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Effects of alloy heat treatment on oxidation kinetics and scale morphology for Crofer 22 APU

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HIGHLIGHTS

- Heat treatment gives a reduction in parabolic oxidation constant of up to 3.5×.
- Scales have a continuous Cr_2O_3 layer and a discontinuous $MnCr_2O_4$ spinel layer.
- The proportion and grain size of the spinel increased with alloy heat treatment.
- Nucleation of the Cr_2O_3 and $MnCr_2O_4$ influences the final scale microstructures.
- Larger alloy grain sizes lead to improved oxidation resistance.

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ABSTRACT

The effect of alloy heat treatment on the oxidation kinetics and oxide scale microstructure of Crofer 22 APU has been studied. Parabolic oxidation rate constants were measured for the as-received alloy and after pre-oxidation heat treatment in argon at 1050 °C for 1 and 4 h. The oxide scale microstructure was investigated using scanning electron microscopy, focused ion beam milling and transmission electron microscopy. It was found that the alloy forms a two-layer scale with a continuous chromia layer and a discontinuous $MnCr_2O_4$ overlayer. Two forms of internal oxides were also formed: subscale pockets of spinel and isolated TiO_x precipitates in the underlying alloy. The pre-oxidation heat treatment had a profound effect on the grain size and morphology of the Cr_2O_3 and $MnCr_2O_4$ layers in the scale. The heat-treated samples exhibit a 3.5× lower parabolic oxidation rate constant than the as-received Crofer 22 APU. This improvement in oxidation resistance is attributed to the dramatic differences in the morphology of the oxide scale that forms during the earliest stages of oxidation (<5 h). The implications of these findings for oxidation mechanisms and long-term SOFC performance are discussed.

1. Introduction

Solid Oxide Fuel Cells (SOFCs) are an attractive option for power generation due to their excellent system efficiencies and fuel flexibility. Recent improvements in electrolyte materials have decreased the operating temperatures for SOFCs to between 650 and 800 °C, which enables metallic interconnects to be used in place of the traditional ceramic interconnect materials. Ferritic stainless steels and Ni-base alloys are currently regarded as the most promising materials for these metallic interconnects due to the semiconducting properties of their native chromia (Cr_2O_3) scales. Unfortunately, such chromia scales can be oxidized further on the cathode side of SOFCs leading to the formation of volatile hexavalent chromium species that can redeposit onto the ceramic cathode causing poisoning [1–3]. Thus, SOFC interconnect alloys typically require protective coatings to suppress the formation of these volatile chromium species [4,5].

Crofer 22 APU (ThyssenKrupp AG, Germany) is a ferritic stainless steel developed specifically for SOFC interconnect applications [6]. The composition limits for the alloy are given in Table 1; the Mn is intended to promote the formation of a $(Mn,Cr)_3O_4$ spinel overlayer on top of the chromia scale and thus to obviate the need for a protective coating. Yang et al. measured an oxidation rate constant (k_g) of 8.0×10^{-14} g^2 cm^{-4} s^{-1} for Crofer 22 APU oxidized in air at 800 °C [7], and this falls within the range of rate constants reported for ferritic stainless steels in a review by Fergus [8]. Unfortunately, this oxidation rate is not sufficiently low to enable uncoated Crofer 22 APU interconnects to meet the current 40,000 h SOFC lifetime

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Table 1
Composition specification for Crofer 22 APU. All values are in wt.%.

	Cr	Fe	C	Mn	Si	Cu	Al	S	P	Ti	La
min	20.0			0.30						0.03	0.04
max	24.0	Bal.	0.03	0.80	0.50	0.50	0.50	0.02	0.05	0.20	0.20

requirement. Life prediction models based on thermal expansion and residual stress calculations performed by Liu et al. indicated that the maximum allowable oxide scale thickness to avoid oxide spallation is around 11 μm [9]. Using the oxidation rate constant measured by Yang et al., this would imply that scale formed on Crofer 22 APU would become mechanically unstable after less than 5000 h exposure. Moreover, SOFC tests performed by Stanislowski et al. using bare Crofer showed a performance degradation rate of 21%/1000 h [2]; this rate is two orders of magnitude higher than the value that can be tolerated for long-term SOFC applications. Thus, as for all other SOFC interconnect alloys, Crofer 22 APU requires a protective coating both to retard the oxidation rate and to prevent the egress of volatile chromium species. The requirements for such coatings are rather stringent. They must be: electrically conductive, oxidation resistant, and have minimal open porosity. The most successful coatings to date have been based on manganese cobaltite ($(Mn,Co)_3O_4$- MCO). The MCO composition that has received most attention is $Mn_{1.5}Co_{1.5}O_4$, which exhibits electrical conductivities of >60 S cm^{-1} at 800 °C [10].

In recent work by the present authors [11] $Mn_{1.5}Co_{1.5}O_4$ coatings were applied to Crofer 22 APU samples using the slurry coating process described by Yang et al. [10]. The coated samples were oxidized at 800 °C in air for times of up to 1000 h and the microstructures of the as-deposited and the oxidized coatings were analyzed by cross-sectional transmission electron microscopy (TEM). It was shown that a complex series of spinel reaction products developed between the MCO coating and the Crofer substrate; these included $(Mn, Co, Cr, Fe)_3O_4$ layers between the chromia and the MCO and pockets of stoichiometric $MnCr_2O_4$ at the chromia/alloy interface. These reaction products could have important consequences for the degradation of MCO-coated Crofer interconnects during long-term service in SOFCs, but a full elucidation of these phenomena will require a more detailed understanding of the basic oxidation characteristics for Crofer 22 APU than is currently available in the literature.

