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Hassan Javed[1], Theo Saunders[2], Michael John Reece[2], Elisa Zanchi[3], Antonio Gianfranco Sabato[4], Aldo R. Boccaccini[5], Federico Smeacetto[3]

1. Sunfire GmbH, Gasanstaltstraße 2, 01237 Dresden, Germany
2. School of Engineering and Materials Science, Queen Mary University of London, UK
3. Department of Applied Science and Technology (DISAT), Politecnico di Torino, Italy
4. IREC-Institut de Recerca en Energia de Catalunya, 08930 Sant Adrià de Besòs, Barcelona, Spain
5. Institute of Biomaterials, Friedrich Alexander University Erlangen-Nuremberg, 91058 Erlangen, Germany

Corresponding author: hassan.javed@sunfire.de

Abstract

Pressure assisted flash sintering was used to process Mn-Co-Cu based spinel coatings, electrophoretically deposited on a Crofer22APU interconnect. This method resulted in highly dense coatings, heat-treated for only a short duration (<10 minutes) at temperatures lower than conventional sintering temperatures. The electrophoretically deposited coatings showed no delamination or cracks after flash sintering at high heating rates (>200 ^{o}C/min). The high heating rate promoted Cu modified Mn-Co spinel and limited the formation of a Cr-oxide scale on the

Crofer22APU substrate. Flash sintering was found to be a promising and time efficient sintering technique to overcome some of the issues related to low coating density and oxide scale formation in solid oxide electrolysis cell conditions.

Key words: Flash sintering, protective coatings, EPD, SOEC, SOFC

1. Introduction

Cr-based steel interconnects such as Crofer22APU and Crofer22H are most commonly used in solid oxide electrolysis cells (SOECs) thanks to their high electrical conductivity, mechanical stability and coefficient of thermal expansion (CTE) matching with other cell components [1,2]. SOECs generally operate at 700-900 °C, which enhances the possibility of Cr evaporation from the interconnect, which can contaminate neighboring electrodes. Deposition of protective coatings on metallic interconnects is considered the most effective way to hinder the Cr evaporation. In this context, Mn-Co based spinel coatings, due to their high electrical conductivity, high Cr retention capability and CTE closely matching with interconnect, are likely to be the materials of choice [3]. Doping and or modification of Mn-Co spinel with transition metal elements (Fe and Cu) is an attractive way to further improve their performance [4–7]. For instance, many researchers have studied Cu doped Mn-Co spinel and found that Cu addition stabilizes the cubic phase ($MnCo_2O_4$) and improves the density of the coatings [8–10].

In general, conventional sintering usually produces coatings with a certain grade of porosity, which might affect the Cr blocking capability of the protective layer. In order to produce dense coatings, conventional sintering should be carried out above 900 °C or for a long dwell time (a matter of hours). In both cases, there is a high possibility of formation of a non-conductive Cr-based oxide scale at the interconnect surface, thus increasing the overall area specific resistance of the interconnect [11].

Pressure assisted flash sintering is a promising technology that can produce dense coatings in just a few minutes by combining simultaneously high pressure and electric current [12]. A limited number of studies has been carried out on flash sintering of Mn-Co based spinel in order to understand its phase stability and densification [11,13,14]. However, up to now, much of the research related to flash sintering of ceramics was mainly carried out on compact of powders. To the best of the author's knowledge, no studies have been conducted to observe the (pressure assisted) flash sintering effect on as-deposited Mn-Co based coatings. Due to high heating and cooling rates, there is a high possibility of stress generation at the coating/substrate interface subjected to flash sintering. The high stress can subsequently lead to delamination at the coating/substrate interface or can even generate cracks within the coatings. Therefore, it is important not only investigate the density of coatings but also the coating/substrate interface.

In our previous studies, $Mn_{1.5}Co_{1.5}O_4$ (MCO) coatings doped with 0-10wt% of Cu were successfully produced using the electrophoretic deposition (EPD) technique [10,15]. MCO and CuO particles were electrophoretically co-deposited to obtain homogenous thick coatings of ~15µm. Two steps sintering of MCO coatings has been repeatedly reported in literature, where first step is carried out in reducing atmosphere with an aim to decompose the spinel and second step in oxidizing atmosphere for reformation of spinel [10,15,16]. In present work, pressure assisted flash sintering is used in addition to conventional sintering to analyze the impact of a different heat treatment process on the density of Cu doped MCO spinel coatings and on the formation of the oxide scale.

