Journal of Power Sources 183 (2008) 247–252

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Conducting oxide formation and mechanical endurance of potential solid-oxide fuel cell interconnects in coal syngas environment

Kejia Liu [a,b], Junhang Luo [b], Chris Johnson [c], Xingbo Liu [d], J. Yang [a], Scott X. Mao [b,*]

[a] Shanghai Institute of Technology, Shanghai 200233, China
[b] Department of Mechanical Engineering and Materials Science, University of Pittsburgh, Pittsburgh, PA 15213, United States
[c] National Energy Technology Laboratory, Morgantown, WV 26507, United States
[d] Department of Mechanical and Aerospace Engineering, West Virginia University, Morgantown, WV 26506, United States

ARTICLE INFO

Article history:
Received 5 March 2008
Received in revised form 3 April 2008
Accepted 4 April 2008
Available online 20 April 2008

Keywords:
SOFC
Metallic interconnects
Spinel
Oxides
Metal dusting
High-temperature alloys

ABSTRACT

The oxidation properties of potential SOFCs materials Crofer 22 APU, Ebrite and Haynes 230 exposed in coal syngas at 800 °C for 100 h were studied. The phases and surface morphology of the oxide scales were characterized by X-ray diffraction, scanning electron microscopy and energy-dispersive X-ray analysis (EDX). The mechanical endurance and electrical resistance of the conducting oxides were characterized by indentation and electrical impedance, respectively. It was found that the syngas exposure caused the alloys to form porous oxide scales, which increased the electrical resistant and decreased the mechanical stability. As for short-term exposure in syngas, neither carbide nor metal dusting was found in the scales of all samples.

1. Introduction

Solid-oxide fuel cells (SOFCs) are electrochemical reactors that convert the chemical energy of the fuel to electrical energy. SOFCs represent the most efficient way to generate electricity from a variety of fuels, such as hydrogen, methane, syngas and other kind of fuel gases due to their operating temperature range of 500–1000 °C [1,2]. One of the most important technical challenges for SOFC is the design of interconnects. Three most important criteria for the SOFC interconnect materials are high electrical conductivity, good stability in both reducing and oxidizing atmospheres at SOFC operating temperature, and close match in coefficient of thermal expansion with other SOFC components.

Metallic interconnects for SOFC offer a large cost advantage over previously used ceramic materials, and thus research on metallic interconnects for SOFCs has attracted considerable attention [2,3]. The metallic interconnect, however, works in a dual-gas environment, i.e., at the cathode side it is exposed to air, and at the anode side it is exposed to various fuel gases at temperature around 800 °C. Moreover, one of the catastrophic carburization phenomena, "metal dusting", might occur at the anode side in an atmosphere containing fuel gas with high carbon activity.

Iron and chromium-based alloys, which are protected by chromia Cr_2O_3-based oxidation scales, are candidate materials for the metallic interconnect of SOFC since Cr_2O_3 shows higher electrical conductivity than that of Al_2O_3 and SiO_2 scales. There are many kinds of fuel gases can be used in SOFC, and their corrosion effect on interconnects depends on the composition of the gas and on other factors, such as temperature and pressure, etc. The fuel gas can be pure hydrogen, but coal syngas represents a more economical option. Coal syngas consists primarily of hydrogen and CO but can contain significant water vapor and some levels of CO_2, H_2S and other minority species. The specific composition depends on the gasification process method as well as the specific coal that is gasified. A typical syngas process with water–coal slurry system contains 15–27.6 vol.% of H_2O, while for a dry fed gasifier the water vapor content is only about 2% water vapor [4]. Corrosion in syngas for metallic interconnect will be different from that in air, and will depend on the specific fuel gas used. Most studies on the scale growth of chromia forming alloys have been carried out under an air environment, only a few studies have examined the oxidation behavior under reducing conditions (some of them see [5–7]). The effect of water vapor on the growth of chromia scales has also been attracting increased attention [8–11]. However, many of these studies only examined the effect of water vapor in air or in oxygen on

* Corresponding author. Tel.: +1 412 624 9602; fax: +1 412 624 4846.
E-mail address: smao@engr.pitt.edu (S.X. Mao).

