Available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he

# Investigation of Mn/Co coated T441 alloy as SOFC interconnect by on-cell tests

*Junwei Wu* [a,b], *Randall S. Gemmen* [a], *Ayyakkannu Manivannan* [a], *Xingbo Liu* [a,b,*]

[a] *National Energy Technology Laboratory, Department of Energy, Morgantown, WV 26507, USA*
[b] *Mechanical and Aerospace Engineering Department, West Virginia University, Morgantown, WV 26506, USA*

ARTICLE INFO

*Article history:*
Received 21 December 2009
Received in revised form
27 March 2010
Accepted 18 April 2010
Available online 26 May 2010

*Keywords:*
SOFC
Interconnect
Laves phase
Electrodeposition
On-cell test

ABSTRACT

T441 has been identified as the candidate for SOFC interconnect material because it is assumed that with the addition of Nb, Ti in T441, the formation of continuous silica sub-layer could be avoided or delayed due to Nb and Si rich secondary phase formation stabilizing silicon migration. Previously, electrodeposition Mn/Co alloys followed by oxidation has been proved as a simple and cost effective method to fabricate (Mn, $Co)_3O_4$ coatings. In this work, Mn/Co coated T441 interconnects were tested as the cathode current collector of solid oxide fuel cells. For comparison, uncoated and 500 h pre-oxidized T441 interconnects were tested as well. The cell with coated interconnect shows stable performance during total 850 h test, even after severe thermal cycles (heating rate 26.7 °C/min). The coating shows good adhesion with substrate and it can prevent Cr poisoning on SOFC cathode. While the cell with uncoated and pre-oxidized T441 interconnects degrade rapidly. XRD results show the coating peaks shifted from mainly $Co_3O_4$ with some little Mn before test to $MnCo_2O_4$ after test due to Mn diffusion from substrate. No Cr penetrated to the coating layer, as further proved by EDX linescan. The effect of laves phase on the $Cr_2O_3$ sub-layer formation and coating thickness was further discussed.


## 1. Introduction

Ferritic stainless steels are the most promising materials for interconnects applications in planar solid oxide fuel cells (SOFCs) at 800 °C or lower, because of its close CTE match with other components of SOFCs, and cost effectiveness as compared with other candidates [1,2]. Crofer 22 APU, E-brite, SUS430, and other alloys have been extensively studied in recent years. It has been found that the oxidation resistance of bare alloys is not enough for the application, and Cr-poisoning can severely degrade cell performance. Therefore, various coatings, nitride [3,4], perovskite [5,6], spinel [7,8], have been tested to prove to be promising for interconnect coatings.

Even with the coatings, some problems still remain during or after long term SOFC operation with the above mentioned interconnects. Firstly, residual silicon in the alloy may diffuse into the substrate/scale interface to form a continuous silica insulation layer, even if the silicon content is as low as 0.1 wt% [9], and with coatings applied. It has also been reported that spallation occurred between silica layer and $Cr_2O_3$ layer [10]. Vacuum melting can effectively remove the residual silicon from the alloy, but with high cost. Secondly, for long-term stack operation, creep resistance of the interconnect material is of great importance to keep gastight [11]. Although no stack degradation has been reported due to poor creep resistance of interconnect by far.

* *Corresponding author*. Mechanical and Aerospace Engineering Department, West Virginia University, Morgantown, WV 26506, USA. E-mail address: xingbo.liu@mail.wvu.edu (X. Liu).
0360-3199/$ – see front matter 
doi:10.1016/j.ijhydene.2010.04.115

Recently, literatures [12,13] have reported that ferritic stainless steels dispersed with laves phases (such as $Fe_2Nb$ type) can not only increase the creep resistance, but also stabilize silicon to prevent continuous silica layer formation during long term test. Addition of little amount of laves phases formation element (Nb, Mo, W, or Ti) into traditional Fe–Cr alloys (such as SUS430) is effective to control the elemental diffusivity at the alloy grain boundaries by forming a laves-type phases in air. T441 is a typical laves phase formation alloy with the addition of Nb, Ti over SUS430 [13]. Yang and co-workers has conducted long term area specific resistance (ASR) test of several ferritic stainless steels with $Mn_{1.5}Co_{1.5}O_4$ spinel. T441 shows 12 m$\Omega$ cm$^2$ after 5000 h test [13], the corresponding ASR values of spinel coated Crofer 22 is 14.3 m$\Omega$ cm$^2$ after 6 months [7] and 40 m$\Omega$ cm$^2$ for coated AISI 430 after only 400 h [14]. Overall, T441 shows the lowest resistance. Another advantage of T441 alloys is [15] that non-stoichiometric $TiO_2$ growth on Ti containing alloys surface may prove to be an effective barrier to both scale growth and Cr vaporization.