In previous oxidation studies it has been shown that a two-layer scale forms on Crofer 22 APU. This microstructure comprises a compact Cr_2O_3 layer on the metallic substrate and an outer $(Mn,Cr)_3O_4$ spinel phase on top of the Cr_2O_3, as intended by the alloy designers. An XRD study of scale development on Crofer 22 APU at 800 °C by Yang et al. showed that both Cr_2O_3 and $(Mn,Cr)_3O_4$ formed after only 2 h of exposure in air [12]. The same two oxidation products have also been reported as being stable in dual atmosphere (moist H_2/air) [13] and in SO_2 containing atmospheres [14]. While there have been several published oxidation studies on Crofer 22 APU, to our knowledge there have been no investigations on the effects of alloy microstructure on oxidation kinetics and scale morphology.

In this paper, we describe a study of the microstructure in the oxide scale formed on Crofer 22 APU in static air at 800 °C. Crofer samples were used in both the as-received (cold-worked and recovered) condition and after pre-oxidation heat treatment to modify the grain size. It is well known that alloy grain boundaries can act as rapid diffusion paths for both anions and cations, and so the starting alloy grain size could have a profound influence on the nucleation and growth of the native oxide scale. However, it is not clear what this effect will be: in some chromia-forming steels a smaller alloy grain size leads to improved oxidation resistance (e.g. Ref. [15]), whereas in others the opposite trend is observed (e.g. Ref. [16]). Here we show that a larger grain size leads to a dramatic reduction in the oxidation rate for Crofer 22 APU and that this is accompanied by changes in the character and morphology of the oxide scale. These observations are used to deduce the role that grain boundary diffusion plays in oxide scale development and to provide a useful baseline for comparison with the microstructures in the oxide scales of coated Crofer 22 APU samples.

2. Experimental

Square coupons (25 mm × 25 mm) were cut from 0.5 mm thick Crofer 22 APU commercial sheet stock. Some of the coupons were heat-treated in a tube furnace under flowing argon for either 1 h or 4 h at 1050 °C to modify the initial alloy grain size. This gave three starting conditions for the subsequent oxidation experiments: as-received (AR), heat-treated for 1 h (HT1h) and heat-treated for 4 h (HT4h). The surfaces of all of the coupons were then prepared by first mechanically grinding with 600 and 1200 grit SiC, followed by polishing with 6 μm and then 1 μm diamond slurry to obtain a mirror finish.

The oxidation behavior of the samples was evaluated by thermogravimetric analysis. First, the dimensions of each coupon were measured precisely to establish the starting surface area. Triplicate samples for each of the three starting conditions were mounted in a slotted alumina d-tube so that the samples were standing upright. Oxidation tests were performed in a tube furnace at 800 °C in static laboratory air for up to 750 h. Samples were cooled periodically, removed from the furnace, and weighed using an AT261 Delta Range balance, which has a precision of 0.01 mg.

The effects of pre-oxidation heat treatment and of thermal exposure during oxidation were evaluated by optical microscopy. Cross-sections through the alloy coupons were prepared using standard metallographic techniques and then etched with oxalic acid to reveal the grain boundaries. Grain diameter measurements were taken from optical microscope images using Image Pro Plus 7 image analysis software. The boundary of each grain was traced in the software and the mean diameter tool was used to obtain the average value of diameters drawn through the grain centroid to the points of intersection on the perimeter in 5° increments for each traced grain. The effects of thermal exposure on the room-temperature hardness of the alloy were evaluated by obtaining Vickers microhardness measurements from the metallographic cross-sections using a 500 g load.

One coupon from each heat treatment condition was used for microstructural analysis of the oxide scale. X-ray diffractometry (XRD) was performed using an INEL diffractometer with a solid state Curved Position Sensitive Detector (CPSD), which collects data simultaneously over a 2θ range of 20–140°. The oxidized coupons were mounted flat and scanned for a total of 60 min using a 30 kV Cu K-α source. The data was analyzed using whole pattern fitting with JADE analysis software. Secondary electron (SE) and backscattered electron (BSE) scanning electron microscopy (SEM) images and Energy Dispersive X-ray Spectrometry (EDXS) analyses of the oxide scales formed were obtained in an FEI Helios 600 Dual Beam focused ion beam (FIB) apparatus equipped with a retractable, low kV, segmented BSE detector and an Oxford 80 mm^2 XMax^N Silicon Drift EDXS detector.

Site selective cross-sectional sample preparation for transmission electron microscopy (TEM) was performed using a FEI Strata 400 Dual Beam FIB apparatus equipped with a flip stage for improved final thinning. Firstly, Pt was deposited *in situ* as a capping layer to protect the original surface of the oxide scale. Rough trench milling was performed at an accelerating voltage of 30 kV with a 2.8 nA ion beam current. Samples were lifted out in