Available online at www.sciencedirect.com

ScienceDirect

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

Short Communication

High temperature cyclic oxidation behavior of ferritic stainless steel with addition of alloying elements Nb and Ti for use in SOFCs interconnect

Azim Safikhani [a,*], *Mohammad Esmailian* [a], *Taleb Tinatiseresht* [a], *Ghasem Barati Darband* [b]

[a] *Advanced Materials and Renewable Energy Dept., Iranian Research Organization for Science and Technology (IROST), Tehran, Iran*
[b] *Tarbiat Modares University, Faculty of Engineering, Iran*

ARTICLE INFO

Article history:
Received 20 December 2015
Received in revised form
12 January 2016
Accepted 17 January 2016
Available online 11 March 2016

Keywords:
Solid oxide fuel cell
Interconnect
Cyclic oxidation
Laves-phase
Niobium
Titanium

ABSTRACT

In the present work, high-temperature cyclic oxidation of ferritic stainless steel (FSS) with minor addition of Nb and Ti elements has been carried out at 800 °C in air for 70 cycles. Thermal cycling consists of 1 h heating in furnace followed by 15 min cooling to room temperature outside the furnace. The weights of all the specimens were measured every 1 cycle. The specimens were examined by scanning electron microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDS). The purpose of making this alloy was for application in solid oxide fuel cells (SOFCs) interconnects. The addition of minor alloying elements, especially Nb, led to formation of Laves phases in oxide/metal interface and prevented the diffusion of cation to the oxide scale. It is also a barrier for the influence of the oxygen anion to the inward of the FSS. The presence of high amount of Nb and low amount of Ti were effective on improving of the oxidation. By increasing amount of Ti compare to Nb in this steel caused the increased oxidation rate.

Introduction

Energy in the form of electricity remains at heart of development of the modern technological civilization. Efficient utilization of natural resources along with exploration of renewable and alternative energy sources is an important challenge facing this generation [1]. Fuel cells have been considered as one of the most promising energy conversion technologies due to their high efficiency, excellent partial load performance, quiet operation and low pollution emissions in comparison with other technologies [2]. Fuel cells are electrochemical devices that convert the chemical energy of a fuel into electrical energy directly. Fuel cells are a clean, quiet and efficient energy conversion technology and have been considered to be an advanced alternative to conventional

* *Corresponding author*. Tel.: +98 915 372 8309.
E-mail address: safikhani_64@yahoo.com (A. Safikhani).
http://dx.doi.org/10.1016/j.ijhydene.2016.01.090
0360-3199/

combustion technologies for power generation [3]. Solid oxide fuel cells offer an efficient means to convert chemical energy to electricity, with potential applications in transportation, distributed generation, remote power, defense, and many others [4]. Depending on the type of the electrolyte, they are operating at temperature levels of more than about 750 °C up to 1000 °C [5]. A single cell of the SOFCs consists of two electrodes (cathode and anode) separated by a solid oxide material acting as electrolyte. To generate adequate system voltages, individual fuel cells are joined by interconnects to form a fuel cell stack The interconnect has two main roles: transmitting the generated electricity to the external circuit and separating the fuel and oxygen paths in the stack [6,7]. The interconnect material must fulfill certain prerequisites. It must have a similar thermal expansion coefficient (TEC) compared to the other ceramic parts in the cell, provide mechanical support to the stack, be gas tight, and have high electrical conductivity as well as low contact resistance with the electrodes. It must also be stable in both high pO_2 (air on the cathode side) and in low pO_2 (the fuel environment on the anode side) environments as well as inexpensive to manufacture [47]. Metallic alloys are able to be used as interconnects in SOFC stacks with benefits of high electrical and thermal conductivity, excellent manufacturability and low cost [48]. Among various metallic materials, Cr_2O_3-forming alloys such as ferritic stainless steel (FSS) has advantages of its thermal expansion coefficient compatible with cell components, cheap material cost compared to Ni base alloys [6,8]. However, the high electric resistivity oxide scales formed on the surface of a metallic interconnect may increase the contact resistance between an interconnect and its adjacent components, thus creating a significant electrical power loss at the electrode/interconnect interface. Moreover, the volatile chromium species, such as CrO_3 or CrO_2 $(OH)_2$, from metallic interconnects have a tendency to be deposited at the triple-phase boundaries of the cathode/electrolyte/gas interface, thus resulting in the rapid degradation of the electrical properties of an SOFC cell [9–11]. There are two ways to solve this problem: a) coating and b) alloy design.

