Variation of Microstructure and Area Specific Resistance with Surface Roughness of a Ferritic Stainless Steel after Long-Term Oxygen Exposure

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Abstract: One of the candidates for metallic interconnects of solid oxide fuel cells is a ferritic stainless steel, Crofer 22 APU. By grinding with different grit SiC grinding paper, Crofer 22 APU specimens with various surface roughness were prepared. The specimens were then thermally cycled by heating them to 1,073 K at a rate of 10 K min⁻¹, holding at 1,073 K for 25 h, and cooling to 298 K at a rate of 10 K min⁻¹. Examinations of the resulting microstructures, measurements of the area specific resistances (ASRs), and analyses of the atomic percentages of elements via energy dispersive X-ray (EDX) spectroscopy were performed. The particle size decreased as the grit number of the grinding paper used to grind the sample surfaces increased. A polished sample exhibited the smallest particle size. Plots of ln (ASR/T) vs. 1/T for the samples ground with grit 80 and grit 400 and the polished sample after 40 thermal cycles exhibited good linearity. At the same measuring temperature, the ASR increased as the surface of the sample became rougher. This suggests that the polished Crofer 22 APU is better than those with rougher surfaces for application as interconnect of SOFC.

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1. INTRODUCTION

Interconnects of a solid oxide fuel cell (SOFC) link cells in series so that the electricity generated by each cell may be combined. An interconnect can be either a metallic or ceramic layer. The interconnect of a solid oxide fuel cell is required to have the following properties; high electronic conductivity (>1 S cm⁻¹) with low ionic conductivity, high chemical stability in both fuel and air, good thermal expansion match to other cell components, high strength and toughness, high thermal conductivity, high chemical stability with regard to other cell components, ease of fabrication to a gas-tight density, the ability to make gas-tight seals with other cell components, and low cost of material [1,2].

As an example, lanthanum chromite, LaCrO₃, is a ceramic interconnect which has high electronic conductivity under fuel and oxidant atmospheres, high stability in the fuel cell environment, and good compatibility with other cell components [3].

Metallic interconnects are feasible and attractive due to the reduction of the cell operating temperature from 1,173~1,273 K down to 873~1,123 K. They have advantages over ceramic interconnects, including lower material and fabrication costs, the possibility of easier and more complex shaping, better electrical and thermal conductivity, and no deformation or failure due to different gas atmospheres across the interconnection. However, oxides form on the metallic interconnects under SOFC operation conditions. The formation of oxides increases the contact resistance and thus decreases the electrical conductivity.

Yang et al. [1] studied the selection and evaluation of heat resistance alloys for SOFC interconnect applications. They reported that ferritic stainless steels with optimized alloy additions are the best candidate materials, chromia-forming alloys need to be either surface or bulk modified, and alumina formers, with better surface stability than the chromia-forming compositions and higher mechanical strength, may find applications in non-conducting stack components.

The oxidation behavior of ferritic stainless steel under SOFC interconnect exposure conditions was investigated by Yang et al. [4]. They reported that an XRD analysis of either side of the coupon, both sides of which were exposed to air during heating, revealed the formation of Cr₂O₃ and M₃O₄ (M = Cr, Mn, and/or Fe) spinel, and that the spinel top layer of the scale on the air side of Crofer 22
Table 1. Chemical composition in wt% of the Crofer 22 APU used in the experiments

<table>
<thead>
<tr>
<th></th>
<th>Cr</th>
<th>Mn</th>
<th>Al</th>
<th>Si</th>
<th>Ni</th>
<th>Ti</th>
<th>V</th>
<th>Co</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crofer 22 APU</td>
<td>23</td>
<td>0.41</td>
<td>0.12</td>
<td>0.1</td>
<td>0.16</td>
<td>0.05</td>
<td>–</td>
<td>–</td>
<td>0.08 La</td>
</tr>
</tbody>
</table>

APU (23 wt% Cr) was enriched in iron during isothermal heating at 1,073 K. Furthermore, increasing both the temperature and thermal cycling accelerated the anomalous oxidation. In addition, they reported that, for ferritic stainless steels with relatively low Cr content, the presence of hydrogen appeared to accelerate iron transport in the scale, leading to enrichment of iron in the scale.

