Journal of Power Sources 180 (2008) 433–439

Contents lists available at ScienceDirect

Journal of Power Sources

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

Oxidation resistance of novel ferritic stainless steels alloyed with titanium for SOFC interconnect applications

Paul D. Jablonski*, David E. Alman

National Energy Technology Laboratory, Process Development, 1450 Queen Avenue SW, Albany, OR 97321, USA

ARTICLE INFO

Article history:
Received 10 January 2008
Received in revised form 5 February 2008
Accepted 6 February 2008
Available online 16 February 2008

Keywords:
SOFC
Interconnect
Oxidation
Ferritic steel
Cr poisoning
Surface treatment

ABSTRACT

Chromia (Cr_2O_3) forming ferritic stainless steels are being developed for interconnect application in Solid Oxide Fuel Cells (SOFC). A problem with these alloys is that in the SOFC environment chrome in the surface oxide can evaporate and deposit on the electrochemically active sites within the fuel cell. This poisons and degrades the performance of the fuel cell. The development of steels that can form conductive outer protective oxide layers other than Cr_2O_3 or $(CrMn)_3O_4$ such as TiO_2 may be attractive for SOFC application. This study was undertaken to assess the oxidation behavior of ferritic stainless steel containing 1 weight percent (wt.%) Ti, in an effort to develop alloys that form protective outer TiO_2 scales. The effect of Cr content (6–22 wt.%) and the application of a Ce-based surface treatment on the oxidation behavior (at 800 °C in air + 3% H_2O) of the alloys was investigated. The alloys themselves failed to form an outer TiO_2 scale even though the large negative ΔG of this compound favors its formation over other species. It was found that in conjunction with the Ce-surface treatment, a continuous outer TiO_2 oxide layer could be formed on the alloys, and in fact the alloy with 12 wt.% Cr behaved in an identical manner as the alloy with 22 wt.% Cr.

1. Introduction

Solid Oxide Fuel Cells (SOFC) are solid state energy conversion devices [1,2] converting a fuel such as H_2 or CO directly into electricity without combustion. In their simplest form they consist of an anode, a cathode and an electrolyte. A single cell can produce current density and voltage in the order of 1 A cm^{-2} and 1 V, respectively. In order to develop greater power output, multiple cells are grouped together. In planar SOFC they are simply stacked together with an "interconnect" separating each cell [2,3]. This interconnect acts as an air/fuel separator and is part of the electrical circuit. Lanthanum chromate is a good choice as an interconnect material for high temperature application (>900 °C), however it is quite expensive. The core goal of the Solid State Energy Conversion Alliance (SECA) is the development of SOFC with a factory cost of \$400 kW^{-1} h^{-1} or less [4–6]. One of the cost enabling developments over the past few years is oxide component materials capable of operating at lower temperatures such as 700–800 °C [7–12]. This lower temperature range has provided for the consideration of metallic materials for interconnect applications [12–18]. Metallic interconnects have several advantages: low cost, ease in manufacturing, and high conductivity. Most metals and alloys will oxidize under both the anode and cathode conditions within an SOFC, thus a chief requirement is that the base metal oxide scale must be electrically conductive since this constitutes the majority of the electrical resistance in a metallic interconnect. Common high temperature metal alloys form oxide scales that contain chrome, silicon and aluminum oxides among others. Under SOFC operating conditions chrome oxide is a semi-conductor while silicon and aluminum oxides are insulators. Several commercial alloys have been developed for SOFC applications such as Crofer 22 APU (ThyssenKrupp VDM), Hitachi ZMG 232 (Hitachi Metals) and Ebrite (Allegheny Ludlum) all of which form chromium-rich oxide scales under oxidizing conditions.

Many SOFC designs will operate at temperatures exceeding 700 °C. At these temperatures in the moist SOFC cathode environment, Cr_2O_3 (chromia) evaporates and deposits on electrochemically active sites at the cathode–electrolyte interface. This degrades the electrical performance of the SOFC [21–27]. The formation of an outer Cr–Mn spinel will reduce Cr evaporation, but will not prevent the Cr poisoning of the electrochemical reactions. Consequently, there has been considerable attention given to developing coatings which prevent Cr migration from the steel interconnects into the cathode [27–30]. Alternatively, the development of steels that can form conductive, protective oxide layers other than Cr_2O_3 may be attractive for interconnect application. For example, TiO_2 may have electrical properties that are attractive for interconnect application [17–20]. This study was conceived to explore steels that could form outer protective TiO_2 scales during oxidation. Further, the effect of alloy Cr content and a reactive

---

* Corresponding author. Tel.: +1 541 967 5982; fax: +1 541 967 5958.
E-mail address: paul.jablonski@netl.doe.gov (P.D. Jablonski).

0378-7753/$ – see front matter. Published by Elsevier B.V.
doi:10.1016/j.jpowsour.2008.02.010

element surface treatment [31–33] on the oxidation of the experimental (Fe–Cr–1Ti–0.5Mn) alloys was investigated.

