

Short communication

# Clad metals, roll bonding and their applications for SOFC interconnects<sup>☆</sup>

Lichun Chen<sup>a,\*</sup>, Zhenguo Yang<sup>b</sup>, Bijendra Jha<sup>a</sup>, Guanguang Xia<sup>b</sup>, Jeffrey W. Stevenson<sup>b</sup>

<sup>a</sup> Engineered Materials Solutions, 39 Perry Avenue, Attleboro, MA 02703, USA

<sup>b</sup> Pacific Northwest National Laboratory, 902 Battelle Blvd, Richland, WA 99352, USA

Received 14 December 2004; accepted 5 January 2005

Available online 22 March 2005

## Abstract

Metallic interconnects have been becoming an increasingly interesting topic in the development in intermediate temperature solid oxide fuel cells (SOFC). High temperature oxidation resistant alloys are currently considered as candidate materials. Among these alloys however, different groups of alloys demonstrate different advantages and disadvantages, and few if any can completely satisfy the stringent requirements for the application. To integrate the advantages and avoid the disadvantages of different groups of alloys, clad metal has been proposed for SOFC interconnect applications and interconnect structures. This paper gives a brief overview of the cladding approach and its applications, and discuss the viability of this technology to fabricate the metallic layered-structure interconnects. To examine the feasibility of this approach, the austenitic Ni-base alloy Haynes 230 and the ferritic stainless steel AL 453 were selected as examples and manufactured into a clad metal. Its suitability as an interconnect construction material was investigated.

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**Keywords:** Clad metals; Roll bonding; SOFC interconnect

## 1. Introduction

Recent advancements in solid oxide fuel cell (SOFC) technologies have allowed a reduction in SOFC operating temperatures to an intermediate range (600–800 °C) [1–3]. This resulted in increased interest in development of cost-effective metallic interconnects to replace the traditional ceramic materials that are used in high temperature (900–1000 °C) SOFC stacks [4–6]. There are three primary functions of interconnects in common SOFC designs: (1) to provide an electrical conductive path that permits an in-series connection of individual cells; (2) to separate the fuel and oxidant gas paths between individual cells; (3) to act as the primary structural element to maintain the overall mechanical support and stability of the stack and to provide mechanical connection surfaces for gas path sealing materials. Therefore, during SOFC

operation, the interconnects must be thermally, chemically and mechanically stable during simultaneous exposure to an oxidizing atmosphere at the cathode side and a reducing atmosphere at the anode side for thousands of hours at elevated temperatures with numerous thermal cycles. The interconnect must be stable towards any sealing materials with which it is in contact. In addition, the interconnects must be chemically compatible with electrical contact materials, which are used to minimize interfacial contact resistance, and/or the electrode materials. More specifically, the metallic interconnect materials are required to have excellent surface stability, i.e. oxidation and corrosion resistance, between 600 and 800 °C, high long-term electrical conductivity, good thermo-mechanical stability and compatibility with other stack components (e.g. seals, electrodes), as well as low cost.

Overall, there are three groups of high temperature oxidation resistant alloys based on what protective oxide scales are formed; these are alumina forming, silica forming and chromia forming alloys [5]. Alumina forming Ni–Cr–Al, Co–Cr–Al and low cost Fe–Cr–Al alloys have extremely slow-growing alumina scale that is protective against oxida-

<sup>☆</sup> This paper was presented at the 2004 Fuel Cell Seminar, San Antonio, TX, USA.

\* Corresponding author. Tel.: +1 508 342 2135; fax: +1 508 342 2535.  
E-mail address: [lchen@emscld.com](mailto:lchen@emscld.com) (L. Chen).

tion and corrosion attack at high temperature. However, the high electric resistance of alumina scales makes these alloys unsuitable to use for interconnects, unless a special measure is taken to overcome this obstacle. Silica forming Ni-, Co- and Fe-based alloys, with protective surface scale to resist oxidation and corrosion, are usually brittle at room temperature, making them unsuitable for forming operations. This, along with the low electric conductivity of silica scales, makes this alloy group unsuitable for interconnects. Chromia scales are protective too while having a reasonable electric conductivity. An additional advantage is that Cr tends to lower the coefficient of thermal expansion (CTE) of alloys.