0378-7753/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jpowsour.2008.04.025

Table 1
Composition (in wt%) of alloys selected for experiments

Alloys	Cr	Fe	Ni	C	Mn	Si	Al	Ti	Cu	Others
Crofer	24	73.2	–	.03	.8	.50	.50	.2	.50	S .02, P 0.05, La .2
Ebrite	26.3	71.86	0.15	–	.1	.21	.05	.05	.05	Mo 1.01, P .01, Cd .12
Haynes 230	22	3	52.7	.1	.5	.4	.3			Co 5, W 14, Mo 2, B .15

the growth of chromia scales but few in the practically used coal syngas.

Whether alloys are attacked by oxidizing and/or metal dusting in carbonaceous gases depends on many factors of the environment. Many works studied dry fuel gases and found metal dusting appeared and even pits formed on the surface of the alloys. However, little research deals with corrosion in wet coal syngas. In this paper, we tested a number of prospective high-temperature alloys in the syngas containing as much as 27.6 vol.% water vapor, simulating the wet coal syngas of the SOFC environment. Although interconnects are expected to have a lifetime of 40,000 h, the samples just tested for 100 h. We expect these experiments can serve as a baseline for further long-term test, as well as reveal the factors affecting the initial steps in scale formation.

2. Experimental procedures

2.1. Materials preparation and syngas composition

Two iron-based and one nickel-based alloys, Crofer 22 APU, Ebrite and Haynes 230 were obtained in sheet form. The nominal compositions of the three alloys were listed in Table 1. Both Crofer and Ebrite are ferritic alloys, whereas Haynes 230 is a nickel-based alloy with high Cr and W.

Rectangular samples of 10 mm × 10 mm × (1–2) mm were cut from the sheets of the three alloys. Each sample was ground up to 800 grits with SiC sand paper, ultrasonically cleaned in acetone, and then dried for further evaluation.

Coal syngas corrosion was conducted in a horizontal furnace. Specimens were put in an alumina boat and exposed to a flowing carburizing atmosphere at 800 °C. The gas was simulation of a reformer outlet one, the compositions were (in vol.%) $29.1CO + 28.5H_2 + 11.8CO_2 + 27.6H_2O + 2.1N_2 + 0.01CH_4$, and also contained 100 ppm H_2S. This was the typical product of one kind of gasifier, the entrained flow one [4].

In order to compare the corrosion effect of the syngas with that of air, other non-syngas treated samples of Crofer were also prepared, one was isothermally treated in the flowing air at 800 °C with 24 h, i.e., the pre-oxidized sample, another one was a the pre-oxidized Crofer sample isothermally exposed in flowing air, and again for an additional 100 h in the syngas mixture. The aim of these samples was to study if the pre-treatment was able to stabilize the alloys.

2.2. Isothermal exposure tests and scale analysis

The isothermal exposure in coal syngas of the four samples were carried out in a continuous exposure at 800 °C for 100 h in the flowing coal syngas with a flow rate of 6 ml min^{-1}.

After isothermally exposure in the syngas, the compositions of the scales formed on the surface of the samples were identi-

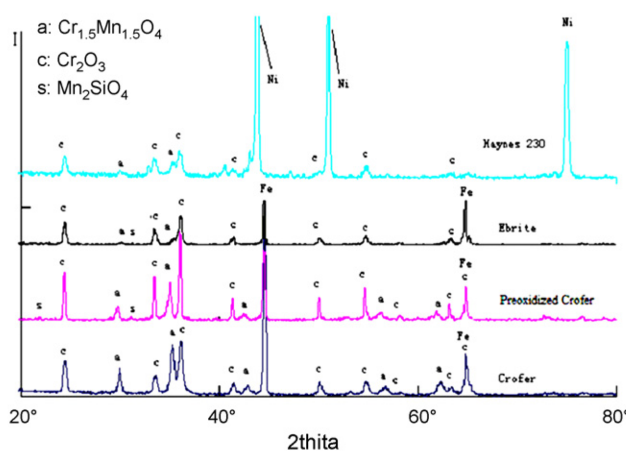

Fig. 2. XRD patterns of Crofer, pre-oxidized Crofer, Ebrite and Haynes 230 samples.