Among the candidates for metallic interconnects, a new ferritic stainless steel, Crofer 22 APU, is an alloy formed by bulk modification with an emphasis in design on both oxidation/corrosion resistance and scale conductivity. Crofer 22 APU was developed by Forschungszentrum Julich of Germany and contains ~23 wt% Cr and small amounts of Mn, Ni, Al, Si, La and Ti.

Works for Crofer 22 APU have been carried out by many researchers [4-17]. However, a few researches [18, 19] have focused on the oxidation behavior of this alloy according to thermal cycling.

In this work, ferritic stainless steel Crofer 22 APU specimens with various surface roughness were prepared by grinding with different grit SiC grinding papers. The samples were then thermally cycled 40 times between 298 K and 1,073 K, resulting in a total oxidation time of 1,000 h at 1,073 K. Variations in microstructure and area specific resistance (ASR) with samples with different surface roughness were studied.

2. EXPERIMENTAL

The chemical composition in wt% of the Crofer 22 APU [17] is listed in Table 1. A Crofer 22 APU plate with a thickness of 0.8 mm was cut into 1 cm × 1 cm squares. Samples with different roughness were prepared by grinding with different grit SiC grinding papers. The specimens were then thermally cycled by heating them to 1,073 K at a rate of 10 K min⁻¹, holding at 1,073 K for 25 h, and cooling to 298 K at a rate of 10 K min⁻¹. The number of thermal cycles, n, for the preparation of the samples was 8, 20, 30, 40, or 120 with the time maintained (oxidation time) at 1,073 K being 200, 500, 750, 1,000, or 3,000 h, respectively.

The surfaces of the prepared samples were examined by cold field emission scanning electron microscopy (FE-SEM) and energy dispersive X-ray spectrometry (EDX, S-4700, Hitachi, Japan).

The electrical resistance of the oxidized samples was measured by a four-probe dc technique (2400 sourcemeter and 2182 nanovoltmeter, Keithley Instruments). A perovskite LaNi₀.₆Fe₀.₄O₃ (LNF) paste was applied between the two oxidized Crofer 22 APU sheets to form a 1 cm² electrode. Two Pt electrical leads were spot welded to the edge of each sheet. The parameters of power and time for spot welding were optimized so as to ensure the formation of a metallurgical bond. The sample assembly was inserted into the furnace, and heated to 873 K for the ASR measurement. ASR measurements were also performed at 923, 973, 1,023, 1,073 and 1,123 K. The inevitable establishment of a thermal gradient between the sample and the voltmeter creates a thermoelectric electromotive force (EMF), which affects the accuracy of low resistance measurements. In order to eliminate errors induced from the thermoelectric EMF, the current reversal technique was employed. The current reversal technique involves measuring the induced voltage in both current directions, computing the corresponding resistance for each direction, and averaging the two measured values.

3. RESULTS AND DISCUSSION

FE-SEM images of the surfaces of Crofer 22 APU samples ground with grit 120 paper after 8, 20, 30, and 40 thermal cycles between 298 K and 1,073 K are shown in Fig. 1 (a)-(d), respectively. As the number of thermal cycles, n, increases from 8 to 20, the particle size increases. The particle sizes of the samples after n=20, 30, and 40 cycles were found to be similar. The ridges that are connected particles are observed in the samples after n=30 and 40. The ridges are in the direction of grinding with emery paper.

Figure 2 shows the SEM images for the surfaces of the Crofer 22 APU samples ground with grit 120 paper after 8, 20, 30, and 40 thermal cycles between 298 K and 1,073 K are shown in Fig. 1 (a)-(d), respectively. The total oxidation times are 200, 500, 750, and 1,000 h at 1,073 K, respectively. The oxide grains are in the form of round scale. The sample subjected to 8 thermal cycles has relatively small particles, and the particle size is quite homogeneous. As the number of thermal cycles, n, increases from 8 to 20, the particle size increases. The particle sizes of the samples after n=20, 30, and 40 cycles were found to be similar. The ridges that are connected particles are observed in the samples after n=30 and 40. The ridges are in the direction of grinding with emery paper.