

Studies of Scale Formation and Kinetics of Crofer 22 APU and Haynes 230 in Carbon Oxide-containing Environment for SOFC Applications

M. Ziomek-Moroz, B. Covino, Jr., G. Holcomb, S. Bullard, L. Penner

U.S. Department of Energy, National Energy Technology Laboratory, Albany, OR

Introduction

Significant progress in reducing the operating temperature of SOFCs below 800°C may allow the use of chromia-forming metallic interconnects at a substantial cost savings. Hydrogen is the main fuel for all types of fuel cells except direct methanol fuel cells. Hydrogen can be generated from fossil fuels, including coal, natural gas, diesel, gasoline, other hydrocarbons, and oxygenates (e.g., methanol, ethanol, butanol, etc.). Carbon oxides present in the hydrogen fuel can cause significant performance problems due to carbon formation (coking).

Also, literature data indicate that in CO/CO₂ gaseous environments, metallic materials that gain their corrosion resistance due to formation of Cr₂O₃, could form stable chromium carbides.¹ The chromium carbide formation causes depletion of chromium in these alloys. If the carbides oxidize, they form non-protective scales.²

Considering a potential detrimental effect of carbon oxides on iron- and nickel- base alloy stability, determining corrosion performance of metallic interconnect candidates in carbon oxide-containing environments at SOFC operating temperatures is a must. In this research, the corrosion behavior of Crofer 22 APU and Haynes 230 was studied in a CO-rich atmosphere at 750°C. Chemical composition of the gaseous environment at the outlet was determined using gas chromatography (GC). After 800 h of exposure to the gaseous environment the surfaces of the corroded samples were studied by scanning electron microscopy (SEM) equipped with microanalytical capabilities. X-ray diffraction (XRD) analysis was also used in this study.

Experimental

The composition (wt%) of the alloys studied are shown below:

Alloy	Mo	Ni	Fe	Mn	Cr	Al	W	Ti	La
Crofer 22 APU	0.002	0.32	Bal.	0.45	22.33	0.13	<0.001	0.1	0.1
Haynes 230	1.32	Bal.	0.74	0.49	22.32	0.42	14.53	0.025	ND

Corrosion experiments were conducted on flat samples in CO-rich atmosphere at 750°C. An example of the chemical composition of the outlet gas determined by GC is shown below:

CO	CO ₂	O ₂	H ₂
92.1mol%	7.3x10 ⁻² mol%	7.81mol%	2.8x10 ⁻³ mol%

The heating and cooling cycles were repeated several times during the 2000 h exposure. One sample out of a 12 sample set of each material was removed after 800 h for the surface studies. X-ray diffraction (XRD) was used to identify possible phases present in the scale and scanning electron microscopy (SEM) was used to determine microstructure and topography of the oxide scales.

Results and Discussion

The results of the gravimetric experiments for the experimental Haynes 230 and Crofer 22 APU in CO-rich 750°C, plotted as (mass change/area)² versus oxidation time, are shown in Figure 1. The plots are non-linear for both materials indicating that the materials do not obey the parabolic rate law of oxidation.

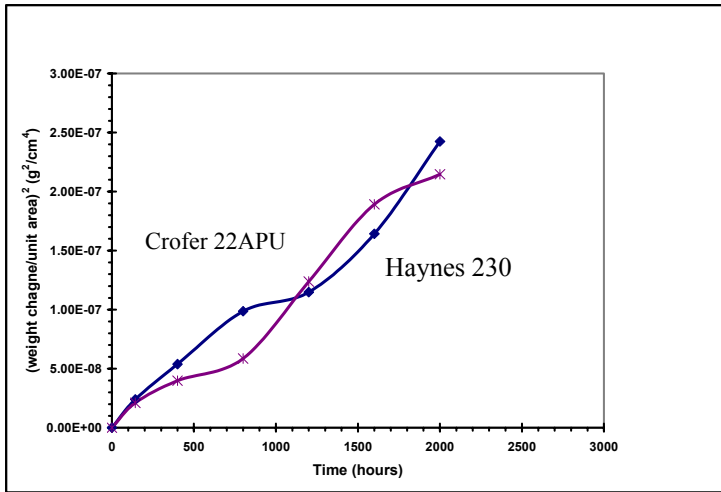


Fig. 1. $(\text{Mass change/area})^2$ versus exposure time for samples oxidized in CO at 750°C.

