

Rolls-Royce Advanced Materials for SOFC Air and Thermal Management Systems Application



Le Ge¹, Atul Verma¹, Prabhakar Singh¹, Richard Goettler² and David Lovett²

¹Center for Clean Energy Engineering. University of Connecticut. Storrs. CT 06269 : ²Rolls-Royce fuel cell systems (US) Inc. North Canton. OH 44720

Objective: The overall objective of the research effort is to identify, test and select candidate iron and nickel base alloys and aluminized coatings for applications in air and thermal management units of advanced SOFC power generation systems. It is also the objective of this study to develop mechanistic understanding of surface and bulk corrosion and degradation, long term protection and chromium evaporation processes.

BACKGROUND: The air and thermal management units of the SOFC systems remain exposed to high temperature and oxidizing environment during the nominal and transient operating conditions. Materials of construction experience surface corrosion and gaseous corrosion products formation resulting in the loss of metal and chromium poisoning of the SOFC cathode

>Chromia forming iron and nickel base alloys have been conventionally used for the fabrication of such sub systems. These alloys remain prone to enhanced metal loss, grain boundary attack and surface oxide evaporation. Presence of water vapor in air has been reported to enhance such evaporation due to the formation of various oxides and hydroxyoxides vapor species 1-3. The long term successful operation of SOFC sub system requires minimization of metal loss as well as Cr-evaporation from the surface oxides.

>Cr evaporation, transport and resulting poisoning of the cathode can be minimized/eliminated by the proper selection of bulk alloys and surface coatings. Alumina forming alloys offer such advantage over chromia forming alloys.

APPROACH: Our approach consists of identifying and selecting Fe and Ni base alloys followed by testing and characterization to assess the metal loss, scale chemistry and morphology, and chromium evaporation. We have utilized isothermal and thermal cyclic oxidation, transpiration and a wide variety of characterization techniques to examine the corrosion products, surface morphology and chemistry, and resulting chromium evaporation rate. Furthermore, we have used a number of coating techniques to deposit uniform aluminized surface layers to further reduce the corrosion rate, minimize the localized corrosion and chromium evaporation rate.

EXPERIMENTAL:

List of alloys and coatings used - AISI 310S, Aluchrom, 602CA, and Aluminized 602CA Two coating techniques were used for aluminizing - Vapor deposition and pack

Alloys were oxidized in humidified air (3-12%H₂O) for up to 500 hrs. Both isothermal and thermal cyclic test were performed in 800-950°C temperature range under flowing gas environment. Cr evaporation rate from the above mentioned bulk and coated alloys were measured using transpiration method (Figure 1). Cr was extracted using two step extraction techniques-nitric acid followed by dissolution in an alkaline solution of potassium permanganate. Inductively coupled plasma mass spectrometer (ICPMS) was used to measure Cr concentration in the condensate.

Samples were analyzed for surface morphology and scale composition using Scanning Electron Microscopy (SEM), Focused Ion Beam (FIB), Energy Dispersive X-Ray Spectroscopy (EDS) and X-Ray Diffraction (XRD)

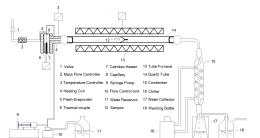
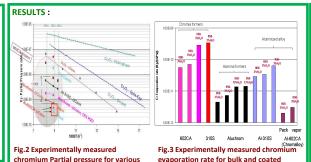


Fig.1 Oxidation and chromium evaporation experimental set-up



alloys

Cr evaporation rate increases as a function of temperature and water content A significantly lower Cr evaporation rate (~ 1/100) is observed for alumina formers compared to chromia forming alloys.

Further reduction (~ 1/200) in Cr evaporation rate is observed for surface aluminized samples

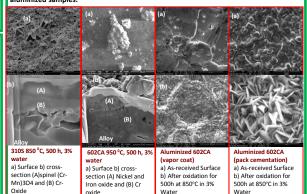
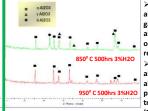


Fig.4 Surface morphology of various alloys and coatings before and after oxidation test



Nickel and iron base chromia forming alloys formed an outer chromia scale (scalegas interface). Doping of chromia scale with alloy constituents such as Mn, Fe, Ni etc. was observed locally2 (Fig 4). Such alloys showed relatively higher Cr evaporation rate.

Dense, continuous and well-adherent alumina scale is observed on Aluchrom and aluminzed-602CA(Fig 4). At 850°C, the scale primarily consists of γ-alumina which transforms to into α-alumina above 900°C3

Fig.5 XRD of the surface scale formed on Aluchrom after oxidation

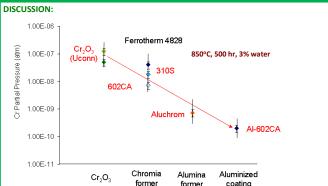


Fig.6 The observed reduction and trend of Cr partial pressure change for alloys and coatings

The decreasing trend in Cr vapor pressure, shown above, for various groups of materials can be rationalized in terms of the decreasing activity of the chromium oxide at the exposed surface.

An early stage transient chromia formation in the case of alumina formers contributes to the observed higher Cr partial pressure than aluminized alloys3.

> A thick aluminized coating serves as large aluminum reservoir which provides longer lasting, dense and thick alumina scale on the alloy surface even under scale spallation conditions.

Alumina scale morphology and crystallographic structure are influenced by the exposure temperature 3.

CONCLUSIONS:

> The metal loss and Cr-evaporation rate are influenced by the scale chemistry and morphology. Aluminized alloys offer significant reduction in corrosion rate due to exclusive alumina scale formation. The γ -alumina forms below 850 0 C which transforms to α -alumina above 900 0 C.

The bulk alumina forming alloys and aluminized coatings exhibit lowest metal loss and chromium evaporation, when compared to conventional alloys. Aluminized coating provides large aluminum reservoir for prolonged exposure and scale spallation conditions.

- Opila, E. J., Myers, D. L., Jacobson, N. S., Nielsen, I. M. B., Johnson, D. F., Olminsky, J. K., and Allendorf, M. D J. Phys. Chem., A, 111, (2007), 1971.
- Stanislowski, M., Wessel, E., Hilpert, K., Markus, E. T., and Singheiser,. L. J. Electrochem. Soc., 154 (4), (2007), A295
- Stanislowski, M., Wessel, E., Markus, E. T., Singheiser, L., and Quadakkers, W. K., Solid State Ionics, 179, (2008), 2406.

ACKNOWLEDGEMENTS:

The authors acknowledge financial support from US Department of Energy Solid State Energy Conversion Alliance Program. Technical discussions with Dr. Jeff Stevenson (PNNL) is gratefully acknowledged.