Among chromia forming alloys, ferritic stainless steels and austenitic Ni(–Fe)–Cr or Fe–Ni–Cr based alloys are considered potential candidates. The ferritic stainless steels are generally more cost-effective and, in some cases, demonstrate good CTE (coefficient of thermal expansion) matching to the other stack components. However, they have issues in terms of (i) high electrical resistance that results from the scale growth over a long period of time, (ii) low mechanical strength at SOFC operating temperatures, and (iii) possible anomalous scale growth under dual atmosphere exposures [7] and corrosion in carbon containing anode side environments [8], both of which can lead to an accelerated metal loss and localized attack. In comparison, Ni(–Fe)–Cr or Fe–Ni–Cr based alloys possess superior high temperature mechanical strength, oxidation and corrosion resistance at both anode and cathode sides under SOFC operating conditions, and are more manufacturable than ferritic stainless steels. These Ni(–Fe)–Cr or Fe–Ni–Cr based alloys, however, are generally more expensive than ferritic compositions and have a relatively high CTE. To integrate the advantages and avoid the disadvantages of these two groups of alloys, cladding, a cost effective approach widely used by industries for the preparation of layered metals, has been investigated for the manufacture of composite or layered-structure interconnects.

## 2. Clad metals

Clad metals are layered metallic composite materials. Clad metals have been widely used in industries as well as in our daily life. They can be produced in plate, strip, foil, tube, rod and wire form. Traditionally, clad metals have provided many solutions in either functionality or cost saving as well as both of them. Functionalities provided by different clad metals can be grouped into structural, thermal expansion management, thermomechanical control (thermostat), electrical, magnetic, corrosion resistant, joining and cosmetic applications. In each function group, there might be several clad metal systems. For example, there are at least three clad metal systems in joining applications: (1) Transition clad metal system that provides an interface between two incompatible metals or alloys [9]. One such application is Al/steel clad metal used in fusion welding between an aluminum part and a steel component in

automotive assembling. (2) Self-brazing clad metal system, in which the thin surface layers of a lower melting point metal or alloy act as brazing filler during brazing joining of the base metal in clad metal as a whole and additional filler or flux is not necessary. Copper-clad stainless steel used for heat exchangers is a good example of this application [10]. (3) Brazing filler clad metal system, in which different metals or alloys in individual layers at designed thickness ratios become a braze filler alloy as a result of in situ alloying at a high temperature during brazing and thus provide brazing joints.

In corrosion resistant applications, clad metals can be divided by the following systems. (1) Noble metal clad system [9]: that is a relatively inexpensive base metal covered with a corrosion resistant metal on the surface. The examples include stainless steel/steel, Ni superalloy/steel, Pt/steel, Au/brass. (2) Corrosion barrier clad system [9]: which is a combination of two or more metals to form a barrier to prevent perforation galvanically, which otherwise will occur on each of the metals due to pitting corrosion. For example, low carbon steel/304 stainless steel for chloride-ion-containing environment applications, Cu/430 stainless steel/Cu for communication cable shielding buried in acidic soil. (3) Sacrificial metal clad system [9]: in this clad metal system, an active metal (Zn, Al, Mg) of the galvanic series is clad to protect a more noble metal. Al/4xx stainless steel and AlClad are good examples of this system. (4) Diffusion-alloyed clad system: a new alloy surface is formed by diffusion where such an alloy or surface is difficult to produce by conventional methods. DuraFoil, a FeCrAl alloy made by diffusion annealing of Al/FeCr/Al clad metal, is a good example of such a system [11]. Finally, a complex multilayer clad system [9] is used for dual environments or multiple requirements. Ti/stainless steel/Ni clad metal sheet used as the bipolar electrode in PEM fuel cell is one such application. Ni/304SS/Cu clad metal used for a bottom battery cap is another example, where the outer Ni surface layer provides low contact resistance, atmospheric corrosion resistance and cosmetic appearance, thick stainless steel in the core is for strength and deep drawing, perforation corrosion resistance and total low cost, and inner Cu surface layer provides a electrode contact surface for electrochemical cell performance.