Figure 2 shows an SEM (secondary electrons) micrograph of the scale formed on the Haynes 230 sample exposed to the CO atmosphere for 800 h at 750°C.

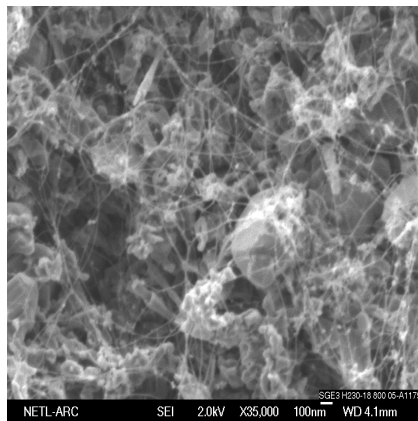


Fig. 2. SEM (backscattered electron) micrograph of Haynes 230 after exposure to CO for 800h at 750°C.

The surface is covered with coarse and fine grains connected by thin carbon filaments. Similar filaments were observed on other metallic materials exposed to carbon oxide-containing atmospheres.²⁻⁴ The crystalline phases determined by XRD in the scale formed are a MCr_2O_4 -like phase and $(\text{Cr, Fe})_2\text{O}_3$ -like phase. In addition to XRD, the energy dispersive spectroscopy (EDS) analysis was performed in different locations of the sample surface. In some areas, high concentrations of carbon (~31at%) were detected along with chromium (~39 at%) and oxygen (~27at%). This indicates carbon deposition onto chromium oxide. In other areas, low concentrations of carbon (~5-7 at%) in comparison to high concentrations of Cr (42at.%) and oxygen (~49at%). Examples of the elemental distributions of carbon, oxygen, and oxygen in the scale by EDS are shown in Figure 3.

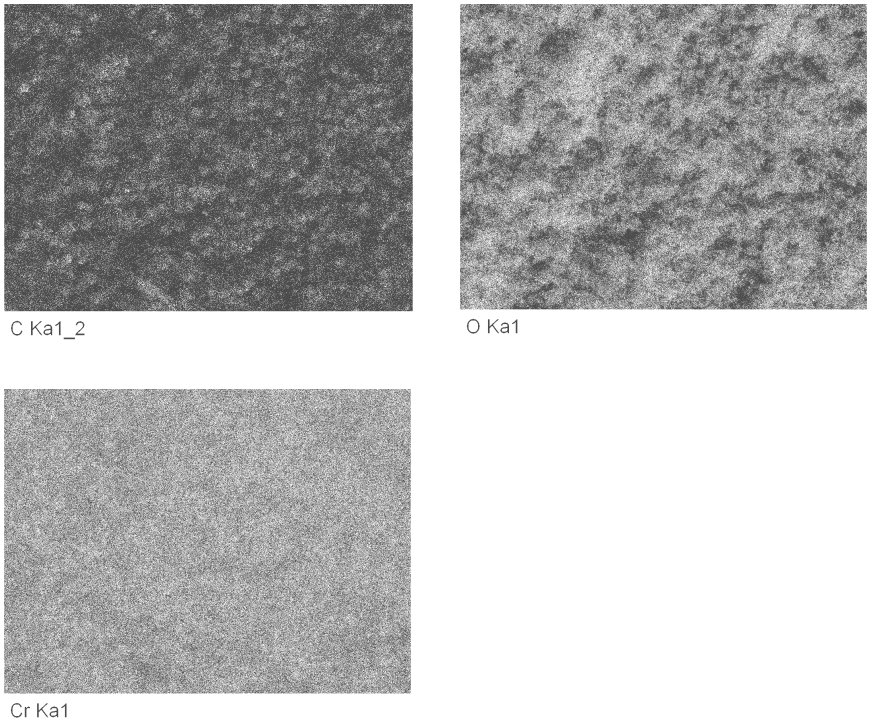


Fig. 3. EDS maps of carbon, oxygen, and chromium for scale formed on Haynes 230 during exposure to CO environment for 800h at 750°C.

Figure 4 shows an SEM micrograph of the scale formed on the Crofer 22 APU sample exposed to the CO atmosphere for 800 h at 750°C. The surface is covered with sponge-like grains. Some coarse grain, few nodules and carbon filaments, are also present in the scale.