2. Experimental

The co-deposition of $Mn_{1.5}Co_{1.5}O_4$ (MCO) and CuO particles was carried out on disc shaped (diameter: 15 ± 0.1 mm, thickness: 2 ± 0.1 mm) Crofer22APU substrates by EPD. A previous study showed that a MCO coating doped with 10 wt% of CuO exhibited higher density as compared with pure MCO and MCO doped with 5 wt% of CuO [10]. Therefore, for this study, a suspension of MCO and CuO (90:10 wt%) was prepared in a solvent composed of ethanol and water in 60:40 vol%, where 37.5g of solid content was added per liter of the solvent. Further details about the EPD deposition parameters can be found elsewhere [15,17]. After the deposition, the samples were dried in air for 24 hours and subsequently sintered.

The EPD coated samples were sintered according to three different heat treatments, referred as S1, S2 and S3. S1 was a single step treatment where the coatings were sintered by flash sintering. Flash sintering was done in vacuum (1 m.bar) using a load of 5 kN. The disc shaped coated samples were introduced into a graphite die and two cylindrical graphite punches were used to hold the sample in the die. Boron nitride (BN) was sprayed on the graphite punches to avoid direct contact with the coated Crofer22APU samples. The samples were heated up to 700°C at a heating rate of 200 °C/min followed by a dwell of 1 min. Afterward, a power pulse of 6.8 V was applied for three seconds to obtain a temperature of approximately 830±30 °C. Subsequently, the samples were cooled down to room temperature at an initial cooling rate of 200 °C/min.

The heat treatment referred to as S2 involved a two steps process; first step sintering in reducing atmosphere (Ar-3% H_2) at 900°C for 2 hours at a heating/cooling rate of 10°C/min, followed by a second sintering step using flash sintering. The S3 treatment involved three steps; first two steps were similar to S2 (first in reducing atmosphere and second by flash sintering), while a third additional step was done in static air at 900°C for 2 hours at a heating/cooling rate of 10°C/min. Flash sintering during S2 and S3 treatment was done under same conditions mentioned for S1.

The microstructure and compatibility of the coatings with the Crofer22APU interconnect was examined by SEM (Merlin ZEISS). For that purpose, the cross sections of Crofer22APU/MnCoCu coated samples were metallographically polished down to 1 μm using diamond paste. The crystalline phase analysis of the deposited and heat-treated coatings was carried out using a PanAlytical X'Pert Pro PW 3040/60 Philips (the Netherlands), with Cu Kα and the X'Pert software.

The XRD analysis were carried out in the range of 2 theta 10°-70°, with a step size of 0.02626° and time per step of 10.20 seconds. Prior to the XRD and SEM analysis, the coated Crofer22APU samples were sonicated for 5 min, in order to remove the BN layer.

3. Results and Discussion

Figure 1 shows XRD analyses carried out on Cu doped MCO coated Crofer22APU substrates after S1, S2 and S3 sintering treatments. The XRD pattern after the S1 treatment (Figure 1(a)) shows the presence of the $(Mn, Co)_3O_4$ phase (PDF # 018-0408) with an intermediate tetragonal spinel structure. The S1 treatment also resulted in the partial reduction of CuO into Cu_2O after flash sintering. The high heating/cooling rates and short dwell time during flash sintering resulted in only partial reduction of the CuO. The presence of BN phase is also visible after the S1 treatment, which is due to presence of residuals of the BN layer. On the other hand, the XRD analysis after the S2 treatment (two steps sintering) shows the decomposition of the MCO spinel into MnO and metallic Co. In contrast to the S1 treatment, the sintering performed during the first step of the S2 treatment in a reducing atmosphere for 2 hours at 900 °C, ensured the complete reduction of the MCO spinel into MnO and metallic Co. These results are in agreement with results found in previous studies for MCO spinel sintered in reducing atmospheres [3,15]. The S2 treatment also resulted in the reduction of the CuO into metallic Cu. XRD analysis after the S3 treatment (figure 1 (c)) carried out in air shows the reforming of the $MnCo_2O_4$ cubic phase spinel (PDF# 023-1237), with the Cu incorporated into the spinel as no distinct peak for a Cu based phase was observed. These results are also coherent with previous studies, where Cu doping was found to stabilize the cubic phase [6,10,15,18] of MCO by partial replacement of Mn [5,19]. The stabilization of the cubic phase is beneficial to minimize the tetragonal-cubic phase transformation that occurs in MCO at around 400 ºC during heating/cooling cycling, consequently limiting the thermal stresses due to difference in volume and coefficient of thermal expansion of both phases. The XRD pattern of the cubic $MnCo_2O_4$ (PDF# 023-1237) is also shown in figure 1d, for better understanding and comparison. A slight shift can be seen between the XRD patterns of the S3 treated sample and that of $MnCo_2O_4$ (PDF# 023-1237), which is most likely due to lattice distortion of Mn-Co spinel as a result of Cu inclusion into the spinel.

