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Clad Metals by Roll Bonding for SOFC Interconnects

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High-temperature oxidation-resistant alloys are currently considered as a candidate material for construction of interconnects in intermediate-temperature solid oxide fuel cells. 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, cladding has been proposed as one approach in fabricating metallic layered interconnect structures. 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. This paper provides a brief overview of the cladding approach and discusses the viability of this technology to fabricate the metallic layered-structure interconnects.

Keywords clad metal, interconnect, roll bonding, solid oxide fuel cell

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) (Ref 1-3). This has resulted in increased interest in the development of cost-effective metallic interconnects to replace the traditional ceramic materials that are used in high-temperature (900-1000 °C) SOFC stacks (Ref 4-6). The primary function of interconnects in SOFCs is to provide an electrical conduit that permits an in-series connection of individual cells. Second, SOFC interconnects separate the fuel and oxidant gas paths between individual cells. Thus, during SOFC operation, the interconnects must be 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. Most applications also require numerous thermal cycles. Finally, the interconnect must be stable toward any sealing materials with which it is in contact and chemically compatible with the electrical contact materials used to minimize interfacial contact resistance and/or the electrode materials.

Considering these service environments, the metallic interconnect materials must have excellent surface stability, i.e., oxidation and corrosion resistance, between 600 and 800 °C, high long-term electrical conductivity, good thermomechanical stability, and compatibility with other stack components (e.g., seals, electrodes), as well as low cost. Overall, high-temperature oxidation-resistant alloys, including ferritic stainless steels and austenitic Ni(-Fe)-Cr or Fe-Ni-Cr based alloys, can be potential candidates. The ferritic stainless steels are generally more cost-effective and, in some cases, demonstrate good coefficient of thermal expansion (CTE) matching to the other stack components. However, they have issues in terms of (a) high electrical resistance that results from the scale growth over a long period of time, (b) low mechanical strength at SOFC operating temperatures, and (c) possible anomalous scale growth under dual atmosphere exposures (Ref 7) and corrosion in carbon containing anode-side environments (Ref 8), both of which can lead to 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 easily fabricated and welded than ferritic stainless steels. These Ni(-Fe)-Cr or Fe-Ni-Cr based alloys, however, are generally more expensive than ferritic stainless steel and have relatively high CTEs. To integrate the advantages and avoid the disadvantages of these two groups of alloys, cladding, a cost-effective approach widely used in industry for preparation of layered metals, has been investigated for the manufacture of composite or layered-structure interconnects.

1.1 Concepts

Two concepts have been evaluated in preparing clad metals for SOFC interconnect applications. The first concept is to make simple clad metals by roll bonding 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, a ferritic stainless steel with an appropriate level of Cr 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 limits the CTE of the clad metal to values that are acceptable to stack designers while it lowers the interconnect cost. The austenitic high-temperature oxidation-resistant alloy, such as a Ni-base superalloy, provides excellent surface stability as well as enhanced structural stability. As a result, the clad metal integrates

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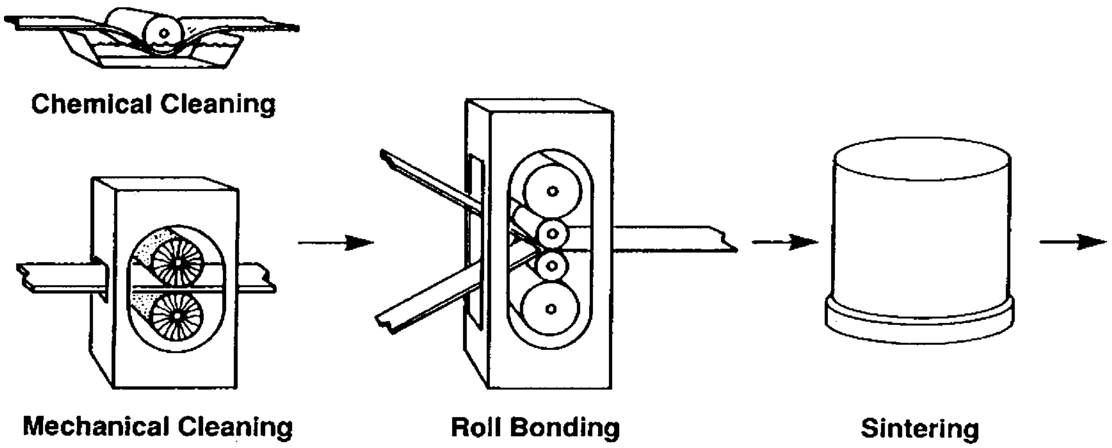

Fig. 1 Schematic of roll-bonding process for manufacturing clad metal

the advantages of Ni-base alloys and ferritic stainless steels while avoiding their disadvantages. 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. In addition to the aforementioned advantages, the flexibility of cladding also allows for addressing cathode- and anode-side issues separately.