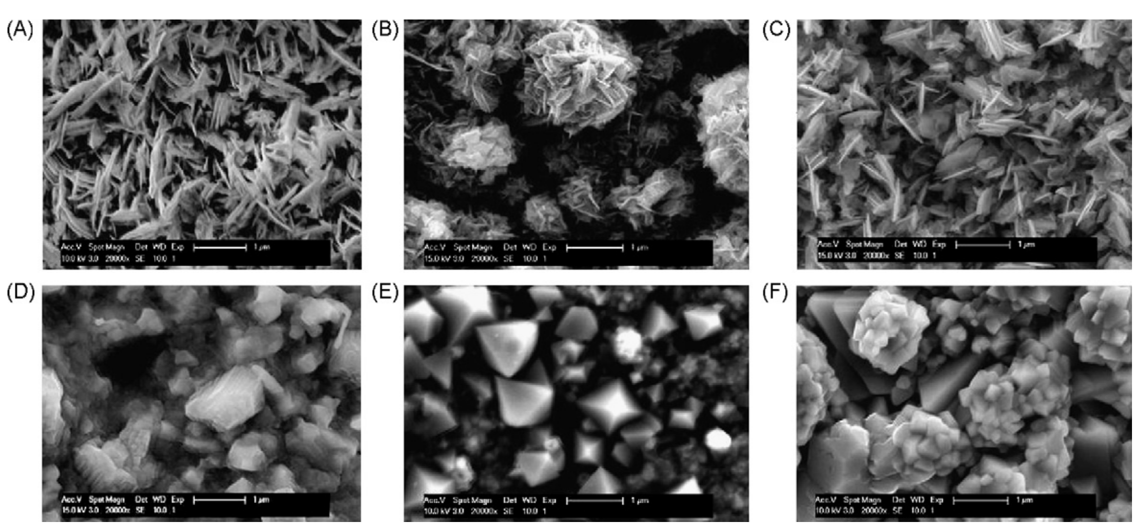

Fig. 1. SEM micrograph of surface of Crofer (A), Ebrite (B) and Haynes 230 (C), pre-oxidized Crofer after exposed to coal syngas at 800 °C for 100 h (D), Crofer exposed in air (800 °C) for 24 h (E) and Crofer in air 124 h (F).

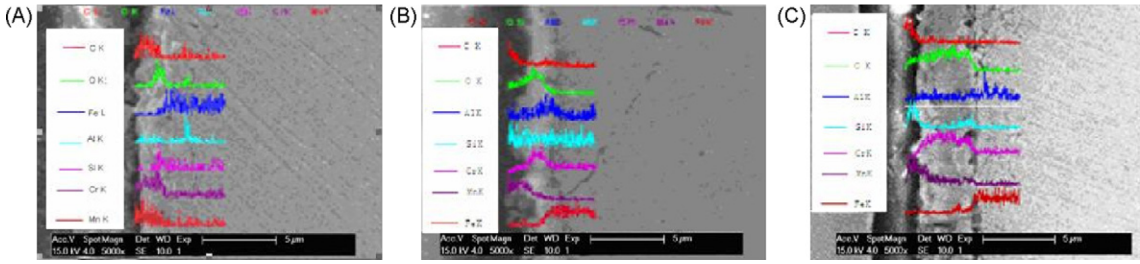

Fig. 3. Cross-sections and EDX line scanning results of Crofers samples of Syngas 100 h at 800 °C (A), the air treated 124 h at 800 °C (B), and pre-oxidized plus syngas exposure sample(C).

fied with X-ray diffraction (XRD). The surface morphologies and cross-section structure were studied by scanning electron microscope (SEM), and the chemical composition and element distribution in the scales were analyzed by energy-dispersive X-ray analysis (EDX). The samples were also tested using impedance measurements and an indentation test, the former was performed in room temperature (20 °C) with the equipment of the Potentiostat EIS 300 system, a product of Gamry instruments, and the latter, the indentation on the conducting oxide layers was carried out by using a Rockwell hardness tester with 60 kg load.

