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Effects of water vapor on oxidation behavior of ferritic stainless steels under solid oxide fuel cell interconnect exposure conditions

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Abstract

The oxidation of ferritic stainless steels has been studied under solid oxide fuel cell (SOFC) interconnect "dual" exposure conditions, i.e., simultaneous exposure to air on one side of the sample, and fuel (hydrogen) on the other. It was found that, under the dual exposures, the oxidation behavior of the stainless steels at the airside differed significantly from that observed during exposure to air at both sides. Increased water vapor partial pressure in the air at the airside further accelerated the anomalous oxidation, resulting in nucleation and growth of hematite in the scale that led to a localized attack. The accelerated oxidation and growth of the hematite nodules was a result of combined effects of hydrogen transport from the fuel side to the airside and the presence of increased water vapor.

Keywords: Oxidation; Stainless steel; Solid oxide fuel cell (SOFC); Interconnect

1. Introduction

Over the past several years, advances in materials and fabrication techniques for planar solid oxide fuel cells (SOFCs) have allowed for a reduction in SOFC operating temperatures (e.g., 650–800 °C) [1–4]. Consequently, the relatively inexpensive ferritic stainless steels that demonstrate a good thermal expansion matching to the ceramic cell components are now considered to be among the most promising candidate materials from which to construct the interconnects in SOFC stacks [5–10]. To function well in the stacks, SOFC interconnects must maintain an excellent stability over thousands of hours in a very challenging "dual" environment, as they are exposed simultaneously to a reducing atmosphere (fuel, such as hydrogen) on one side and an oxidizing atmosphere (air) on the other side. Similar dual exposures can be also found in the SOFC balance of plant and other power systems that use hydrogen as fuel.

The stability (specifically the oxidation and corrosion behavior) of stainless steels in various environments has been extensively investigated in the past for a number of traditional applications [11–15]. Recently, studies focusing on the applicability of ferritic stainless steels for the SOFC interconnect applications have also been carried out and reported [10,16–20]. All of these studies, however, were carried out using single atmosphere exposure conditions (i.e., either an oxidizing or reducing environment), and were presumably based on the implicit assumption that oxide scale growth and oxidation behavior as measured in either an oxidizing or reducing environment will be essentially identical to the scale growth and oxidation occurring on the air or fuel side of the material when it experiences the dual atmosphere exposure conditions characteristic of the SOFC interconnect environment.

However, our recent investigation of ferritic stainless steels under dual atmosphere conditions that have moist hydrogen at one side and air at the other clearly indicates that the oxidation behavior (i.e., scale growth and composition) on the airside differs significantly from the behavior observed when the steels are exposed to air only [21,22]. While no substantial difference was observed between the scales grown on the fuel side of the dual exposure samples and scales grown on samples exposed to the fuel only, it was

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found that the anomalous oxidation behavior of steels on the airside under these dual exposure conditions was highly dependent on the Cr content of the alloy and heating mode. AISI430, with 17% (wt.%) Cr, suffered localized attack via formation of hematite (α-Fe_2O_3) rich nodules on the airside of dual exposure samples. As the chromium content increased to 22% in Crofer22 APU and 27% in E-brite, no hematite phase was found in the scale on the airside, but it was noticed the microstructure as well as composition of the scale grown at the airside could be different from those of the scale grown in air only. The anomalous oxidation behavior of ferritic stainless steels on the airside of dual exposure specimens, and the growth of iron oxides that result from enhanced iron transport in the scale, was attributed to the diffusion of hydrogen through the steel and its subsequent presence in the airside scale. Similar anomalous oxidation behavior was also reported by Ziomek-Moroz et al. [23] for 316L stainless steel under simulated SOFC interconnect environments (moist hydrogen/air dual exposures).

In addition to hydrogen/air dual environments, Nakagawa et al. [24], recently examined the oxidation behavior of ferritic stainless steels in (argon+hydrogen)/air dual environments as well as the steam/air dual environment that simulated boiler tube exposure conditions. Fe_2O_3 formation was found on the top scale grown on the airside and a significantly increased oxidation rate was observed as well, both of which were attributed to hydrogen permeation from the (argon+hydrogen) side or the steam side to the airside of stainless steels.