1.2 Roll-Bonding Process for Clad Metals

A clad metal is a metallic composite that is made up of layered metals or alloys. The clad metal can be produced by explosion, forging, diffusion bonding, friction welding, or coaxial extrusion. Among these different approaches, the most economic and productive manufacturing process for large-sized flat clad metal sheets and foils is roll bonding. As a solid-state welding process to join dissimilar metals, roll bonding is a well established and widely used manufacturing technology (Ref 9). In this process (shown schematically in 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 produce a solid-state joint between the original individual metal pieces. During roll bonding, no filler or adhesive agent is involved nor is metal fusion. 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, whereas no external heat is applied during a cold roll bonding. In comparison with the hot roll bonding, the cold roll bonding demonstrates advantages of having a 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. Chemical and mechanical cleanings are two common methods used to remove organic matter and 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 process, high reduction in thickness of the materials (up to 60% or more in a single pass) is achieved under high pressure at the roll bite. 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 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." Upon completion of the above processes, the clad metal can be further processed by any of conventional strip-metal manufacturing methods (e.g., rolling, annealing, pickling, leveling, and slitting) to specific customer requirements. It can be roll-formed, stamped, drawn, and joined into a required component or part. As clad metals can be produced by roll bonding and further processed in coil form, their manufacturing has high productivity and is economically cost-effective.

2. Experimental Procedures

In this proof-of-concept work, AL 453, a chromia-forming ferritic stainless steel that was initially developed for roll bonding, and Haynes 230, a Ni-base austenitic alloy, were selected and investigated. Haynes 230 was produced by Haynes International (Kokomo, IN) and AL 453 by Allegheny Ludlum (Brackenridge, PA). Their compositions are listed in Table 1. A three-layer clad metal system, Haynes 230/AL 453/Haynes 230, was prepared with the AL 453 as the center core and the Haynes 230 as the outer layers. A thick AL 453 plate was clad between two pieces of thin Haynes 230 sheets by cold roll bonding to form Haynes 230/AL 453/Haynes 230 clad metal in one rolling pass. High-temperature annealing was then carried out to establish a metallurgical bond along the metal interfaces. The clad metal was then processed to 0.5 mm final thickness with a thickness ratio of approximately 8:84:8 (in %). The final annealing was performed at a temperature well above intermediate SOFC operating temperatures (600-800 °C), with the hope of ensuring that the microstructure developed during the annealing could be retained during SOFC operation.

Table 1 Chemical composition of alloys (wt.%)

Alloy	AL 453	Haynes 230
Cr	22	22
Mn	0.3	0.5
Si	0.2	0.4
Al	0.8	0.3
Mo	<0.1	2.0
W	…	14
Co	…	5.0
C	0.02	0.1
Others	0.05(Ce+La)	0.02La, 0.015B
Ni	0.2	57
Fe	Balance	3

To examine its compositional and structural stability, the clad metal was heat-treated at 800 °C for 300 h in moist air containing ~3% water vapor. Samples (before and after heat treatment) 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 kV. The thermal-expansion behavior of the clad metals was also analyzed using a dilatometer (Theta Industries [Port Washington, NY], Dilatronic with 7200 series controllers).

3. Results and Discussion

Figure 2 shows the cross section of the clad metal Haynes 230/AL 453/Haynes 230 after cold rolling and 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 ~60 μm 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 energy-dispersive spectroscopy (EDS) 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 manual 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 debonding of any layer in the clad metals.

To further examine its structural stability under SOFC interconnect working conditions, the clad metal was subjected to an oxidation test at 800 °C in moist air containing ~3% H_2O. After 300 h, very thin scales had grown on the surfaces of the clad metal (Fig. 3a 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 steel such as AL 453 (Ref 6). As a result, the clad metal demonstrated 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. 3a). Microscopically, the interdiffusion resulted in formation of additional phases in the diffusion zone at the interface (Fig. 3b) between AL 453 and Haynes 230. Second phases, such as carbides, were identified along grain boundaries in the Ni-base outer layers. 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.