In our previous study, electrodeposition Mn/Co alloys followed by oxidation has been successfully utilized to fabricate Mn and Co containing spinel coatings [16,17]. By means of interconnect on-cell test, dramatical performance improvement has been exhibited, as compared with uncoated interconnect based on SUS430 [18]. In this work, the performances of solid oxide fuel cells will be evaluated with Mn/Co coated T441 interconnect as cathode current collector, as well as with uncoated, 500 h pre-oxidized T441 interconnect for comparison. Additionally, the effect of laves phases will be discussed on $Cr_2O_3$ sub-layer growth and substrate element diffusion.

## 2. Experimental

### 2.1. Interconnect and coating process

T441 substrate alloys were obtained from Allegheny Ludlum, with chemical composition of 17.6% (weight) Cr, 0.33% Mn, 0.47% Si, 0.46% Nb, 0.18% Ti, 0.20% Ni, 0.01% C, 0.045% Al, 0.024% P, 0.001% S, balance Fe [13]. Substrates were machined as button cell interconnect, as shown in previous publication [18]. Mechanical grinding and electrochemical polishing were conducted before Mn/Co alloys deposition on the machined coupon. After being oxidized at 800 °C for 2 h, the coated coupon is ready for test. The detailed Mn/Co alloy electrodeposition and interconnect on-cell test process were also described in previous work [18]. SOFC button cells were purchased from MSRI. The anode is Ni/YSZ cermet, the electrolyte is yttria-stabilized zirconia (YSZ), and the cathode lanthanum strontium manganate (LSM). Interconnect on SOFCs were tested at 800 °C. The oxidant flow rate was at 500 cm$^3$ min$^{-1}$ (97% air + 3% $H_2O$) and the fuel flow rate was 100 cm$^3$ min$^{-1}$ (97% $H_2$ + 3% $H_2O$). Load of 0.75A (0.375 A cm$^{-2}$ relative to the cathode area) were added after open circuit voltage (O.C.V) were stabilized. During the test, thermal cycles were also conducted to test the thermal coefficient. For comparison, bare T441 and 500 h pre-oxidized T441 interconnect were tested as well.

### 2.2. Interconnect and cell characterization

Surface morphology and composition of the coatings were assessed by a JEOL JSM 6300 scanning electron microscopy (SEM) equipped with a Thermo Electron energy dispersive X-ray analysis (EDX) system. To characterize the phase formation, X-ray diffraction (XRD) data were obtained with a Panalytical MRD diffractometer equipped with a thin film stage. Additionally, cross section of coated interconnect was also analyzed by SEM/EDX to study the $Cr_2O_3$ sub-layer formation and elemental diffusion.

## 3. Results and discussions

### 3.1. Interconnects before test

Fig. 1 shows the surface morphologies of interconnects before on-cell test. After 500h oxidation, cubic particles start to appear (Fig. 1 (a)), but the surface is not uniform, some big clusters were discovered. EDX result shows surface has large amount of Mn, Cr and little Ti, which matches the results from literature [15]. It shows alloys with titanium addition will form $TiO_2$ after oxidation. Literature also shows the oxidized structure has Mn-rich spinel top layer and chromia-rich sub-layer, which is similar to other Mn containing stainless steels [13], such as Crofer 22 APU. Fig. 1 (b) and (c) display the surface morphologies of Mn/Co as-deposited and oxidized (800 °C for 2 h) surfaces. Both of them display uniform structure, and no pores or cracks were observed. As-deposited surface has 8 at.% Mn (cobalt of balance) by EDX.

### 3.2. Cell performance

Fig. 2 shows the cell performances as function of time. Curves 1 and 2 are corresponding to cell performances with bare and 500 h pre-oxidized T441 interconnect, respectively. Both of the cells were tested at constant current of 375 mA cm$^{-2}$ with close initial power densities. The corresponding voltages of the cells are just above 0.7V. The one with bare interconnect was tested for total 380 h. Performance dropped rapidly in the initial 100 h and decrease linearly at a much lower rate in the rest of 280 h. Much lower degradation rate was observed for the cell with pre-oxidized T441 interconnect during 408 h test, because lower Cr evaporation rate are from Mn-rich spinel formed on T441 after oxidation. Big spikes exhibited on the both curves are due to the V/I curve measurement interruption.

The cell with Mn/Co coated interconnects displayed much lower power density at the beginning of the test. In order to make the tests comparable, load of constant voltage 0.7 V are applied instead of constant current 0.75A. The performance increased rapidly and reached a plateau from 100 h to 170 h, and another plateau with the same level is observed between 480 h and 546 h. Note that fluctuation of performance is observed between 170 h and 480 h, the reason is not clear yet. After the performance is stabilized at 546 h, two thermal cycles were conducted. Firstly, the cell and interconnect were cooled down from 800 °C to room temperature (RT) in 2 h. Then, they were heated up to 800 °C within 30 min (heating rate 26.7 °C/min) and cooled down to RT in 2 h. Next, they were