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Short communication

Oxidation of Haynes 230 alloy in reduced temperature solid oxide fuel cell environments

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Abstract

Haynes 230 alloy was exposed to reducing and oxidizing environments at 750 °C for 1000 h, simulating the conditions in a reduced temperature solid oxide fuel cell (SOFC). The oxidized specimens were characterized in terms of the oxide morphology, composition and crystal structure. The oxide scale in each environment was identified as Cr_2O_3 with the existence of Cr_2MnO_4. Ni remained metallic in the reducing atmosphere, and NiO was detected in the sample exposed to air. The oxide scale is around 1 μm thick after 1000 h of oxidation in both situations. The area specific resistance (ASR) contributed by the oxide scale is expected less than 0.1 $\Omega\,cm^2$ after 40,000 h of exposure when a parabolic oxide growth rate is assumed, demonstrating the suitability of the interconnect application of this alloy in the reduced temperature SOFCs.

Keywords: Ni-based alloy; Interconnects; Solid oxide fuel cells; Area specific resistance; Oxidation

1. Introduction

Solid oxide fuel cells (SOFCs) offer a high-energy conversion efficiency of fossil fuels to electricity at a low emissions level. With a high operating temperature in the range of 600–1000 °C, the fossil fuels can be directly internally reformed to provide hydrogen to the fuel cell, eliminating the need for an external reformer and allowing increased compactness. Furthermore, rapid kinetics can be achieved with non-precious electrode materials and high quality heat is produced as a byproduct for co-generation.

However, the high temperature of the SOFC places rigorous requirements on its component materials. Among the most critical needs for the commercial deployment of SOFCs are the interconnects, which separate the fuel and oxidant and provide electric connection between the anode and cathode of adjacent cells. Close thermal expansion match to the fuel cell components, sufficient electronic conduction at the operation temperature, good chemical stability in both reducing and oxidizing environments and adequate thermal cyclicability are fundamental requirements. Previously, interconnect materials for SOFCs operated at ∼1000 °C are complex perovskite ceramic oxides, typically, the Sr- or Ca-doped $LaCrO_3$ [1]. However, this ceramic interconnect is mechanically brittle, difficult to manufacture in a large planar form, deforms due to the loss of oxygen at the fuel-side, and represents a significant portion of the product cost in a planar SOFC stack design. Therefore, metallic-type interconnects for planar SOFCs are desirable, offering excellent ductility, higher electronic conductivity, higher heat conductivity, lower cost and flexible fabricability. In turn, significant performance and cost advantage can be realized.

So far, metallic interconnects have not been successfully deployed, since the oxidation of metallic materials forms an electrically insulating surface oxide, leading to undesirable increase in contact electrical resistance. Furthermore, the incompatibility in thermal expansion between the metal-

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lic interconnect and cell component materials (electrolyte and electrodes) causes the interfacial contact breakdown. A Cr-based alloy, Cr–5Fe–1Y_2O_3, manufactured by Plansee Ltd., is a well-known metallic material proposed for planar high-temperature SOFC interconnect. It is a pre-alloyed ODS powder; therefore, material cost is significant. The sintered Cr–5Fe–1Y_2O_3 offers thermal expansion compatibility with stabilized zirconia and excellent oxidation resistance [2], however, rapid electrochemical degradation was observed with this Plansee interconnect. This degradation was found to be related to the evaporation of Cr from the interconnect followed by its deposition on the cathode surface [3].

Recent progress in reduced temperature SOFCs (<800 °C) have provided a valuable opportunity for replacing the ceramic interconnects by metallic alloys. The reduced temperature SOFCs that maintain the cell power density and durability at the same level as those operated at temperatures near 1000 °C are achieved by reducing the thickness of the electrolyte [4,5], and/or by the identification of new electrolytes with improved oxygen ion conductivity [5–8]. High-temperature oxidation-resistant alloys are generally considered to be the candidate materials for reduced temperature SOFC interconnects [9–13]. Such alloys contain Cr and/or Al as the alloying elements to form a protective oxide scale, by preferential oxidation of Cr (Cr_2O_3) or Al (Al_2O_3). Al_2O_3-forming alloys are less interesting for SOFC interconnect application due to the low electrical conductivity of the oxide scale. Studies have focused on the Cr_2O_3-forming alloys, especially the Cr-containing ferritic stainless steels [14–29] with a thermal expansion coefficient in the neighborhood of 12×10^{-6}. Austenitic alloys, such as austenitic stainless steels and superalloys [30,31] have rarely evaluated as an interconnect candidate material due to their relatively high thermal expansion coefficients.