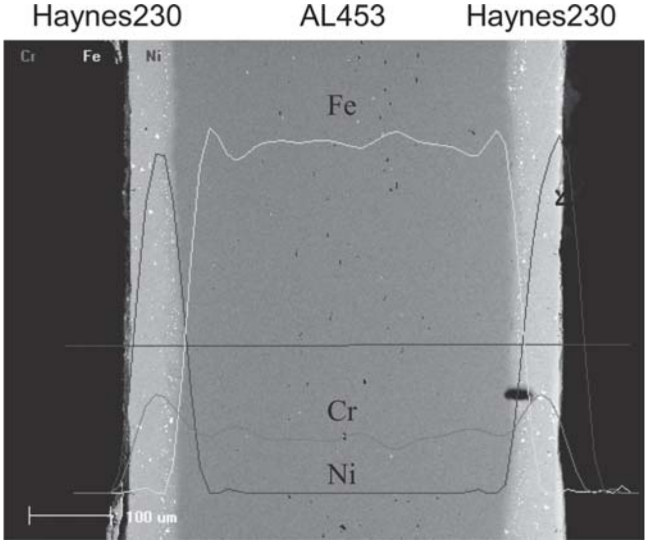

Fig. 2 SEM micrograph and elemental distribution across the cross section of the clad metal system Haynes 230/AL 453/Haynes 230 prepared via roll bonding followed by annealing

The thermal expansion behavior of the three-layer clad metal was also investigated. Figure 4 shows the thermal expansion of the clad metal as a function of temperature, in comparison with those of Haynes 230 and AL 453. At temperatures below ~600 °C, 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 to deviate 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 thermomechanical 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, 28% and 87% reductions, respectively (Ref 10). In contrast, Haynes 230 demonstrates high yield strength that decreases only slightly from 395 MPa at room temperature to 280 MPa at 538 °C and 255 MPa at 760 °C, corresponding to 29% and 35% reductions, respectively (Ref 11). 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. Figure 5 shows the CTE of the clad metal Haynes 230/AL 453/Haynes 230 as a function of temperature. The clad metal demonstrates a CTE at 13.5×10^{-6} from room temperature to 800 °C, compared with 15.3×10^{-6} for Haynes 230 and 12.5×10^{-6} for AL 453 in the same temperature range. The linearity of the thermal expansion of the clad metal is also improved, particularly in comparison with AL 453 in the low-temperature regimen. It is expected that a further decrease in CTE can be achieved by adjusting the thickness of the core and outer layers and also by considering other alloy pairings.