2. Experimental techniques

2.1. Alloy design and manufacture

Experimental alloy formulation was first evaluated theoretically with the use of Thermo-Calc (version r) and the TcFe5 database. High purity starting materials were used to formulate the series of alloys shown in Table 1. Approximately 6800 g of high purity raw materials was induction melted under inert gas and poured into a cylindrical mold for each alloy. These cylindrical ingots were machined and subsequently homogenization heat treated at 1150 °C/12 h/FC in vacuum. The homogenized ingots were bagged in protective stainless steel foil pouches and preheated to 900 °C for 3 h prior to fabrication. Hot working consisted of forging and rolling to fabricate the round ingot into a slab shape and ultimately form a strip product. These strips were hot worked to a thickness of 3 mm. Subsequently, these strips were conditioned to remove oxidation products and any residual surface defects prior to cold rolling. Each alloy was subsequently cold rolled to approximately 1 mm thickness.

2.2. Alloy testing and evaluation

Oxidation test coupons were cut from each of the alloys with the dimensions of approximately 12 mm × 24 mm × thickness and polished through 600 grit prior to testing. Some samples were drilled with a 3 mm diameter hole near one end to provide for hanging from a quartz rack while others were stood upright inside alumina crucibles. Further, some duplicate samples were surface treated with cerium oxide [31–33] before testing. Prior to oxidation testing the starting weights and physical dimensions of the coupons were measured and recorded. Oxidation tests were conducted at 800 °C in moist air. The moist air was generated by bubbling commercial purity dry air through two glass columns (2.54 cm in diameter by 120 cm in height) filled with distilled water just ahead of the furnace entrance. This was intended to generate air saturated with 3% H_2O, the maximum amount of moisture dissolvable in air at ambient conditions. After a predetermined time interval, the coupons were removed from the heated furnace, cooled and the weight of each coupon was measured and recorded. The samples were then reinserted into the heated furnace for the next cycle. Oxide scale surfaces were examined by standard X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. Chemistries of the oxidized surfaces were determined by energy dispersive X-ray analysis (EDX). Oxidized coupons were also sectioned and polished via standard metallographic procedures to view the scales in cross section. These were analyzed by SEM with WDX analysis using in situ standards for metal and oxide scale chemistry.

Table 1
The design chemistries (weight percent) for the experimental series of alloys are found in the table below

	F7	F8	F9	F10	F11
Fe	Bal.	Bal.	Bal.	Bal.	Bal.
Cr	6	9	12	18	22
Ti	1	1	1	1	1
Al	0	0	0	0	0
Si	0	0	0	0	0
Mn	0.5	0.5	0.5	0.5	0.5
C	0	0	0	0	0

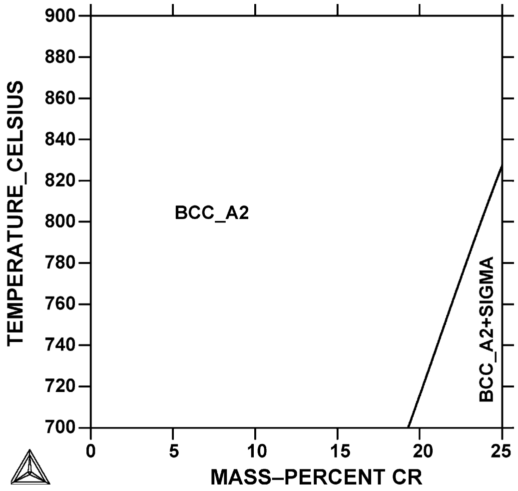

Fig. 1. Phases calculated to be present in an Fe–1Si–0.5Mn × Cr alloy (Thermo-Calc Classic version r used along with TcFe5 database).

3. Results

3.1. Alloy phases and chemistry

Thermo-Calc showed that all of the experimental alloys are expected to be single phase at the test conditions, similar to a simple ferritic stainless steel containing Si rather than Ti. However, it was observed that with high Cr and at lower temperatures (>22Cr and <800 °C) Sigma phase is predicted in the simple Si containing ferritic alloy (typical of many commercial ferritic stainless steels) while Laves phase is predicted in the experimental Ti containing alloy (Figs. 1 and 2). The possibility of Laves phase formation was not considered to be undesirable in these alloys. In fact, some researchers [34–36] are considering Laves phase as a way to tie up residual Si for a cost effective way of dealing with undesirable SiO_2 formation in ferritic alloy interconnects. However, is not a consideration in the present experimental alloys since they contain Ti but no Si. Furthermore, the experimental alloys were single phase under the test conditions.

The measured chemistry of the experimental alloys is found in Table 2. Good correlation was observed between the actual alloy composition and target composition. Furthermore, the alloys contained very low levels of “tramp” or undesirable elements. A

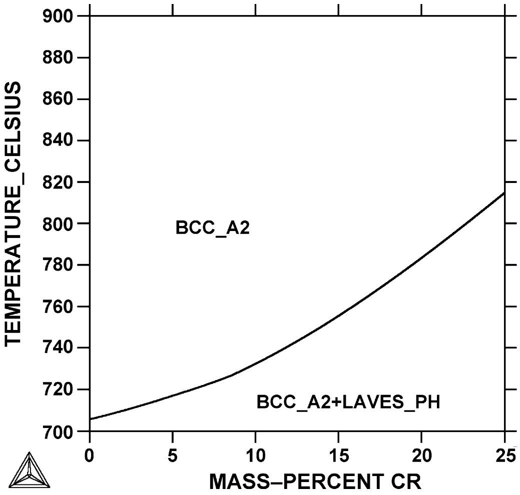

Fig. 2. Phases calculated to be present in an Fe–1Ti–0.5Mn × Cr alloy (Thermo-Calc Classic version r used along with TcFe5 database).