Figure 1. XRD characterization of sintered coatings after (a) S1, (b) S2, (c) S3 treatments and (d) XRD simulated pattern of Co_2MnO_4 phase

Figure 2 shows the cross sections of EPD deposited Mn-Co-Cu spinel coatings on Crofer22APU, sintered in three different ways, as previously described. The sintered coatings were uniform, with a thickness of ~15 µm. By the introduction of pressure-assisted flash sintering, coatings with negligible porosity were obtained at temperatures lower than conventional sintering temperature (approx. 950 ^{o}C) of Mn-Co based spinel coatings. Despite of fast heating and cooling rates (>200 °C/min) during the flash sintering, no cracks or delamination effects between the Crofer22APU substrate the Mn-Co-Cu spinel coatings were observed.

Figure 2. EPD deposited Mn-Co-Cu coating on the Crofer22APU substrates. Sintering was performed according to (a,b) S1, (c,d) S2 and (e,f) S3 treatment

Figure 3 shows the EDS mapping carried out on Crofer22APU/Mn-Co-Cu coatings, sintered by the three different heat treatments. After the S1 and S2 treatments, different phases are clearly visible in the Mn-Co-Cu coating, while after the S3 treatment, the coating becomes homogenous with no distinct phases. In particular, the EDS mapping shows Cu rich zones after the S1 and S2 treatments, while after the third step sintering (S3), no Cu rich areas were observed. These EDS analyses are in agreement with the XRD investigation and previous studies, where sintering of MnCoCu spinel coatings in a reducing atmosphere results in decomposition of the spinel, and reforming of the MnCo spinel after sintering in air. It is also worth pointing out that flash sintering (S1) did not resulted in the formation of a Cr oxide scale on the Crofer22APU substrate. Nevertheless, a Cr rich scale of~1μm was formed after the S3 treatment, as clearly visible from the corresponding EDS mapping (Figure). The formation of the oxide scale is due to third step sintering carried out in air at 900 ^{o}C. The oxidizing sintering step in S3 could be potentially carried out during the consolidation/sealing procedure of a real SOCs stack.

Figure 3. EDS mapping carried out at Mn-Co-Cu coated Crofer22APU substrates sintered by S1, S2 and S3 treatments

4. Conclusions

Flash sintering was employed to rapidly sinter of Cu doped MnCo spinel (MCO) coatings electrophoretically deposited on a Crofer22APU interconnect.

The findings in this study provide the following insights for future research:

- The proposed approach, EPD co-deposition and flash sintering can be further expanded to study the in-situ formation of new spinel structures (i. e. avoid Co), by a proper selection of precursors.
- The one-step sintering treatment (S1) could be directly converted in Cu doped MCO, by a stack consolidation treatment in air.
- A natural progression of this work is to analyse the effect of the pressure-assisted flash sintering on the electrical properties of the coated samples

Flash sintering was found to be a promising sintering method that involves short sintering times (<10 min) to obtain high densification with respect to conventional sintering. The high heating and cooling rates during flash sintering did not produce any cracks within the coatings as well as no delamination at the Crofer22APU/coating interface. Moreover, the use of a reducing atmosphere during flash sintering did not promote the formation of a Cr-rich oxide scale at the Crofer22APU substrate. These results confirm that flash sintering could be an attractive way to minimize the current issues /challenges related to coatings degradation under SOEC conditions at 850°C.

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6. References

[1] R. Sachitanand, M. Sattari, J.E. Svensson, J. Froitzheim, Evaluation of the oxidation and Cr evaporation properties of selected FeCr alloys used as SOFC interconnects, International Journal of Hydrogen Energy. 38 (2013) 15328–15334. doi:10.1016/j.ijhydene.2013.09.044.

[2] Y. Zheng, J. Wang, B. Yu, W. Zhang, J. Chen, J. Qiao, J. Zhang, A review of high temperature co-electrolysis of H2O and CO2 to produce sustainable fuels using solid oxide electrolysis cells (SOECs): advanced materials and technology, Chem. Soc. Rev. 46 (2017) 1427–1463. doi:10.1039/C6CS00403B.