## 3. Roll bonding process for clad metals

The clad metal can be produced by explosion, forging, diffusion bonding, friction welding, or co-axial extrusion. However, the most economic and most productive manufacturing process for large size flat clad metal sheets and foils is roll bonding. Roll bonding is a solid state welding process to join dissimilar metals and a well-established and widely used manufacturing technology [9,10]. In this process (Fig. 1), two or more sheets, plates or strips of metals or alloys are stacked together and then passed through a pair of rolls until proper deformation has been achieved to pro-

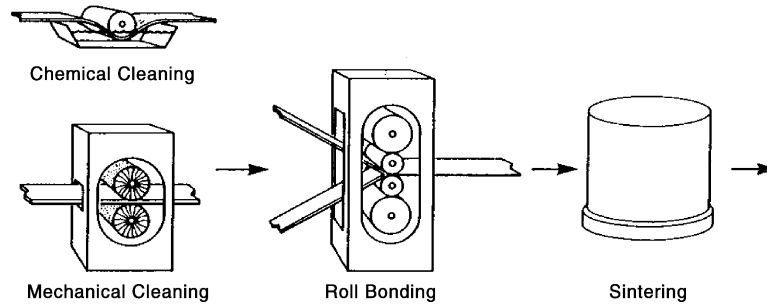


Fig. 1. Schematic of roll bonding process for manufacturing clad metal.

duce a solid state joint between the original individual metal pieces. During roll bonding, no filler or adhesive agent is involved. Generally there are two types of roll bonding: hot roll bonding and cold roll bonding. Hot roll bonding is a process that involves external heating, while no external heat is applied during cold roll bonding. Cold roll bonding has several advantages over hot roll bonding, including more uniform individual layer thickness ratio, good surface quality and lower cost. Before roll bonding, the surfaces to be bonded must be properly cleaned and prepared to remove any barriers to bonding (Fig. 1). Chemical and mechanical cleanings are two common methods used to remove organic matter and surface oxides. An alkaline detergent is normally applied to remove oil or organic matter and a diluted acid solution is used to remove surface oxides. Mechanical cleaning may also provide rough surfaces, which provide a greater amount of surface asperities and promote localized shear deformation to break unavoidable surface oxide films during cold roll bonding. During the bonding process, high reduction in thickness of the materials (capable of up to 60% or more in a single rolling pass) is achieved under high pressure at the roller. The high reduction generates a great amount of heat and creates virgin surfaces on the materials being bonded. The fresh, virgin surfaces along the bond interface are in a self-enclosed environment, where oxidation cannot occur, and therefore do not have bond-impeding oxide barriers. A bond (normally a mechanical bond) in the layered composite is thus obtained through interfacial mechanical locking and atomic affinity between the two metals. After roll bonding, annealing is normally performed (Fig. 1) to obtain or secure a metallurgical bond. In addition to recovery and recrystallization of highly cold-worked microstructures during annealing, residual organic impurities can be gasified and diffused away from the bond interface, and diffusion can occur along and across the bond interface, creating a “common lattice structure”. Some of the clad metal systems do not need a separate annealing process after cold-roll bonding because self-annealing occurs during and after bonding. After the above processes, the clad metals can be further processed by any of conventional strip metal manufacturing processes (e.g., cold-rolling, annealing, pickling, leveling and slitting) to specific required sizes and temper. They can be roll-formed, stamped, drawn and joined into a required component or part. As clad met-

als can be produced by roll bonding and further processed in coil form, their manufacturing has high productivity and is economically cost-effective.

#### 4. Concepts for SOFC interconnects

Two concepts have been proposed in preparing clad metals for SOFC interconnect applications. The first concept is to make simple clad metals by roll bonding of two or three layers of metals that typically have different compositions and properties. The second concept is to surface-alloy or -modify the clad metals through roll bonding and diffusion. In the first concept, for example, a ferritic stainless steel with an appropriate level of chromium and relatively low CTE can be used as the center core or back base in a clad metal system while a relative high CTE austenitic high temperature oxidation resistant alloy is used to form a thin surface layer in the clad metal. The ferritic stainless steel keeps the CTE of the clad metal to a value that is acceptable to stack designers, while lowering the interconnect cost. The austenitic high temperature oxidation resistant alloy, such as a Ni-base superalloy, provides excellent surface stability as well as enhances the structural stability. As a result, the clad metal integrates the advantages of Ni-base alloys and ferritic stainless steels, while their disadvantages are avoided. In the second concept, a clad metal is first made by roll bonding of a base metal with one thin outer layer at one side or two thin layers at both sides of the base metal. This is followed by a special heat treatment during which diffusion alloying occurs on the surface of the clad metals. The surface alloying or modification offers the flexibility to modify the surface alloy composition of clad metals for improved chemical, electrical, and thermomechanical stabilities. For example, spinel phase is expected to form on the chromia scale to prevent chromium specie from volatilization which poises the cathode in the cell. Another hypothesis approach is to modify the surface of alumina forming alloys to make the surface more conductive.

