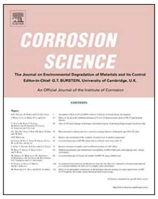
Corrosion Science xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Corrosion Science

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



Effects of alloyed La, Cu and B on the oxidation of Fe-22Cr ferritic stainless steels under simulated cathode side atmosphere of solid oxide fuel cell interconnects

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ARTICLE INFO

Keywords:
A. Stainless steel
A. Copper
A. Rare earth elements
B. SIMS
C. Oxidation
C. Segregation

ABSTRACT

Discontinuous oxidation of La (0.14–0.52 wt.%), Cu (0.17–1.74 wt.%) and B (48–109 ppm) alloyed Fe-22Cr ferritic stainless steels, and Crofer 22 APU (0.047 wt.% La), have been studied at 800 °C, in flowing air-2% H_2O atmosphere, for 1300 h. The determined parabolic rate constants ($1.65–2.58 \times 10^{-4}\ mg^2\ cm^{-4}\ h^{-1}$) are quite close to each other. Benefits of high La-alloying are not caused by the reduction in oxidation, but rather by the alteration in scale growth direction. On the other hand, high Cu-alloying promotes the segregation of Cu at the scale/alloy interface, which suppresses the sub-surface and/or internal oxidation.

1. Introduction

Fuel cell technology has gained huge attention over the past years as a promising alternative to the current combustion based energy technologies, because it converts the chemical energy of a fuel directly into electricity. In particular, solid oxide fuel cells (SOFCs) outweigh the benefits of any fuel cell technology with respect to its high efficiency in energy conversion, fuel flexibility, low noise and low emissions of toxic pollutants. Due to such attractiveness, SOFC technology is an interesting option, which is applicable extensively in a diversified (high-efficient) power generation such as small, distributed stationary power systems, as well as auxiliary power units (APUs) for transportation use. Basically, the high operating temperatures (≤ 800 °C) provide additional positive features, such as potential use of SOFCs in highly efficient cogeneration (combined heat and power) applications [1–4]. While SOFCs offer several advantages, they also impose serious technical challenges in terms of long-term stability, particularly the material degradation under high temperature and corrosive environments.

One of the key components for the successful fabrication and operation of SOFC stacks is the interconnect. With the reduction of operating temperature, presently, the metallic interconnects are used, which not only provide the electrical connection between individual cells, but also serve as a key support structure to cells in a stack. Among the four major components (such as cathode, anode, solid electrolyte and interconnect), the interconnect is the one which operates in both oxidizing (cathode side) and reducing (anode side) atmosphere, and therefore, requires the most demanding material selection criteria [5,6]. Several Ni-Cr and Fe-Cr based alloys have been considered as candidates for the intermediate temperature (i.e. 600–800 °C) SOFCs interconnect applications. Although Ni-Cr based alloys exhibit excellent oxidation resistance and form oxide scales with satisfactory electrical conductivity, their potential mismatch of thermal expansion coefficient (TEC) to cell components is unacceptable and hindered their application as SOFC interconnects. On the other hand, Fe-Cr based ferritic stainless steels are most promising because their thermal expansion behavior matches well with the adjacent cell components. Furthermore, compared with Ni-Cr based alloys, Fe-Cr based alloys are cost-effective [7,8]. Still, the major challenge concerning the use of Fe-Cr based chromia forming alloys under the SOFCs operating conditions (such as intermediate operating temperature: 600–800 °C; longer operating time: 40,000 h; simultaneous exposure to oxidizing and reducing environments) is high temperature corrosion/oxidation. The resistance to corrosion/oxidation under these specific conditions, largely depends on the alloy composition as well as their microstructure such as grain size, grain boundary characteristics and the texture, i.e. distribution of grain orientation [9–11]. Essentially, an inadequate oxidation resistance of interconnect alloys brings up series of issues in SOFCs, for example, the rapid growth of oxide scale and their increase in thickness with time, which can spoil the electrical conductivity [12]. Also, the spallation of oxide layers leads to a failure in electrical contact between electrodes and interconnects. Another major challenge is the Cr-containing vapor species that form over chromia forming Fe-Cr based alloy interconnects, resulting Cr-deposition and poisoning the cathode, which ultimately brings down the electrochemical performance of SOFCs [13]. In order