3. Results and discussion

3.1. Morphology and phase characterize for syngas exposure samples

SEM micrographs of the interconnect samples exposed only in coal syngas for 100 h were shown in Fig. 1A–C. The morphology of Crofer, Ebrite and Haynes 230 (cf. Fig. 1A–C) had whiskers or ridges-like surface grains. The morphology of Crofer consisted of uniformly distributed whiskers or ridges, while in the Ebrite and Haynes 230 samples larger nodules were present, and each of the nodules was made up of the same tiny whisker structures. The size of the wiskers was ∼1 μm in length and 0.1 μm thick on the nodulous surfaces.

The morphology of pre-oxidized Crofer before syngas exposure was shown in Fig. 1E, were the typical pyramid-like grains of the spinel were present. After syngas exposure, its morphology had only a small change (Fig. 1D), and the surface grains were still pyramid-like with a size of 0.2–1 *μm,* but with a somewhat less-defined appearance.

The sample exposed first for 24 h at 800 °C followed by 100 additional hours at 800 °C in air (cf. Fig. 1F) showed clusters of small pyramid-like grains grown on each big grain. Comparison with Fig. 1A–C, one can find that the air exposure samples shown in Fig. 1D–F were significantly different in morphology from those formed in syngas. The former had the pyramid-like grains, while the latter had the whiskers or ridges-like grains.

XRD patterns of scales on Crofer, pre-oxidized Crofer, Ebrite and Hynes 230 after syngas exposure were shown in Fig. 2. The main phases of the four samples were chromia (Cr_2O_3), spinel ($Cr_{1.5}Mn_{1.5}O_4$) and the substrate (α-Fe for iron-based or Ni for nickel-based) of the alloys. Both Ebrite and Haynes 230 samples had very strong substrate peaks (lines) and relatively weak spinel lines, indicating the oxide scales on them were thin and the main phase on the both of the scales was Cr_2O_3, and the spinel phase not present or only present as a minority phase.

In both pre-oxidized and non-pre-oxidized Crofer samples, both chromia and spinel were indicated by XRD analysis. The spinel

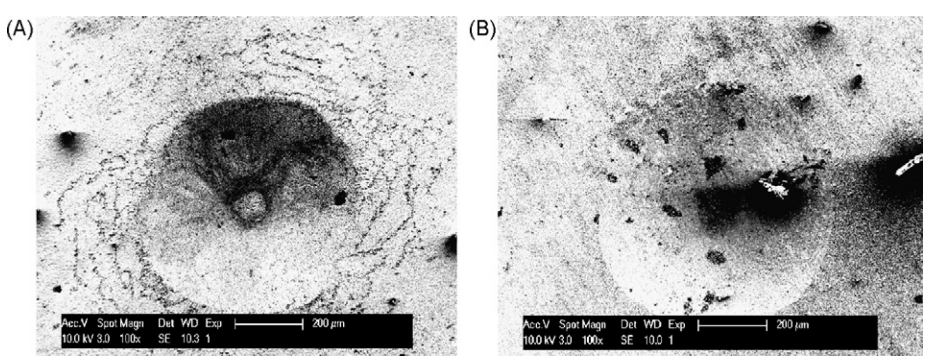

Fig. 4. Indentation for syngas exposed Crofer sample (A), and air exposed Crofer sample (B) after indentation with a load of 60 kg.

