_4$ protective layers were deposited on the Crofer 22 APU steel substrate by a spray pyrolysis method. Steel samples were laser cut from a 0.3 mm thick sheet forming a 25.4 mm diameter discs. Subsequently, they were cleaned in acetone and used for the deposition. The liquid precursor was prepared from $Mn(NO_3)_2{\cdot}4H_2O$ (Panreac, 98% purity) and $Co(NO_3)_2{\cdot}6H_2O$ (Chempur, 99% purity) dissolved in solution made of 90 vol% tetraethylene glycol (Sigma-Aldrich, 99% purity), and 10 vol% ethanol (POCH, 99.8% purity). The total concentration of cations in precursor was fixed at 0.2 mol/L. A molar ratio of Mn:Co = 1:2 was chosen to obtain the $MnCo_2O_4$ composition. The precursor was sprayed using the Paasche VL airbrush placed 600 mm above the hot plate heated to the temperature of 390 °C. The gun nozzle was set to the flow rate of 7.5ml/h with the air pressure of 2 bars. 100, 200 and 400 ml of the precursor solutions were used to obtain the ~2 µm, ~5 µm and ~10 µm layer thicknesses, respectively (after initial internal calibration). Samples were examined after the deposition and after sintering for 2h in air at 600 °C and 800 °C.

Microstructure of the prepared materials have been studied by X-ray diffraction technique (XRD) using the Philips X'Pert Pro MPD with $CuK_{\alpha 1}$ λ=0.15406 nm. The average crystallite size was determined using the Scherrer formula, using constant K = 0.9.

The morphology of the obtained samples was observed by a Scanning Electron Microscopy (SEM) using the FEI Quanta FEG 250 microscope. The SEM images were collected using an ETD detector for secondary electrons at an acceleration voltage of 10 kV(surface)/20kV(cross-sections). Atomic Force Microscopy (AFM) using the Nanosurf EasyScan 2 device in the contact mode was performed to determine the effect of the sintering temperature on grain dimensions. Additional reference sample deposited on a sapphire substrate was prepared for the electrical conductivity measurements using the van der Pauw method.

Measurements were carried out in air. Sample was heated to 800°C, held isothermally for 10 hours and then cooled in steps of 100 °C down to 200 °C. For the measurement, 100 mV DC excitation signal was used and the current was measured by Keithley 2400.

Results and discussion

Surface SEM and AFM images of coated Crofer 22 APU steel are shown in Figure 1 A-C. The samples were deposited using 100 ml, 200 ml and 400 ml of the precursor solution which should yield coatings with a thickness of 2 µm, 5 µm and 10 µm respectively. In the Figure 1 A, substrate roughness is still visible, a bit less in Figure 1 B. Surface on sample with 10 µm coating seems very different. Coating formed some repeating structure with "valleys" and "hills" with a characteristic size (~diameter) of ~50 µm. Sample surfaces were covered completely and uniformly. No surface defects were detected on any samples. AFM images (area of 2.5 x 2.5 μm^2, Figure 1 D-F) were taken for the 2 µm coating after different heat treatment steps (as-produced, 600 °C, 800 °C). For the 800 °C a noticeable grain growth occurred. This is also evidenced by surface roughness. RMS roughness (S_q) is measured to be 1.0 nm, 1.6 nm and 8.4 nm for the as-produced, 600 °C and 800 °C processed sample, respectively. The roughness measured for the 800 °C sample does not include the waviness of the coating.