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https://doi.org/10.1016/j.corsci.2018.01.025
Received 11 August 2017; Received in revised form 11 January 2018; Accepted 19 January 2018

Please cite this article as: Swaminathan, S., Corrosion Science (2018), https://doi.org/10.1016/j.corsci.2018.01.025

to overcome the issue of Cr-volatility, several surface overlay coating treatments have been explored so far [14,15] and references therein]. But for the broad technological point of view, issues related with materials as well as manufacturing cost, reproducibility, fabricability/scalability and controllability are making the coating technique not so easy to be implemented [15,16].

Basically, the properties of the oxide scales, such as electrical conductivity and Cr-volatility, depend largely on the chemical composition and structure of the oxide scales developed at the surface as well as at their (oxide scale/alloy) interface. While plenty of publications deal with the coating approaches for SOFC interconnects [14,15,17–19], up to now there are relatively few studies on improving the long term stability through alloy modification [20–22]. As a possible route to overcome the coating difficulties, variety of metal matrix composites (MMC such as TiC and TiN based cermets with 30–70 wt.% Ni, Ni_3Al, Ti_3Al, also with Ni-based hastelloy) are proposed [23,24]. However, the alloy modification strategy is more simplistic, scalable and moreover, technologically highly relevant for the commercialization of SOFCs. Basically, optimization of alloy composition, and the systematic analysis of oxidation mechanism are the key factors in the alloy development [25]. As a part of such efforts, herein, La (0.14–0.52 wt.%), Cu (0.17–1.74 wt.%) and B (48–109 ppm) alloyed Fe–22 wt.% Cr ferritic stainless steels have been developed, and their oxidation characteristics are investigated under a simulated cathode side atmosphere (i.e. flowing air with 2% water vapor) at 800 °C, in a discontinuous manner for up to 1300 h. The oxidation behavior of these developed steels (i.e. La, Cu and B-alloyed Fe-22Cr ferritic stainless steels) are compared with that of Crofer 22 APU steel (containing 0.047 wt.% La), which is commonly known to be a state of the art construction material for SOFC interconnects. The present authors' publication clearly showed that Fe-22Cr ferritic stainless steel alloyed with 1.57 wt.% Cu exhibits improved oxidation resistance, whereas 0.6 wt.% La does not [26]. Moreover, high lanthanum ($>$ 0.5 wt.%) containing steel is susceptible to cracking during hot rolling, and this issue has been solved with the addition of small amount (50–100 ppm) of boron, which is known to enhance the hot workability processes. Additionally, boron was found to be efficient in improving the mechanical properties of superalloys [27] and to enhance the scale adhesion and oxidation resistance of NiCrAl alloys and Fe-based low Cr alloys [28,29]. Despite such encouraging findings, astonishingly, none of the Fe-Cr ferritic stainless steels applicable for SOFC interconnects is alloyed with boron. The present authors' recent work demonstrated that modification of oxide scale structure and its constituents by high La, Cu and B-alloying of Fe-22Cr ferritic stainless steel, is an effective method to improve the electrical performance (i.e. lowering the area specific resistance) of the interconnect material [30]. However, the oxidation characteristics presented in Ref. [30] is solely based on the continuous isothermal exposure in a static dry air condition. In general, water vapor is the most common gas species present in SOFC cathode side environment. Even though its concentration usually does not exceed a few percent, water vapor induced Cr evaporation may alter the oxidation behavior of the interconnect material [31]. Therefore, high temperature corrosion/oxidation under the cathode side service condition is an important avenue of SOFC interconnect research. In the present work, the oxidation behavior of the La, Cu and B-alloyed Fe-22Cr ferritic stainless steels is examined in SOFC cathode side relevant (flowing gaseous (air + $2\%H_2O$)) environment in a discontinuous manner. The main focus is on how the alloyed elements such as La (0.14–0.52 wt.%), Cu (0.17–1.74 wt.%) and B (48–109 ppm) response to the humid air atmosphere in the cathode side of SOFC. In particular, the extent of oxidation depth and/or reaction kinetics are of interest in this context. It will be shown here that the oxidation in flowing humid air atmosphere is much faster than that of stagnant dry air. Furthermore, in the present work, it will be revealed from the dynamic SIMS depth profiling that boron contributes to oxide scale in sizable proportion if not dominates entirely in scale growth process. Numerous studies have reported that the reactive element addition improves oxide scale adherence and modifies the scale growth mechanism by promoting a preferential anionic (oxygen) diffusion [32–34]. This strategy of microstructural modification of oxide scale, i.e. obtaining less external oxidation or substantial internal oxidation, has been achieved in the current research via high La-alloying. Impressively, it will be shown in the present work that the addition of Cu impedes the sub-scale formation and thus the overall scale thickness is comparable to that of Crofer 22 APU. In spite of dominant internal oxidation observed for high La-alloyed steel in this work, formation of the Fe-Cr alloy protrusions within the scale structure and incorporation of the active element (herein La) into a scale are expected to be beneficial not only to promote electrical conductivity of the scale but also to inhibit the Cr-volatilization.