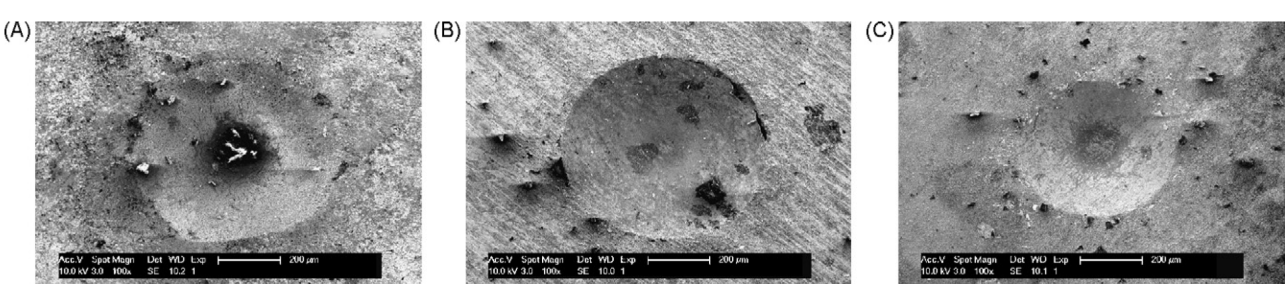

Fig. 5. SEM micrograph of pre-oxidized Crofer (A), Ebrite (B) and Haynes 230 (C) after indentation with a load of 60 kg.

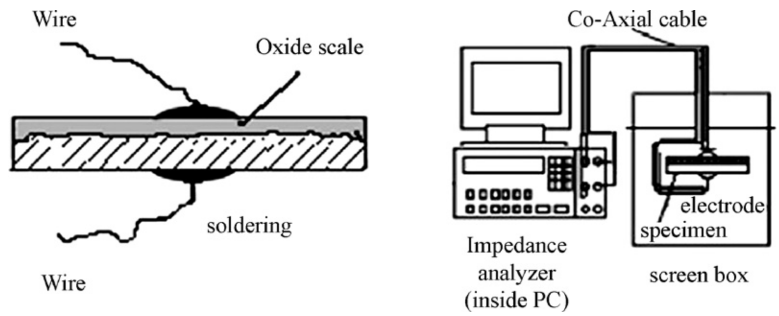

Fig. 6. Schematic of the sample and impedance measurement.

phase can be more clearly seen in the pre-oxidized sample. The substrate lines were weak for the two samples, implying the oxide scales were thicker than those of Ebrite and Haynes 230 after syngas exposure.

One may note that no carbide phase was identified in the three iron-based samples. However, we cannot exclude the possibility of there might be some amorphous carbon, which could not be identified by XRD.

3.2. Cross-section and EDX scanning for Crofer samples

Fig. 3A shows the cross-section SEM image of the scale formed on the surface of syngas exposed Crofer sample. The EDX line scan of this sample indicated that chromium (Cr), manganese (Mn) and oxygen (O) peaks were uniformly distributed throughout the layer, indicating the scale had only one layer and it was a mixture of spinel ($Mn_{1.5}Cr_{1.5}O_4$) and chromia (Cr_2O_3) phases. In contrast, the cross-section of air exposure Crofer sample, shown in Fig. 3B, showed a two-layer scale structure, with Mn-rich in the outer layer consistent with spinel formation, while the chromium-rich inner layer was consistent with chromia. EDX analysis of the surface also showed a Mn composition difference between the sample, the air exposed sample contained as much as 11.6 wt% of Mn while the syngas exposed sample had only 6.6 wt% Mn. The thickness of the scale for both samples was about 2 μm.

Cross-section image for pre-oxidized Crofer sample was similar to that of the air exposure sample as shown in Fig. 3C. It can be found that the line scan results were similar to that of the air sample (Fig. 3A), as it had a Mn-rich outer layer and a chromium-rich sublayer. The scale thickness was about 4 μm, thicker than that of the air and syngas-treated samples.

Cross-section and EDX line scanning for both Ebrite and Haynes 230 showed one thin layer of oxide scale, which was similar to Fig. 3A and both of their thickness were less than 1 μm.

3.3. Indentation results

The micrographs of indented area are shown in Figs. 4 and 5. There were many cracks around the indentation for the syngas exposure sample of Crofer (cf. Fig. 4A), whereas little or no cracking was found in the air exposure sample (Fig. 4B), suggesting that the porous scale formed in syngas was more brittle than that formed in air.