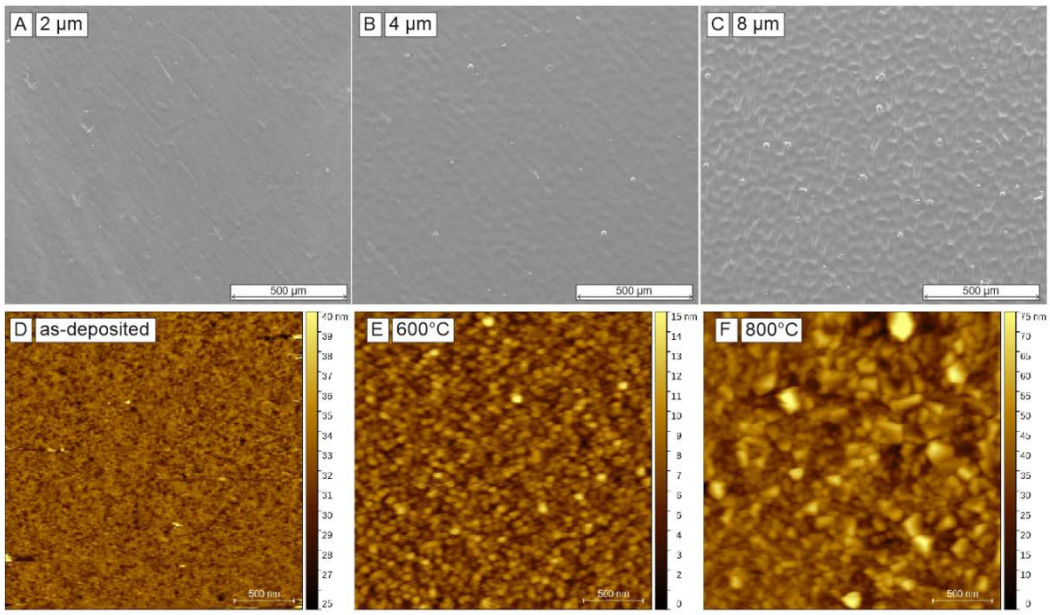

Figure 1. A-C) SEM images of the "as-deposited" samples with 2/5/10 um spinel coatings after 800 °C and D-F) AFM images of a 2 µm spinel coating on steel after different heat treatment steps.

Phase composition of the spinel coatings was analyzed by X-ray diffractometry. Steel with a 2 µm coating was analyzed in the as-produced state (390 °C) and after annealing at 600 °C, 700 °C and 800 °C for 2 hours. For the thinnest sample it should be possible to notice the substrate peaks and possible oxides peaks (formed due to oxidation). Results are presented in Figure 2. Already for the as-deposited coating the expected $MnCo_2O_4$ spinel phase structure is recognized. Besides the two peaks from the steel substrate, no other peaks are detected what indicates that the obtained coatings are single-phase. For the heat treated samples, diffraction peaks become narrower indicating crystallite size increase. The average crystallite sizes determined by Scherrer formula are (14 ± 2) nm, (25 ± 6) nm, (48 ± 9) nm

and (102 ± 14) nm for temperatures 390, 600, 700 and 800 °C, respectively, as shown in Figure 2 C. Moreover, peaks shift towards lower 2θ values is observed, indicating a slight unit cell size increase.

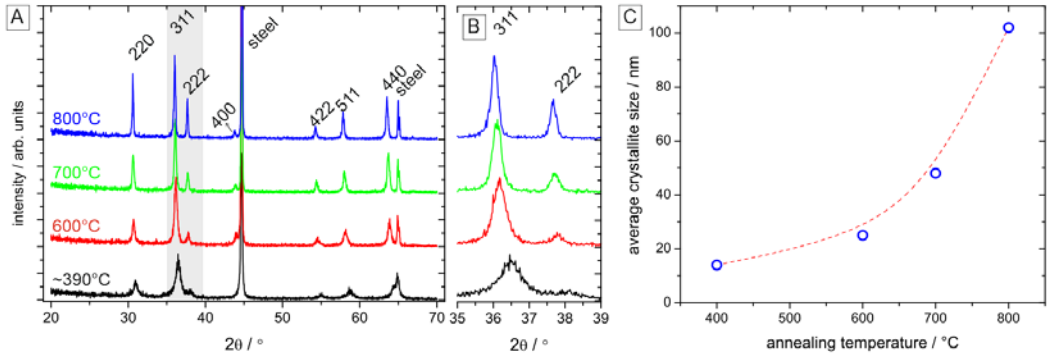

Figure 2. A) XRD patterns of 2 µm spinel coating on steel in the as-deposited and heat treated condition. B) Close-up view of the main 311 peak, C) average crystallite size as a function of temperature.