2. Experimental method

2.1. Materials and samples preparation

The Fe-22 wt.% Cr ferritic stainless steels of the present investigation, with varying La (0.14–0.52 wt.%), Cu (0.17–1.74 wt.%) and B (48–109 ppm) composition have been manufactured using the vacuum induction melting (VIM) process, by Hankook Vacuum Metallurgy Co., South Korea. These experimental steel grades are designated by their composition of La, Cu and B. The Fe-22Cr steel containing higher La (0.52 wt.%), 0.17 wt.% Cu and 109 ppm B, is designated as 0.52La-0.17Cu–0.011 B steel. Similarly, higher Cu (1.74 wt.%), 0.14 wt.% La and 48 ppm B, alloyed Fe-22Cr steel is designated as 0.14La-1.74Cu-0.005 B steel. The chemical composition of the steels (in wt.%) developed is given in Table 1. The ingots of 300 kg in each category, were subjected to homogenization at 1150 °C for 2 h and subsequently hot rolled at 1150 °C to 18 mm. For the discontinuous oxidation experiment, the samples of 10 mm × 10 mm with a thickness of 2 mm were machined from the as-delivered hot rolled sheets, and all sides of the samples were ground till 2000 grit surface finish using SiC abrasive papers. Following ultrasonic cleaning in acetone for 10 min, the samples were washed in ethanol and finally, dried by blowing hot air. For the purpose of comparison with the experimental steels (0.52La-0.17Cu-0.011 B and 0.14La-1.74Cu-0.005B), Crofer 22 APU (ThyssenKrupp VDM GmbH, Germany), a commercial interconnect material for SOFCs, has been included in the present investigation and its chemical composition, expressed in wt.%, is also presented in Table 1. The Crofer 22 APU steel used in the present work contains 0.047 wt.% La, and therefore, labelled as 0.047La steel. The 0.047La steel was manufactured using VIM process and this material prevailed

Table 1
Chemical composition of the Fe-22Cr ferritic stainless steels investigated in this study.

Element	Chemical composition of the Fe-22Cr ferritic stainless steels (wt.%)		
	0.52La-0.17Cu-0.011B	0.14La-1.74Cu-0.005B	0.047La (Crofer 22 APU)
Cr	22.9	22.6	22.487
Mn	0.38	0.38	0.441
Ti	0.060	0.059	0.052
Al	0.08	0.08	–
C	0.003	0.004	0.008
La	0.52	0.14	0.047
Cu	0.17	1.74	–
B	0.0109	0.0048	–
Ni	0.60	0.63	0.052
P	0.005	0.005	–
S	0.001	0.001	–
Si	0.04	0.04	0.084
V	–	–	0.012
W	–	–	0.104
Mo	–	–	0.017
N	–	–	0.013