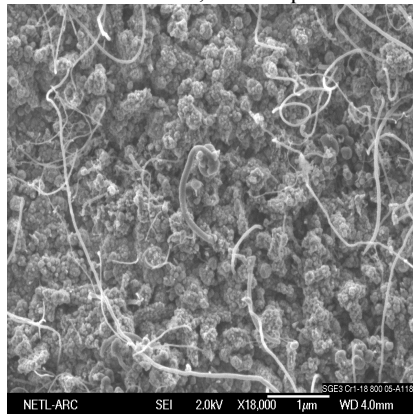


Fig. 4. SEM (secondary electron) micrograph of Crofer 22 APU after exposure to CO for 800h at 750°C.

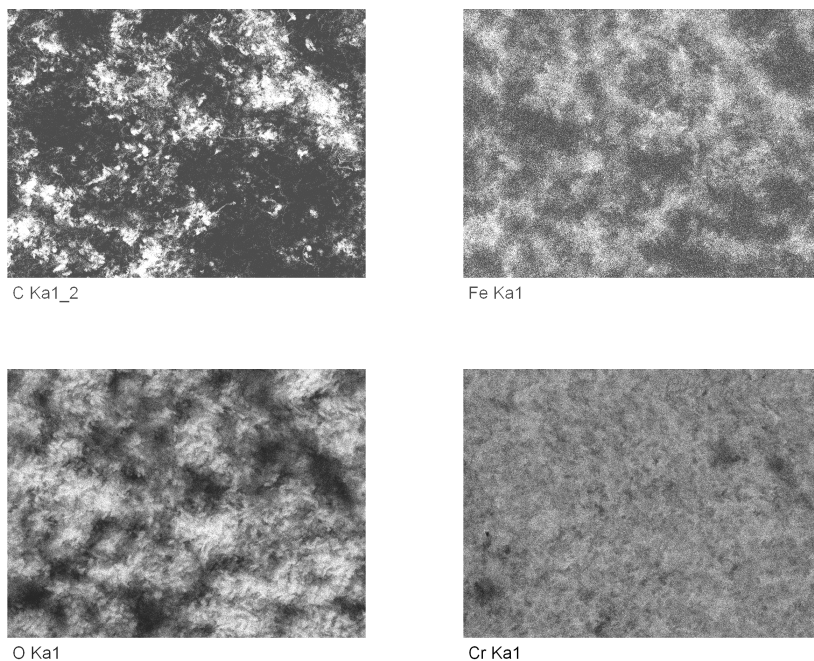


Fig. 5 EDS maps of carbon, iron, oxygen, and chromium for scale formed on Crofer 22 APU during exposure to CO environment for 800h at 750°C.

The crystalline phases determined by XRD are FeCr_2O_4 -like phase, Cr_2O_3 -like phase, and some traces of Cr_7C_3 -like phase. The X-ray maps for carbon, chromium, iron, and oxygen shown in Figure 5, indicate non-uniform carbon, iron, and oxygen distribution. Although some areas of the Fe X-ray map overlap with some areas of the C x-ray map, the presence of Fe_3C was not detected.

Conclusions

Based on the kinetic results, in CO Haynes 230, and Crofer 22 APU do not obey the parabolic rate law of oxidation.

SEM investigations of the Haynes 230 and Crofer 22 APU after exposure to the CO environment for 800 h at 750 °C revealed the presence of carbon filaments.

Cr_7C_3 -like phase was found in the scale formed on the Crofer 22 APU sample.

References

1. S. Mrowiec and T. Werber, Gas Corrosion of Metals, The Foreign Scientific Publications Department of the National Center for Scientific, Technical and Economic Information, for the National Bureau of Standards and the National Science Foundation, Washington, D.C., Warsaw, Poland 1978.
2. M. Ziomek-Moroz, et al. CORROSION 2006, paper 06480.
3. C.H. Toh, P.R. Munroe, D.J. Young and K. Fogar, Materials at High Temperatures, Vol. 20, 2003, p. 129.
4. Z. Zeng, K. Natesan, Solid State Ionics, Vol. 167, 2004), p.9.
5. Z. Zeng, K. Natesan, Chem. Mater., Vol. 17, 2005, p.3794.