Result of the electrical conductivity measurement of the deposited layer measured by the van der Pauw method is shown in Figure 3. In this case the MCO was deposited on a polished sapphire substrate. Measurement of the in-plane conductivity of the MCO layer deposited on the steel, would be impossible due to conductivity of the substrate. After reaching 800 °C (maximum processing temperature), the sample was held isothermally for 10 hours to evaluate possible changes and stability. During this period, electrical conductivity has visibly decreased (from ~70 S cm^{-1} to ~60 S cm^{-1}). The decrease is not influenced by the electrical current, as it also continued upon a failure of the power supply. The obtained conductivity of ~60 S cm^{-1} is a typical value reported for these materials in the bulk and coatings form. For the layers deposited by spray pyrolysis, upon their exposure to higher temperatures, grain growth occurs which can influence the electrical conductivity [18]. After isothermal hold the sample was cooled in 100 °C steps down to 200 °C. The plot of electrical conductivity vs. the inverse of temperature is shown in Figure 3B. For the electrical conductivity plots, between 800 °C-600 °C and 600 °C-200 °C activation energies of 0,48 eV and 0.36 eV are obtained after fitting with the Arrhenius equation. These data are well in line with results reported by other groups [19].

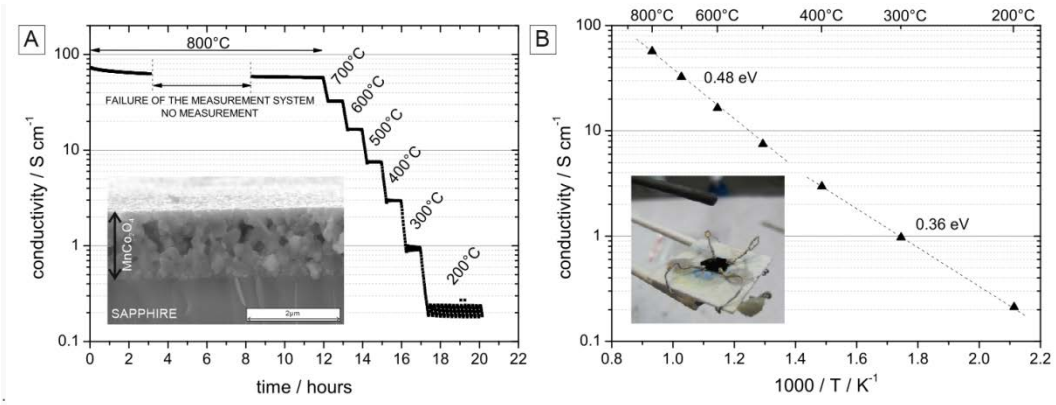

Figure 3. Electrical conductivity of the $(Mn,Co)_3O_4$ thin film (~1.5 µm) on a sapphire substrate. A) time/temperature dependence and B) Arrhenius plot.

Spray pyrolysis offers deposition of coatings with a scalable thickness in the range between 1 µm and 20 µm. Cross-sections of the coatings developed in this work are presented in Figure 4 A-C. Coatings, as seen previously from the surface images, are dense and defect free. For the thickest coating with surface waviness, the observed thickness is between 8-15 µm. No cracks or major defects were found throughout the sample. Chemical composition by EDS is shown in Figure 4 D. The Co/Mn ratio is constant (~2) throughout the coating and close to the desired one. No diffusion of Cr to the coating has been noticed after the initial processing with a maximum temperature of 800 °C. In comparison to other reports, the obtained microstructure is much denser than typically obtained for higher sintering temperatures and/or dual-atmosphere (redox) sintering [4,20–22].

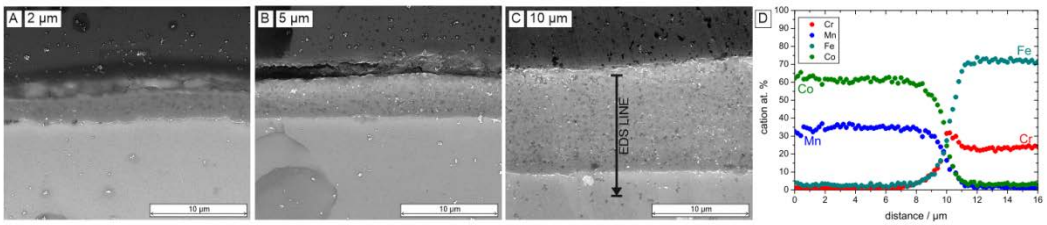

Figure 4. Cross-section SEM images of MCO coatings on steel. Coatings were deposited at 390 °C and annealed at 800 °C.