Protective coatings can be useful; such as perovskite coating materials: (LaSr) CoO_3, (LaSr)CrO_3, (LaSr)MnO_3, have been studied extensively and they are not very effective in general because of the diffusion of chromium through the coatings and potential formation of thick interfacial reaction layers. There are several conductive spinel coatings, such as $MnCo_2O_4$, $Mn_{1.5}Co_{1.5}O_4$, $(Cu,Mn)_3O_4$ [12]. There are also other covers such as $NiFe_2O_4$ spinel coating [13], yttrium/cobalt [14], novel Nb doped $Ti_3(Si_{0.95}Al_{0.05})C_2$ solid solution [15], a spinel $Mn_{1.5}Co_{1.5}O_4$ and perovskite $La_{0.60}Sr_{0.40}FeO_3$ mixture is coated on Crofer alloy by Fatma Aydin Unal et al. [42], for corrosion and chromium protection in the cathode side of a SOFC. Their Results show that uncoated interconnect experienced a significant performance lost from 4.5 W to 3.8 W. On the other hand the cells with screen printing coated with a mixture $Mn_{1.5}Co_{1.5}O_4$ and $La_{0.60}Sr_{0.40}FeO_3$ exhibited decreases only from 5.78 W to 5.42 W in the short-term performance tests. There are also dual layer coatings method on SUS430 steel by in-situ phase formation for solid oxide fuel cell interconnects. The duel layers are Co_3O_4 and $La_{0.6}Sr_{0.4}CoO_{3-\delta}$− $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ [43]. Their results show that the interconnect with dual layer coatings exhibits a reduced area-specific resistance (ASR) of 22.8 mΩ cm^2 as compared to uncoated one with ASR of 64 mΩ cm^2 after isothermal oxidation at 800 °C for 200 h. Also in the case, Kathryn O. Hoyt et al. [44] were investigated oxidation behavior of $(Co,Mn)_3O_4$ coatings on preoxidized stainless steel for solid oxide fuel cell interconnects. Recently, Jinhua Xiao et al. [45] improved the performance of SUS 430 alloy as a metallic interconnect material for intermediate-temperature solid oxide fuel cell by coating $MnCu_{0.5}Co_{1.5}O_4$ spinel.

Alloy design is another approach that is receiving some attention as well. In particular, minor alloying additions of Mn, Ti and/or of reactive elements like Y, Ce and La, have been shown to be very effective in alleviating scale volatilization by promoting formation of spinel or second phases with lower chromia activity on the scale surface [16]. Some of alloying elements in the FSS such as Y, La, Ce [17] and Zr [18], are reaction elements where the alloys are also known for promoting oxidation resistance, scale adherence and conductivity. Adding a low amount of laves phase formation elements (Nb, W, Ti, Mo) to traditional Fe-Cr alloys (such as SUS430) is effective to control the elemental diffusivity at the alloy grain boundaries by forming a laves type phase in air [19]. Reported that Nb, W and Mo are commonly added to FSS to improve the mechanical property of the high temperature strength, oxidation resistance, creep resistance and reduction of ASR [20,21]. However, adding excessive amounts of these elements can also have disadvantages such as formation of brittle intermetallic secondary phases. These brittle intermetallic phases are generally known to degrade the impact toughness and corrosion resistance of the alloys [22]. For example, if the high amount of Nb is added to the FSS, the Nb will precipitate as Fe_2Nb in the grain boundaries [23]. The addition of Ti is also effective to reduce Cr evaporation rate of ferritic stainless steel [24,25]. However, if the amount of Ti is too high, oxidation rate and ASR will increase [24] and it is reported that by increasing in amount of Ti from 0.25wt% to 0.50wt% in the FSS, the Cr evaporation resistance decreases [26]. In recent years, a new strategy has proposed to control the cation diffusivity at the alloy grain boundaries: the addition of Mo into FeeCr alloy is effective to control the cation diffusivity at the alloy grain boundaries by forming Laves-type phases in air atmosphere [36]. In this case, Safikhani et al. [46] by addition Ni and Mo in ferritic stainless steel witch was used for solid oxide fuel cells interconnect, their results show that the doped elements in the steel can improve performance of the SOFCs such as increase the electrical conductivity and improve the oxidation rate. Therefore, this work has been focused to investigate the high temperature cyclic oxidation behavior of ferritic stainless steel for use in SOFCs interconnects in air at 800 °C.

About Nb and Ti

Fig. 1 shows the Ellingham diagram for the oxidation reaction of the Fe, Cr, Nb and Ti elements. Ti and Nb are oxygen active elements. The applications of Nb are a result of several favorable properties: has a relatively low density, high melting temperature (2468 °C), corrosion resistance against many acids, low neutron capturing cross section, as well as excellent