[3] S.-I. Lee, J. Hong, H. Kim, J.-W. Son, J.-H. Lee, B.-K. Kim, H.-W. Lee, K.J. Yoon, Highly Dense Mn-Co Spinel Coating for Protection of Metallic Interconnect of Solid Oxide Fuel Cells, Journal of the Electrochemical Society. 161 (2014) F1389–F1394. doi:10.1149/2.0541414jes.

[4] A. Masi, M. Bellusci, S.J. Mcphail, F. Padella, P. Reale, J. 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, Journal of the European Ceramic Society. 7 (2016) 661–669. doi:10.1016/j.jeurceramsoc.2016.09.025.

[5] B. Talic, P.V. Hendriksen, K. Wiik, H.L. Lein, Thermal expansion and electrical conductivity of Fe and Cu doped MnCo2O4spinel, Solid State Ionics. 326 (2018) 90–99. doi:10.1016/j.ssi.2018.09.018.

[6] A. Masi, M. Bellusci, J. Stephen, F. Padella, P. Reale, R. Steinberger-wilckens, A. Masi, M. Bellusci, S.J. Mcphail, F. Padella, P. Reale, J. Hong, R. Steinberger-wilckens, The Effect of Chemical Composition on High Temperature Behaviour of Fe and Cu Doped Mn-Co spinels, Ceramics International. 43 (2016) 2829–2835. doi:10.1016/j.ceramint.2016.11.135.

[7] J.C.W. Mah, A. Muchtar, M.R. Somalu, M.J. Ghazali, J. Raharjo, Formation of sol–gel derived (Cu,Mn,Co)3O4 spinel and its electrical properties, Ceramics International. 43 (2017) 7641–7646. doi:10.1016/j.ceramint.2017.03.060.

[8] R. Wang, Z. Sun, U.B. Pal, S. Gopalan, S.N. Basu, Mitigation of chromium poisoning of cathodes in solid oxide fuel cells employing CuMn1.8O4spinel coating on metallic interconnect, Journal of Power Sources. 376 (2018) 100–110. doi:10.1016/j.jpowsour.2017.11.069.

[9] W. Huang, S. Gopalan, U.B. Pal, S.N. Basu, Evaluation of Electrophoretically Deposited CuMn1.8O4 Spinel Coatings on Crofer 22 APU for Solid Oxide Fuel Cell Interconnects, Journal of The Electrochemical Society. 155 (2008) B1161. doi:10.1149/1.2975367.

[10] A.G. Sabato, S. Molin, H. Javed, E. Zanchi, A.R. Boccaccini, F. Smeacetto, In-situ Cu-doped MnCo-spinel coatings for solid oxide cell interconnects processed by electrophoretic deposition, Ceramics International. 45 (2019) 19148–19157. doi:10.1016/j.ceramint.2019.06.161.

[11] A.L.G. Prette, M. Cologna, V. Sglavo, R. Raj, Flash-sintering of Co2MnO4 spinel for solid oxide fuel cell applications, Journal of Power Sources. 196 (2011) 2061–2065. doi:10.1016/j.jpowsour.2010.10.036.

[12] M. Biesuz, V.M. Sglavo, Flash sintering of ceramics, Journal of the European Ceramic Society. 39 (2019) 115–143. doi:10.1016/j.jeurceramsoc.2018.08.048.

[13] A. Gaur, V.M. Sglavo, Tuning the flash sintering characteristics of ceria with MnCo2O4, Materials Science and Engineering B: Solid-State Materials for Advanced Technology. 228 (2018) 160–166. doi:10.1016/j.mseb.2017.11.026.

[14] A. Gaur, V.M. Sglavo, Flash-sintering of MnCo 2 O 4 and its relation to phase stability, Journal of the European Ceramic Society. 34 (2014) 2391–2400. doi:10.1016/j.jeurceramsoc.2014.02.012.

[15] S. Molin, A.G. Sabato, H. Javed, G. Cempura, A.R. Boccaccini, F. Smeacetto, Co-deposition of CuO and Mn1.5Co1.5O4powders on Crofer22APU by electrophoretic method: Structural, compositional modifications and corrosion properties, Materials Letters. 218 (2018) 329–333. doi:10.1016/j.matlet.2018.02.037.

[16] 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, Journal of the European Ceramic Society. 37 (2017) 4781–4791. doi:10.1016/j.jeurceramsoc.2017.07.011.