Comparison of the three air-oxidized samples by indentation, i.e., the Crofer, Ebrite and Haynes 230, indicates that all the samples had similar adhesion properties. However, the results of Ebrite and Haynes 230 may be due to the thinness of the scales.

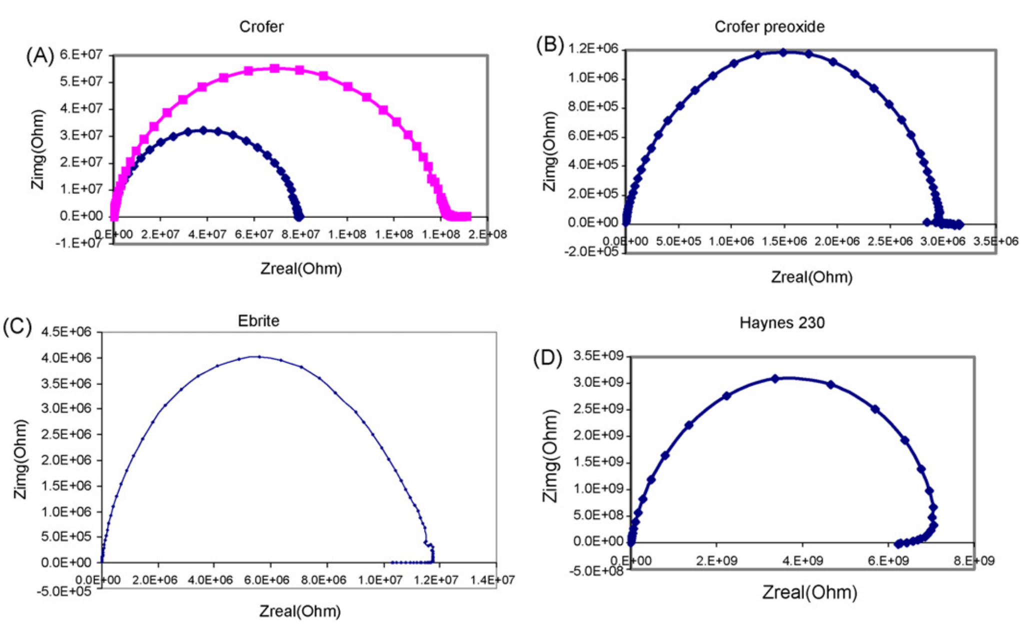

Fig. 7. Illustration for impedance measure results of air exposure Crofer (small semicircle) and syngas exposure Crofer (A), pre-oxidized Crofer (B), Ebrite (C) and Haynes 230 (D).

3.4. Measurement of electrical impedance of the scale

The schematic of the sample and instrument configuration for impedance analysis are shown in Fig. 6. The measurements were carried out with ac current with an amplitude of 1500 mV and a frequency range from 1×10^{-3} Hz to 1×10^{5} Hz.

The Nyquist plots of Crofer samples treated in syngas and air is shown in Fig. 7A, where the plot for air sample showed a perfect semicircle. It can be found from Fig. 7A that the resistance of the syngas exposed sample was much higher than that of the air exposed sample. The plots of both pre-oxidized and un-oxidized Crofer samples (cf. Fig. 7A as the bigger semicircle and Fig. 7B), had a “tail” in the semicircles, which might be related to the scale with porous whisker-like morphology (Fig. 1C) and ridges-like grains (Fig. 1D). Nyquist plots of both Ebrite and Haynes 230 had similar shapes (cf. Fig. 7C and D), and the patterns were different from that of Crofers (Fig. 7A and B). The resistances of the Ebrite and Haynes 230 were also higher than that of Crofer. The maximum real parts of the impedance, Z_{real}, for all samples were different. The Haynes 230 sample had the highest resistance ($\sim 6 \times 10^{9}\ \Omega$) and the pre-oxidized Crofer sample had the smallest one ($\sim 3 \times 10^{6}\ \Omega$). The lower resistance for the pre-oxidized sample was likely due to lower porosity (Fig. 1D), giving a much more direct and shorter electron conduction path than that of the more porous samples (Fig. 1C).