In the previous dual environment studies, ambient air was used on the airside. To understand the effects of water vapor on the anomalous oxidation behavior of ferritic stainless steels, moist air (air saturated with water vapor, ~3% H_2O) was used instead of ambient air in the current work. This paper reports details of this work and discusses the effects of water vapor on the oxidation behavior of ferritic stainless steels under dual exposure conditions.

2. Experimental

The dual atmosphere study was carried out in a specifically designed apparatus that allows for simultaneous testing of separate alloy coupons in 3 different atmospheres (air, fuel and dual atmosphere) [21]. The material under investigation is Crofer22 APU, a ferritic stainless steel that was developed by Forschungszentrum Julich for SOFC interconnect applications [25] and commercialized by ThyssenKrupp VDM. It has the following nominal composition (wt.%): 22.8 Cr, 0.45 Mn, 0.08 Ti, 0.06 La, 0.005 C, $\leq$0.03 P, $\leq$0.03 S, balance Fe. The dual atmosphere specimen was prepared by sealing a 0.5 mm thick, 25 mm diameter circular disk of Crofer22 APU to the end of an E-brite tube (outside diameter of 25 mm; inside diameter of 20 mm) using BNi-2 braze, an Ni-based braze. The brazing was carried out in a vacuum furnace by heating from room temperature to 1050 °C in 3 h, holding for 0.5 h, and then cooling to 300 °C in 3 h, after which the furnace was turned off and allowed to cool to room temperature. Before brazing, the disk of Crofer22 APU was polished on both sides using 1200 grit SiC sandpaper. The disk was cleaned by ultrasonication in acetone for 10 min and subsequently rinsed with alcohol. After brazing, a helium leak test was performed to assure that the ferritic stainless steel disk was hermetically sealed to the E-brite tube.

After assurance of hermetic sealing, the E-brite tube and the ferritic stainless steel disk were placed in the test-stand, along with the coupons which would be exposed to air only or fuel only. Before starting the heating program, the tube was flushed with helium for 30 min, after which wet hydrogen was introduced at a rate of 5 ml/min. The moist hydrogen (with ~3 vol.% moisture) was prepared by flowing hydrogen through a porous stone water bubbler at room temperature. Air was introduced using a Tetratec AP200 pump. The ambient air was determined to contain ~1% H_2O by the Traceble Hydrometer. Moist air (~3% H_2O) was prepared by flowing ambient air through a porous stone water bubbler at room temperature. The furnace was then heated to 800 °C at 10 °C/min, and held at that temperature for 300 h before cooling down to room temperature. After the test, the sample was removed by cutting out the inner area of circular disk, avoiding the Ni-diffusion zone (from the Ni-based braze) near the edge of the sample. The sample was then ultrasonicated in acetone for 5 min to remove oil contaminants from the cutting process, and subsequently rinsed with alcohol.

The surfaces of the cleaned samples were first analyzed on a Philips XRG-3100 X-ray Generator with Cu K_α radiation and then under a JEOL scanning electron microscope (model 5900LV) equipped with energy-dispersive spectroscopic (EDS) capability at an operating voltage of 20 kV. After surface analysis, the coupon samples were epoxy-mounted, sectioned, polished, and examined under the SEM.

3. Results

3.1. Moist hydrogen/moist air dual environment

Fig. 1 shows the XRD pattern of the scale grown on the airside of the Crofer22 APU coupon that was exposed to moist air at one side and moist hydrogen at the other during an isothermal oxidation at 800 °C for 300 h, in comparison with the pattern of the scale grown on the sample exposed to moist air at both sides during the same thermal history. XRD analysis of either side of the coupon exposed to moist air only revealed the formation of Cr_2O_3 and M_3O_4 (M=Cr, Mn, and/or Fe) spinel. Due to the similar ionic radii of Mn, Cr, and Fe [26], it is difficult to determine the exact composition of the spinel solely based on the positions of the spinel peaks in the XRD pattern.