In addition to the aforementioned advantages, the flexibility of cladding also allows for addressing cathode and anode side issues separately, because multilayer clad metals can have different alloys at each side surface.

Table 1  
Chemical composition of alloys (wt.%)

Alloys	Chemical compositions (wt.%)									
	Cr	Mn	Si	Al	Mo	W	C	Others	Ni	Fe
AL 453	22	0.3	0.2	0.8			0.02	0.05(La + Ce)	0.2	Balance
Haynes 230	22	0.5	0.4	0.3	2.0	14	0.1	5Co, 0.02La, 0.015B	57	3

## 5. Experiments

A proof-of-concept experiment has been conducted in this work. AL 453, a chromia-forming ferritic stainless steel, and Haynes 230, a Ni-base austenitic alloy, were selected as core base and surface layer materials, respectively, for a clad metal. Haynes 230 was produced by Haynes International, and AL 453 by Allegheny Ludlum. Table 1 lists their compositions. A thick AL 453 plate was clad with two pieces of thin Haynes 230 sheets, one at each side, by cold roll bonding to form three layer Haynes 230 | AL 453 | Haynes 230 clad metal, with a thickness ratio of approximate 8%/84%/8%. A rolling reduction of  $\sim 60\%$  was achieved in one rolling pass during bonding. High temperature annealing was subsequently carried out to establish a metallurgical bond along the metal interfaces. The clad metal was cold-rolled into a 0.5 mm final thickness. The final annealing was then performed at a temperature well above intermediate SOFC operating temperatures (600–800 °C), in order to ensure that the microstructure developed during the annealing can be retained during SOFC operation.

The clad metal sample was tested at 800 °C for 300 h in moist air ( $\sim 3$  vol.% water vapor) to examine its oxidation resistance and microstructural stability. The moist air was generated by flowing air through a water bubbler at the room temperature. Samples before and after the oxidation testing were cross-sectioned, polished and examined on a JEOL scanning electron microscope (model 5900LV) equipped with energy-dispersive X-ray (EDX) capability at an operating voltage of 20 keV. The thermal expansion behavior of the clad metals was also analyzed using a dilatometer (Dilatronic by Theta Industries).

## 6. Results and discussion

Fig. 2 shows the microstructure of the cross-section of the clad metal Haynes 230 | AL 453 | Haynes 230 after cold-rolling and a subsequent annealing. The difference in contrast between the Ni-base alloy and the ferritic stainless steel clearly reveals the center core of AL 453 and a uniform layer of Haynes 230 with a thickness of about 60  $\mu\text{m}$  at each side of the clad metal. The Ni-base alloy outer layers are well bonded to the ferritic stainless steel core via metallurgical bonds that were established during the annealing through alloy element interdiffusion across the interfaces between AL 453 and Haynes 230. The interdiffusion appears to be very limited under the current processing, as evidenced by the EDS