In the present paper, Haynes 230, a Ni-based alloy, was investigated in the SOFC environments. Special attention was given to the oxidation behavior in both oxidizing (cathode) and reducing (anode) atmospheres, including the morphology, thickness, crystal structure, and composition of the oxide scales. The purpose of the present study is to examine the possibility of Haynes 230 for the interconnect application in the reduced temperature SOFCs. Haynes 230 has a mean coefficient of thermal expansion (CTE) 15.2×10^{-6} between 25 and 800 °C [32], which is slightly higher than that of the SOFC cell components ($(10–13) \times 10^{-6}$ [33]), however, the difficulty caused by the minor mismatch in CTEs can be alleviated through the design of the SOFC stack configuration.

2. Experimental procedures

A Ni-based alloy, Haynes 230, with an nominal composition (in wt.%) 57Ni–22Cr–14W–2Mo–0.5Mn–0.4Si–0.3Al–0.10C–0.02La–5Co–3Fe–0.015B, was provided by Liyuan Precision Materials Ltd. Coupon specimens with dimensions of 20 mm × 20 mm × 1 mm were cut by using a Buhler slow diamond saw, and were placed in an atmosphere controlled furnace for oxidation in both oxidizing and reducing environments, respectively, simulating the cathode (air) and anode (humidified H_2) conditions in a reduced temperature SOFC. The oxidation temperature was 750 °C, and the oxidation duration was 1000 h.

Small specimens with dimensions of 5 mm × 5 mm × 1 mm were obtained from the oxidized samples for the observation of the surface morphology of the oxide scales; the samples for the cross-section examination were mounted in a Buhler epoxide and polished on a Buhler automatic polisher. A D/Max-3B X-ray diffractometer was employed to identify the crystal structure of the oxide; a JSM-5510LV scanning electron microscope (SEM) with energy dissipation spectrum (EDS) attachment was used for the oxide scale examination.

3. Results and discussions

3.1. Oxidation in oxidizing (cathode) environment

Fig. 1 shows the typical morphology of the surface oxide scale of Haynes 230 exposed to air at 750 °C for 1000 h, which consists of fine oxide particles and is much more compact than that formed in the SS 430 and other ferritic stainless steels in similar conditions. The EDS result obtained from the surface, shown in Fig. 2, indicates that the oxide scale may contain O, Cr, Mn, Ni and insignificant amount of W and other elements. The electrons penetrated the oxide scale, X-rays might also be generated from the substrate, and therefore, the exact oxide composition cannot be determined in this way. However, compared with the substrate composition, it can be seen that the Cr and Mn contents in the oxide scale are significantly higher than that in the substrate, indicating Cr and Mn outward migrations to the surface and subsequent oxidation. Fig. 3 is a typical cross-section SEM micrograph of the oxidized Haynes 230 exposed to air at 750 °C for 1000 h. It confirms a very thin oxide scale of ∼1 μm. At the oxide scale/substrate interface, no voids and cracks are observed,

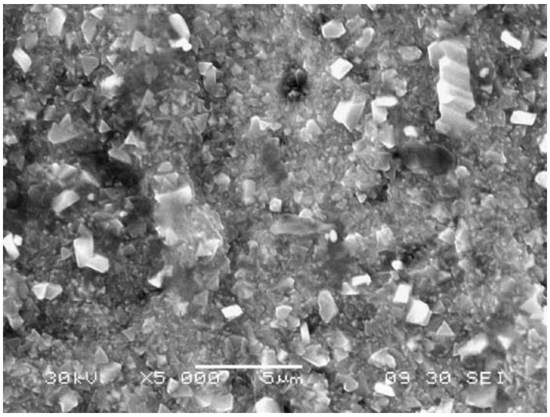

Fig. 1. SEM micrograph of the surface oxide of Haynes 230 exposed to air at 750 °C for 1000 h, showing a dense oxide scale with fine particles.