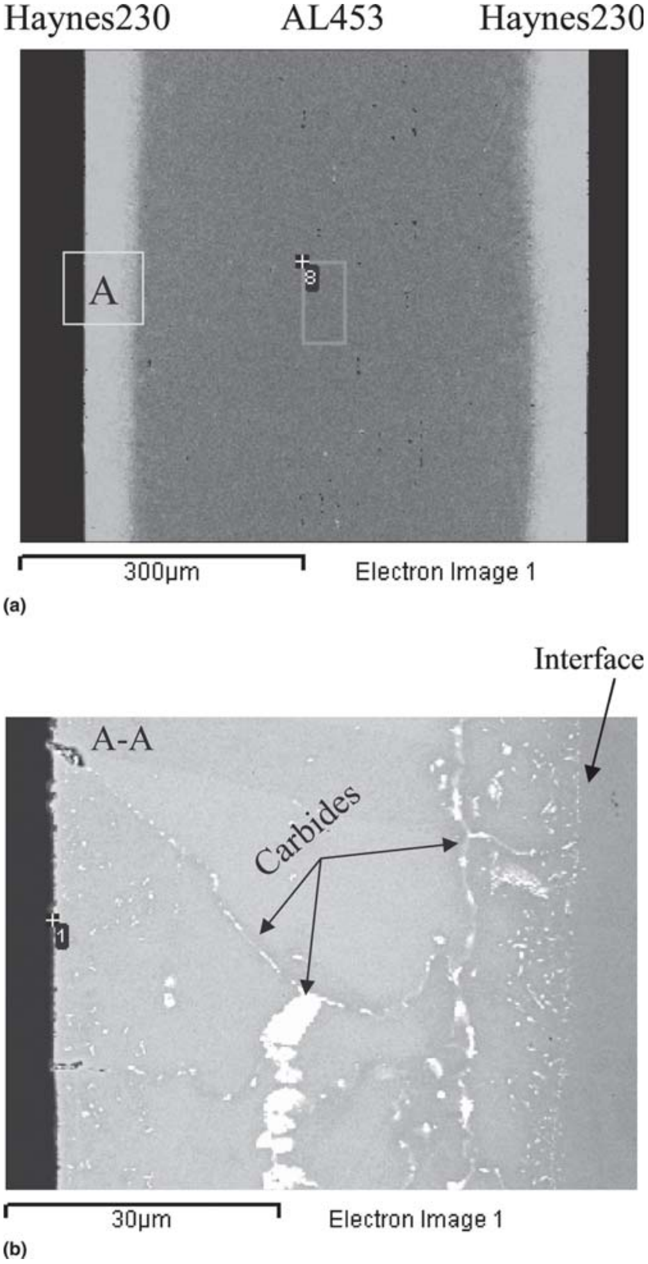

Fig. 3 SEM micrograph of the clad metal system Haynes 230/AL 453/Haynes 230 after heat treatment at 800 °C for 300 h in moist air (~3% H_2O): (a) cross section and (b) an image from area "A" in (a)

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.

4. Conclusions

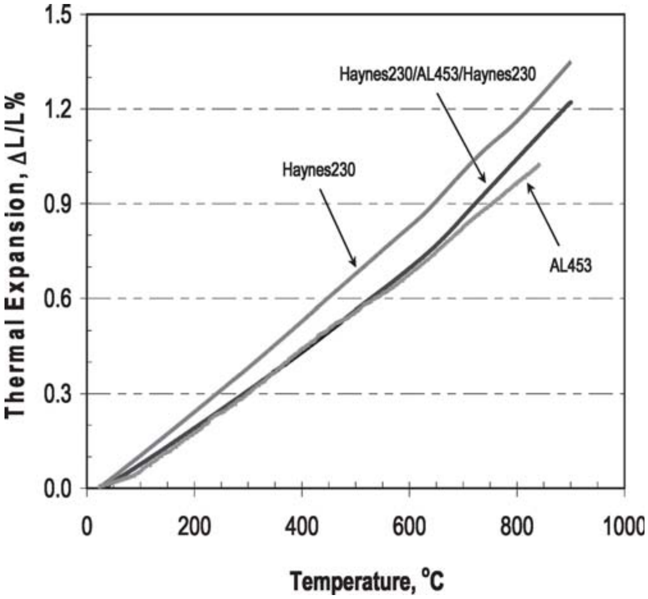

Fig. 4 Thermal expansion of the clad metal system Haynes 230/AL 453/Haynes 230 in air as a function of temperature

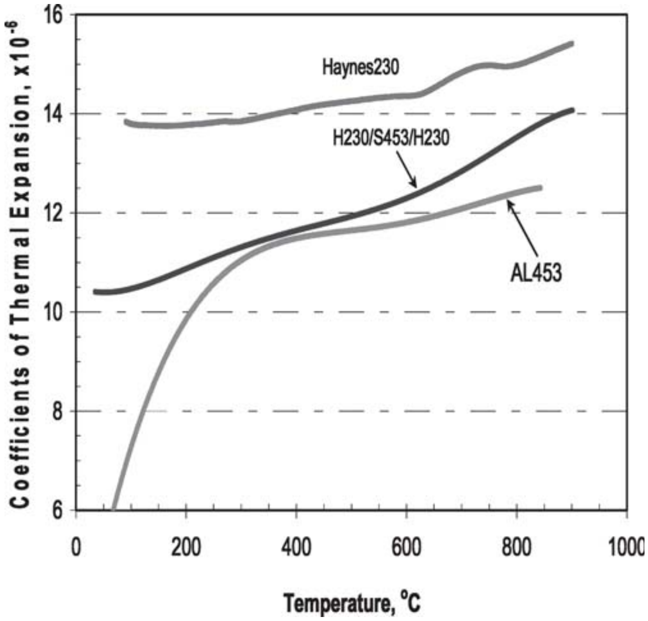

Fig. 5 Coefficients of thermal expansion of the indicated metals in air as a function of temperature

The proof-of-concept work on the clad metallic composite materials indicates that cladding is a viable means of manufacturing layered structures for SOFC interconnect applications. Specifically, the three-layer clad system, composed of a ferritic stainless steel core and symmetrical, thin Ni-base alloy outer layers on each side of the core, 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.

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