[17] F. Smeacetto, A. De Miranda, S. Cabanas Polo, S. Molin, D. Boccaccini, M. Salvo, A.R. Boccaccini, Electrophoretic deposition of Mn1.5Co1.5O4 on metallic interconnect and interaction with glass-ceramic sealant for solid oxide fuel cells application, Journal of Power Sources. 280 (2015) 379–386. doi:10.1016/j.jpowsour.2015.01.120.

[18] Z. Sun, R. Wang, A.Y. Nikiforov, S. Gopalan, U.B. Pal, S.N. Basu, CuMn1.8O4protective coatings on metallic interconnects for prevention of Cr-poisoning in solid oxide fuel cells, Journal of Power Sources. 378 (2018) 125–133. doi:10.1016/j.jpowsour.2017.12.031.

[19] T. Brylewski, A. Kruk, M. Bobruk, A. Adamczyk, J. Partyka, P. Rutkowski, Structure and electrical properties of Cu-doped Mn-Co-O spinel prepared via soft chemistry and its application in intermediate- temperature solid oxide fuel cell interconnects, Journal of Power

Sources Journal. 333 (2016) 145e155 Contents. doi:10.1016/j.jpowsour.2016.09.136.

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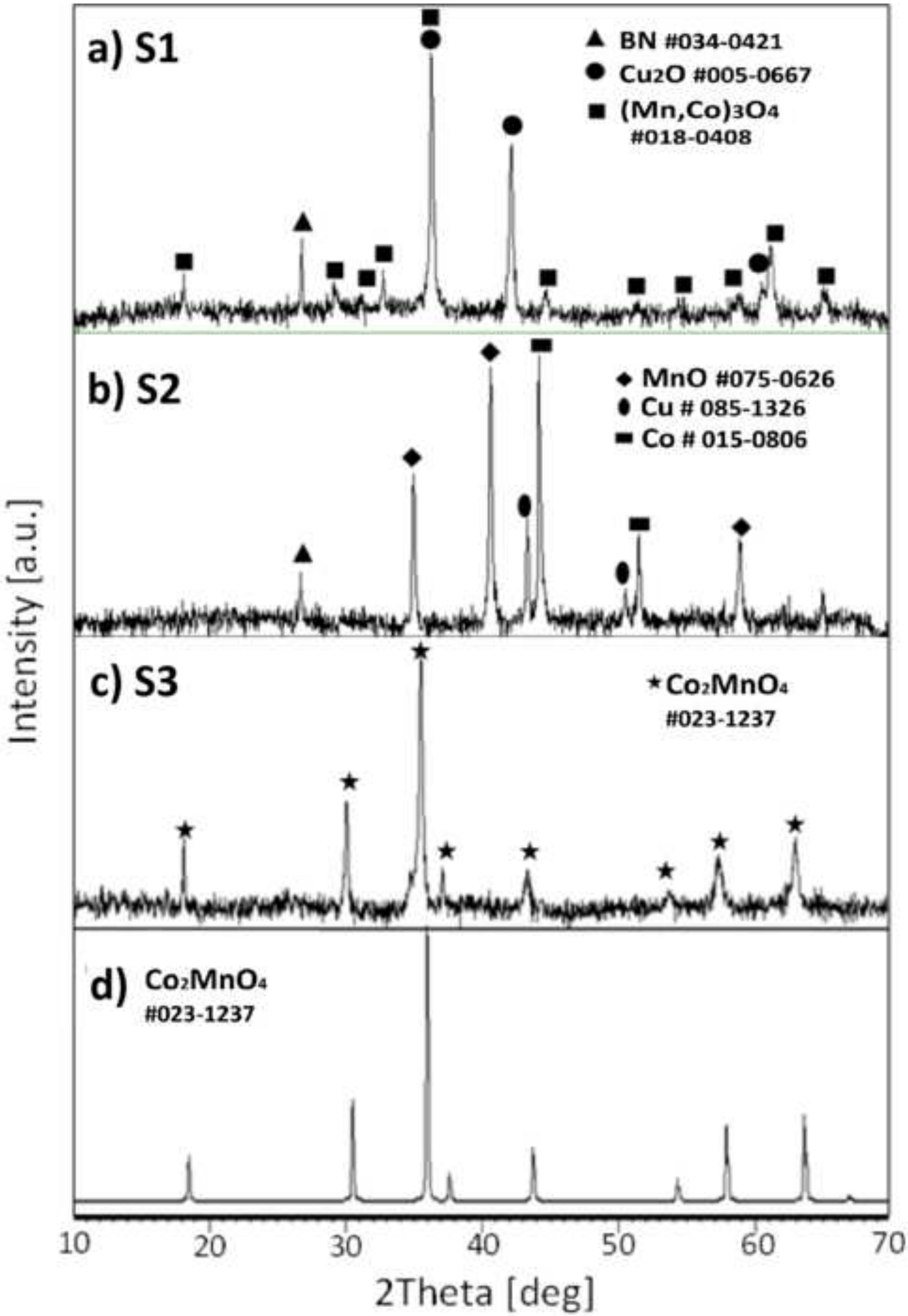