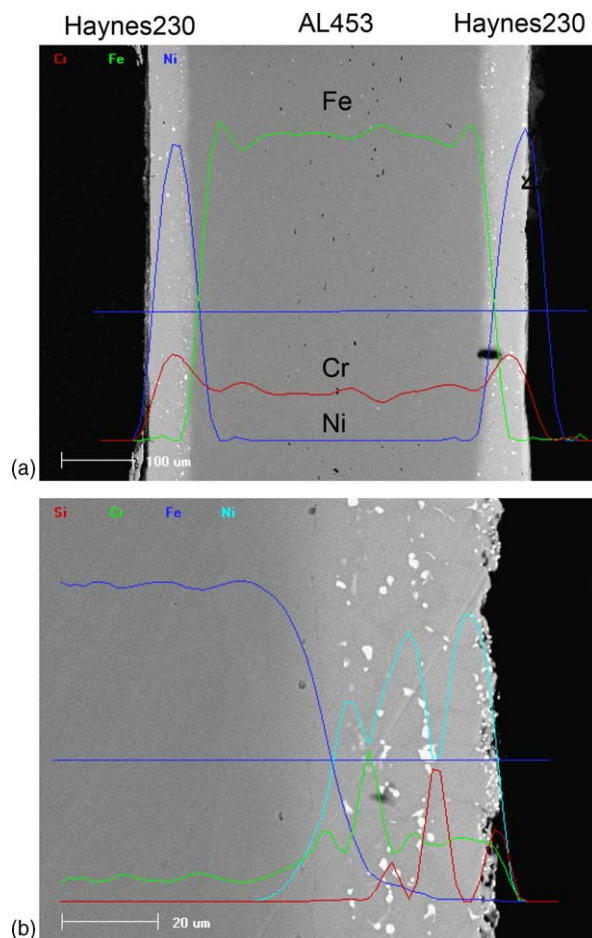


Fig. 2. SEM micrograph and elemental distribution across the cross-section of the clad metal system Haynes 230 | AL 453 | Haynes 230 prepared via roll bonding followed by annealing.

linear analysis. No obvious intermetallic phases or Kirkendall diffusion porosity are observable along the bonding interfaces in the clad metal system. The quality of the bond-strength of the clad metal was confirmed by the fact that manually mechanical chiseling into the adjacent area of the clad interface on a sample cutting edge or heating by a torch flame over the clad metal sample did not cause de-bonding of any layer in the clad metals.

After the oxidation test at 800 °C in moist air containing  $\sim 3$  vol.%  $\text{H}_2\text{O}$  for 300 h, it was observed that very thin scales were grown on the surfaces of the clad metal, as shown in Fig. 3(a) and (b). The scale was essentially identical to that grown on unclad Haynes 230, and thus its growth rate was much slower than that of a chromia-forming ferritic stainless

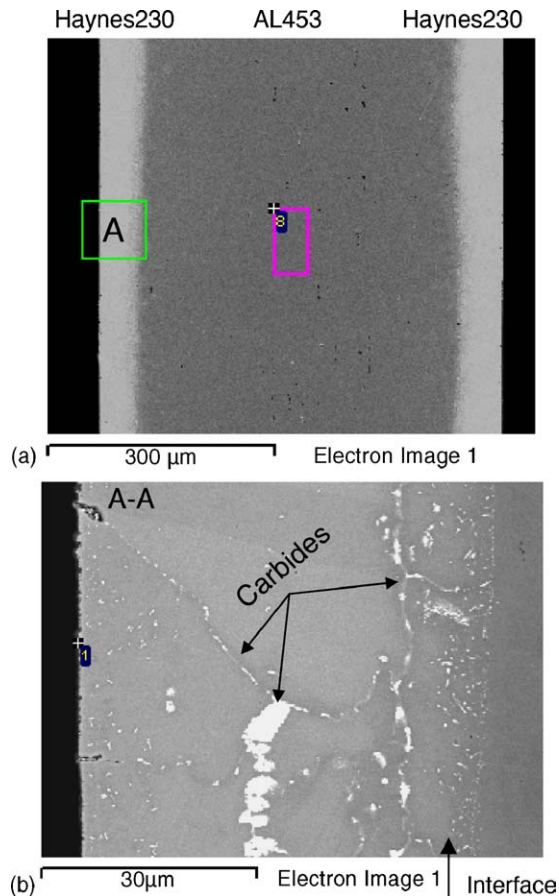


Fig. 3. SEM micrograph of the clad metal system Haynes 230 | AL 453 | Haynes 230 after heat-treatment at 800 °C for 300 h in moist air (~3% H<sub>2</sub>O): (a) cross-section, and (b) an image from area “A” in (a).

steel such as AL 453 [6]. As result, the clad metal demonstrated an oxidation resistance equivalent to that of Haynes 230. Overall the clad metal remained structurally stable during the oxidation. A limited amount of interdiffusion occurred during the test, leading to only a slight increase in the thickness of the Ni-base outer layers, as defined by the contrast difference (Fig. 3(a)). Microscopically, the interdiffusion resulted in formation of additional phases in the diffusion zone at the interface (refer to Fig. 3(b)) between AL 453 and Haynes 230. Second phase along grain boundaries in the Ni-base outer layers was identified as tungsten rich carbides. As expected, the thin scales grown on the clad metal provided a good protection to the substrate and no obvious internal oxidation were observed in the austenitic outer layers and the ferritic core. It was noted from the semi-quantitative EDS analysis that the compositions of Cr, W, Fe and Ni in Haynes 230 near a narrow inter-diffusion band parallel to the bond interface were still at their original levels of 22, 14, 3 and 57%, respectively, and that the Cr% in AL-453 also did not change after 300 h oxidation testing at 800 °C.