3.5. Discussion

Scale morphologies of wet syngas-exposure samples of three kinds of alloys had similar whiskers or ridge-like grain structures (cf. Fig. 1A–C). The scale structure formed in the syngas was porous and uncompact. In contrast, the morphology of air exposure sample was pyramid-like, compact and uniform (cf. Fig. 1E and F) and the morphology was independent of exposure time. The pyramid-like morphology is the typical spinel structure formed in high-temperature air of Crofer 22. It was reported [5] that the chromia scale on alloys could be formed in both oxidant and reduce environments such as in hydrogen or in water vapor. However, the morphologies in both cases were different. The whiskers and ridges-like morphology obtained in syngas was characteristic formed in a reducing environment.

It has been argued [5] that whiskers or ridges-like morphologies were caused by vaporization of chromium species during the exposure period. Therefore, the morphologies for un-oxidized samples imply that the vaporization of chromium was severe. In addition, the large surface area of these porous scales may continuously increase corrosion in further exposures.

We found, by XRD, the main phases in the scale for four syngas samples, the un-oxidized Crofer, and primarily Cr_2O_3 for Ebrite and Haynes 230, were chromia and spinel (cf. Fig. 2), in. Results for cross-section and EDX analysis indicated that the Crofer sample in syngas exposure had only one oxide scale layer (Fig. 3A), whereas the air exposure Crofer had two scale layers with a manganese-rich layer as the outer layer and a chromium-rich inner layer (Fig. 3B). The structure of the two layers may reduce the volatility of chromium, since the MnCr spinel is known to be more stable than Cr_2O_3. The two layers structure remained in the pre-oxidized Crofer (Fig. 3C) after syngas exposure, suggesting that pre-oxidation may be used as surface modification method for samples intended for the syngas exposure use.

No carbide phase was found in the scale of the iron-based alloys. Carbide formation is thought to be one of the first stages in metal dusting. This is likely due to the high humidity in the syngas used for this test, which is consistent with the results of Ref. [3]. The absent of metal dusting was also supposed by the thermochemical calculations in equilibria [12] of C–H–O ternary diagram (cf. Fig. 8), where carbon deposition region is at the upper part of the diagram, and the regional boundary line is dependent on the temperature. It can be seen that our wet syngas is in the region out of the carbon deposition boundary line for 800 °C, which gives the theoretical verification of our result.

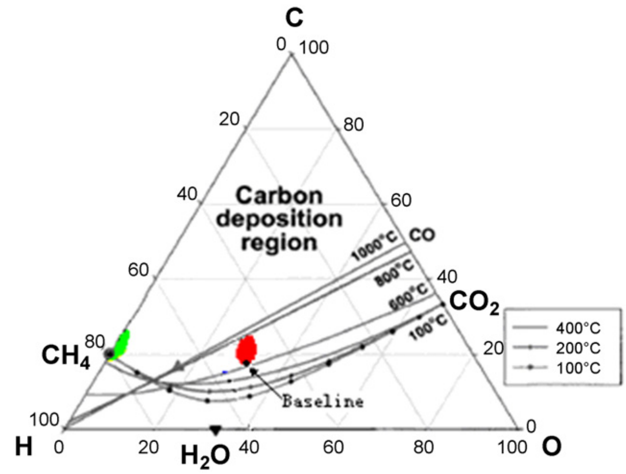

Fig. 8. Carbon deposition limit lines in the C–H–O diagram [12].

Results obtained by electrical impedance test experiments were sensitive to the microstructure of the scale. It was found that the compact and dense scales (Crofer treated in air or pre-oxidized sample in syngas) had relatively smaller electrical resistance and had perfect semicircle in the Nyquist plot, whereas the porous scale (Crofer in syngas) had higher resistance as well as distorted semicircle in the Nyquist plots, although the detailed explanation needs further study.