Conclusions

This study has shown a potential to deposit $MnCo_2O_4$ ceramic coatings on stainless steel at 390 °C, i.e. at much lower temperature than typically used. Spray pyrolysis is a simple and cheap deposition method. Crystalline, phase pure coatings are obtained during the deposition. No further heat treatment is necessary. Electrical conductivity of the layers is the same as for bulk spinel samples. Dense microstructures of the coatings, both on steel and sapphire substrates, are obtained. Coatings are well adhered and crack-free. Though the protective character of the coating still needs to be demonstrated in a dedicated corrosion study, spray pyrolysis seems very attractive for deposition of protective interconnect coatings for Solid Oxide Cell stacks.

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Bibliography

[1] N. Shaigan, W. Qu, D.G. Ivey, W. Chen, A review of recent progress in coatings, surface modifications and alloy developments for solid oxide fuel cell ferritic stainless steel interconnects, J. Power Sources. 195 (2010) 1529–1542.

[2] Y. Larring, T. Norby, Spinel and Perovskite Functional Layers Between Plansee Metallic Interconnect (Cr-5 wt % Fe-1 wt % Y[sub 2]O[sub 3]) and Ceramic (La[sub 0.85]Sr[sub 0.15])[sub

0.91]MnO[sub 3] Cathode Materials for Solid Oxide Fuel Cells, J. Electrochem. Soc. 147 (2000) 3251–3256. doi:10.1149/1.1393891.

[3] S. Molin, A.G. Sabato, M. Bindi, P. Leone, G. Cempura, M. Salvo, S. Cabanas Polo, A.R. Boccaccini, F. Smeacetto, Microstructural and electrical characterization of Mn-Co spinel protective coatings for solid oxide cell interconnects, J. Eur. Ceram. Soc. 37 (2017) 4781–4791. doi:10.1016/j.jeurceramsoc.2017.07.011.

[4] M. Bobruk, S. Molin, M. Chen, T. Brylewski, P.V. Hendriksen, Sintering of MnCo<inf>2</inf>O<inf>4</inf>coatings prepared by electrophoretic deposition, Mater. Lett. 213 (2018) 394–398. doi:10.1016/j.matlet.2017.12.046.

[5] A. Gaur, V.M. Sglavo, Flash-sintering of MnCo2O4 and its relation to phase stability, J. Eur. Ceram. Soc. 34 (2014) 2391–2400. doi:10.1016/j.jeurceramsoc.2014.02.012.

[6] A. Masi, M. Bellusci, S.J. McPhail, F. Padella, P. Reale, J.-E. Hong, R. Steinberger-Wilckens, M. Carlini, Cu-Mn-Co oxides as protective materials in SOFC technology: The effect of chemical composition on mechanochemical synthesis, sintering behaviour, thermal expansion and electrical conductivity, J. Eur. Ceram. Soc. 37 (2017) 661–669. doi:10.1016/j.jeurceramsoc.2016.09.025.

[7] D. Perednis, L.J. Gauckler, Thin film deposition using spray pyrolysis, J. Electroceramics. 14 (2005) 103–111. doi:10.1007/s10832-005-0870-x.

[8] S. Molin, P.Z. Jasinski, Improved performance of LaNi0.6Fe0.4O3 solid oxide fuel cell cathode by application of a thin interface cathode functional layer, Mater. Lett. 189 (2017) 252–255. doi:10.1016/j.matlet.2016.11.101.

[9] J.L.M. Rupp, L.J. Gauckler, Microstructures and electrical conductivity of nanocrystalline ceria-based thin films, Solid State Ionics. 177 (2006) 2513–2518. doi:10.1016/j.ssi.2006.07.033.