The thermal expansion behavior of the three-layer clad metal was also investigated. Fig. 4 shows the thermal expansion of the clad metal as a function of temperature, in compar-

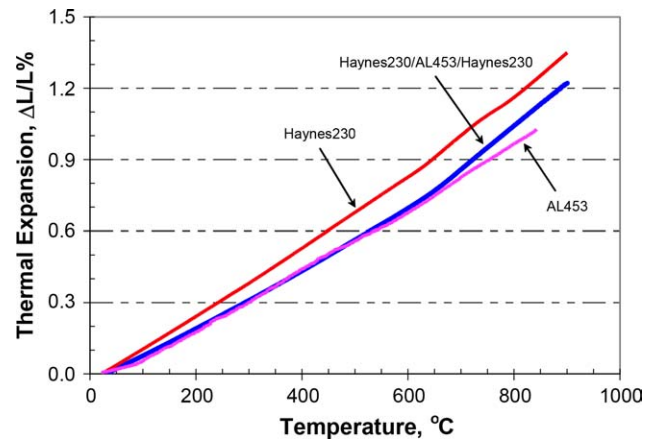


Fig. 4. Thermal expansion of the clad metal system Haynes 230 | AL 453 | Haynes 230 in air as a function of temperature.

ison with those of Haynes 230 and AL 453. At temperatures below about 600 °C, the thermal expansion of the clad metals was dominated by the AL 453 core. As the temperature increased over 600 °C, the thermal expansion curve began deviating slightly from the AL 453 curve toward the Haynes 230 curve. The thermal expansion behavior of the clad metal as a function of temperature is likely associated with the thermo-mechanical properties of the core stainless steel and the outer layer Ni-base alloy. It is known that, typically, the mechanical strength of ferritic stainless steels experiences a dramatic drop as the temperature increases over 550–600 °C. For example AL 453 has a yield strength of 310 MPa at room temperature that drops to 173 MPa at 538 °C and 39 MPa at 760 °C, a 28 and 87% reduction, respectively [12]. In contrast, Haynes 230 demonstrates a high yield strength that only slightly decreases from 395 MPa at room temperature to 280 MPa at 538 °C and 255 MPa at 760 °C, corresponding to 29 and 35% reduction, respectively [13]. Thus at temperatures lower than 600 °C, the thermal expansion behavior is dominated by the large volume fraction of the core stainless steel AL 453. Above this temperature, the stronger Haynes 230 outer layers start to play a significant role in the overall behavior of the clad metal.

It is noted that the current testing was of fairly short duration. Obviously, longer oxidation testing and further analysis need to be performed to fully characterize and understand the performance behavior of the clad metal in SOFC operating conditions. Nevertheless this preliminary study suggests that cost-effective cladding may be a promising technology for fabrication of metallic layer-structure interconnects for SOFC applications.

## 7. Conclusions

Two conceptual approaches of clad metals, a simple multilayer clad system and a surface-alloyed/modified clad alloy system, for SOFC interconnects have been proposed. The

proof-of-concept work on the first concept clad system indicated that cladding is a viable means of manufacturing layered structures for SOFC interconnect applications. Specifically, the three-layer clad system, comprised of a ferritic stainless steel core and symmetrical, thin Ni-base alloy outer layers at each side of the core substrate, demonstrates an oxidation resistance identical to the Ni-base alloy and a thermal expansion similar to that of a ferritic stainless steel. The well-bonded layer structure was stable under preliminary testing. Further improvement in desired properties relative to SOFC interconnect applications can be achieved by optimizing materials and design parameters for the clad structure.

### Acknowledgements

The authors would like to thank William Gorman at Engineered Materials Solutions (EMS) for his assistance in clad metal processing and thermal expansion measurement, Nat Saenz, Shelly Carlson, and Jim Coleman at Pacific Northwest National Laboratory for their assistance in metallographic and SEM sample preparation and analysis. The authors would like to express their gratitude to EMS management for their support in financial and human resources on this work and permission to publish this paper. Part of this work, specifically SEM analysis, was funded as part of the Solid-State

Energy Conversion Alliance (SECA) Core Technology Program by the U.S. Department of Energy's National Energy Technology Laboratory (NETL). PNNL is operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.

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