Results obtained from indentation experiment indicated the pre-oxidized Crofer scale had higher mechanical toughness endurance, as it was little apparent cracking after indentation, whereas the un-oxidized Crofer samples had poor mechanical endurance due to its porous and noncompact microstructure.

It was found that pre-oxidized Crofer was an effective way to reinforce the alloy from corrosion in the wet syngas environment. As shown in Fig. 1D, the pre-oxidized sample still retained some of the pyramid-like morphology after being exposed in wet coal syngas for 100 h. On the other hand, as the pre-oxidized sample was thicker than the air exposure (24 h) sample, the new pyramid structure must grow in the syngas exposure, therefore the morphology of the newly growing grains must had inherited that of the pre-oxidized one (Fig. 3C). Thus, the morphology of materials (at least in these short-term tests) depends not only on the environment of isothermal treatment but also on the morphology created by pretreatment. XRD (Fig. 2) results indicated the pre-oxidized one had more spinel than that of Ebrite and Haynes 230. Cross-section and EDX showed that it had a two-layered scale which was very similar to that of the air exposure sample. Indentation test indicated it had better mechanical toughness than the un-oxidized sample and it had the best electrical conductivity among all samples tested (at room temperature).

4. Conclusion

High-temperature alloys Crofer 22 APU (with and without pre-oxidation), Ebrite and Haynes 230 potentially, which are expected to be used for coal-based SOFC as interconnects in wet syngas environment, was studied. The following conclusion can be drawn:

(1) The scale formed in syngas was a porous structure compared with scale formed in air environment for Crofer 22. There was no clear spinel layer formed in the syngas while clear spinel layer formed in air. The scale formed in the syngas had lower mechanical endurance and lower electrical conductivity compared with the scale formed in air.
(2) The pre-oxidized Crofer sample performed best in comparison with Ebrite and Haynes 230 in syngas. The formed spinel had the pyramid-like morphology due to pre-oxidized treatment in air, and the oxidized scale remained dense after wet syngas exposure. XRD results indicated the phases of the scale were chromia and spinel, and no carbide phase was found. Cross-section EDX analysis showed the two layers structure of the scale had spinel phase in the outer layer and chromia phase in the inner layer, which appeared to be a better structure for corrosion resistance in syngas environment.

Acknowledgements

This technical effort was performed in support of the National Energy Technology Laboratory's on-going research in University of Pittsburgh under contract #DE-AC26 -04NT41817. K. Liu was visiting scholar in University of Pittsburgh supported by Shanghai Leading Academic Discipline Project with project number P1502.

References

[1] W.Z. Zhu, S.C. Deevi, Mater. Sci. Eng. A348 (1–2) (2002) 227–243.
[2] W. Jeffrey, Fergus, Mater. Sci. Eng. A 397 (1–2) (2005) 271–283.
[3] Z. Zeng, K. Natesan, Solid State Ionics 167 (2004) 9–16.
[4] R.S. Gemmen, J. Trembly, J. Power Sources 161 (2006) 1084–1095.
[5] L. Mikkelsen, S. Linderoth, Mater. Sci. Eng. A361 (2003) 198–212.
[6] E.A. Polman, T. Fransen, P.J. Gellings, Oxid. Met. 32 (1989) 433.
[7] P. Kofstad, K.P. Lillerud, J. Electrochem. Soc. 127 (1980) 2410.
[8] T. Norby, J. Phys. IV 3 (1993) 99.
[9] G. Hultquist, B. Tveten, E. Hornlund, Oxid. Met. 54 (2000) 1.
[10] H. Asteman, J.E. Svensson, M. Norell, L.G. Johansson, Oxid. Met. 54 (2000) 11.
[11] K. Hilpert, D. Das, M. Miller, D.H. Peck, R. Weiss, J. Electrochem. Soc. 143 (1996) 3642.
[12] K. Sasaki, Y. Teraoka, J. Electrochem. Soc. 150 (7A) (2003) 885–888.