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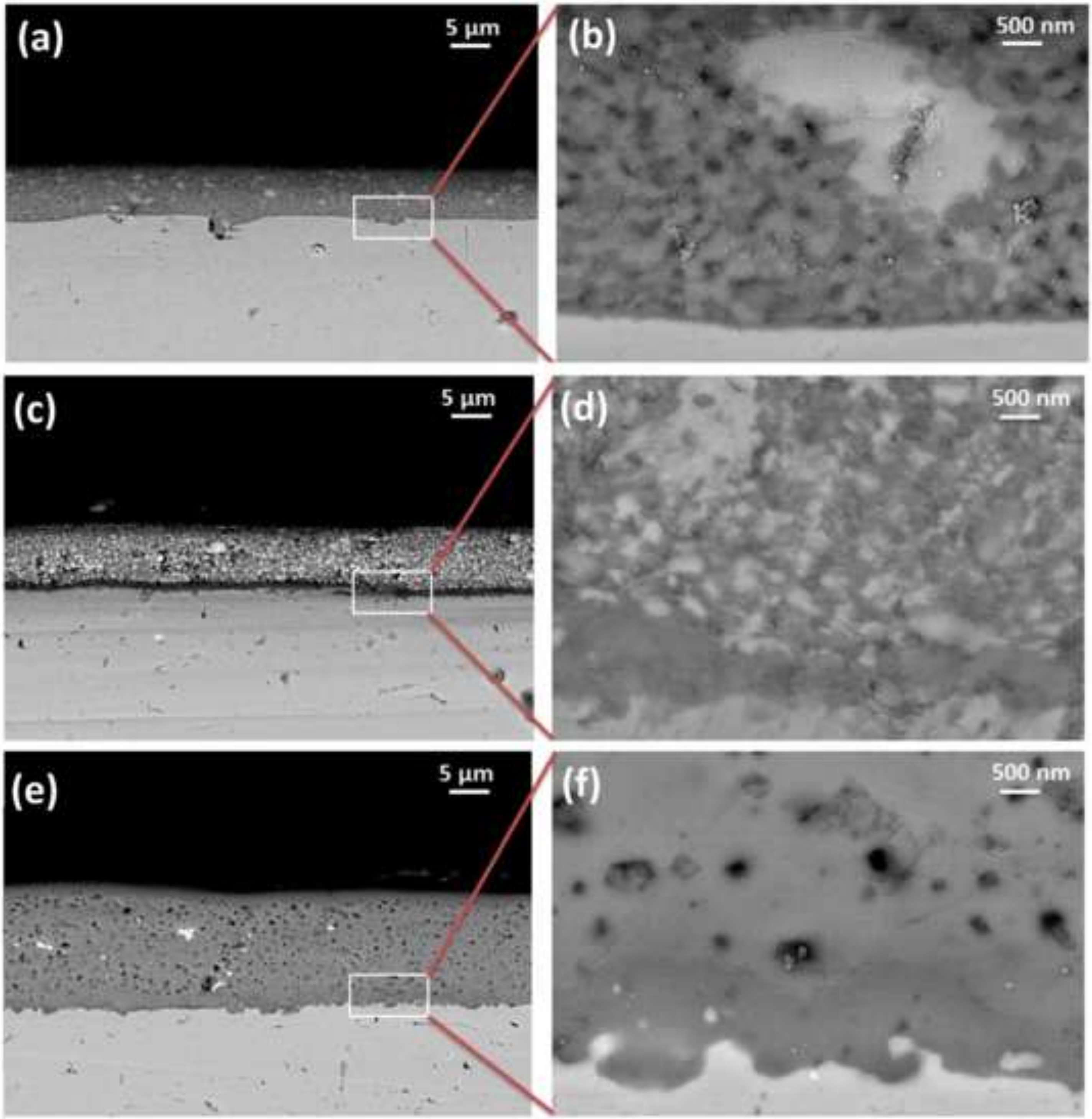

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