[10] L. Santos-gómez, J.M. Porras-vázquez, E.R. Losilla, F. Martín, J.R. Ramos-barrado, LSCF-CGO nanocomposite cathodes deposited in a single step by spray- pyrolysis, J. Eur. Ceram. Soc. 38 (2018) 1647–1653. doi:10.1016/j.jeurceramsoc.2017.10.010.

[11] Z. Shao, W. Zhou, Z. Zhu, Advanced synthesis of materials for intermediate-temperature solid oxide fuel cells, Prog. Mater. Sci. 57 (2012) 804–874. doi:10.1016/j.pmatsci.2011.08.002.

[12] A.B. Haugen, F. Madaro, L.P. Bjørkeng, T. Grande, M.A. Einarsrud, Sintering of sub-micron K0.5Na0.5NbO3powders fabricated by spray pyrolysis, J. Eur. Ceram. Soc. 35 (2015) 1449–1457. doi:10.1016/j.jeurceramsoc.2014.11.011.

[13] C. Goulart, E. Djurado, Synthesis and sintering of Gd-doped CeO2nanopowders prepared by ultrasonic spray pyrolysis, J. Eur. Ceram. Soc. 33 (2013) 769–778. doi:10.1016/j.jeurceramsoc.2012.09.029.

[14] N. Betancur-Granados, O.J. Restrepo-Baena, Flame spray pyrolysis synthesis of ceramic nanopigments CoCr2O4: The effect of key variables, J. Eur. Ceram. Soc. 37 (2017) 5051–5056. doi:10.1016/j.jeurceramsoc.2017.06.024.

[15] H. Abdoli, P. Alizadeh, Electrophoretic deposition of (Mn,Co)3O4 spinel nano powder on SOFC metallic interconnects, Mater. Lett. 80 (2012) 53–55. doi:10.1016/j.matlet.2012.04.072.

[16] Z. Yang, G. Xia, S.P. Simner, J.W. Stevenson, Thermal Growth and Performance of Manganese Cobaltite Spinel Protection Layers on Ferritic Stainless Steel SOFC Interconnects, J. Electrochem. Soc. 152 (2005) A1896–A1901. doi:10.1149/1.1990462.

[17] D. Szymczewska, S. Molin, P. Hendriksen, P. Jasiński, Microstructure and Electrical Properties of Fe,Cu Substituted (Co,Mn)3O4 Thin Films, Cryst. 2017, Vol. 7, Page 185. 7 (2017) 185. doi:10.3390/CRYST7070185.

[18] J.L.M. Rupp, B. Scherrer, A.S. Harvey, L.J. Gauckler, Crystallization and grain growth kinetics for precipitation-based ceramics: A case study on amorphous ceria thin films from spray pyrolysis, Adv. Funct. Mater. 19 (2009) 2790–2799. doi:10.1002/adfm.200900255.

[19] T. Brylewski, W. Kucza, A. Adamczyk, A. Kruk, M. Stygar, M. Bobruk, J. Dąbrowa, Microstructure and electrical properties of Mn1+xCo2−xO4 (0≤x≤1.5) spinels synthesized using EDTA-gel processes, Ceram. Int. 40 (2014) 13873–13882. doi:10.1016/j.ceramint.2014.05.106.

[20] A. Kruk, M. Stygar, T. Brylewski, Mn–Co spinel protective–conductive coating on AL453 ferritic stainless steel for IT-SOFC interconnect applications, J. Solid State Electrochem. 17 (2012) 993–1003. doi:10.1007/s10008-012-1952-8.

[21] B. Talic, S. Molin, K. Wiik, P.V. Hendriksen, H.L. Lein, Comparison of iron and copper doped manganese cobalt spinel oxides as protective coatings for solid oxide fuel cell interconnects, J. Power Sources. 372 (2017) 145–156. doi:10.1016/j.jpowsour.2017.10.060.

[22] B. Talic, H. Falk-Windisch, V. Venkatachalam, P.V. Hendriksen, K. Wiik, H.L. Lein, Effect of coating density on oxidation resistance and Cr vaporization from solid oxide fuel cell interconnects, J. Power Sources. 354 (2017) 57–67. doi:10.1016/j.jpowsour.2017.04.023.