Corrosion Science 106 (2016) 172–178

Contents lists available at ScienceDirect

Corrosion Science

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

Reduction of chromium volatilisation from stainless steel interconnector of solid oxide electrochemical devices by controlled preoxidation

Wichitra Wongpromrat[a,b], Grégory Berthomé[b], Valérie Parry[b], Somrerk Chandra-ambhorn[c], Walairat Chandra-ambhorn[a], Céline Pascal[b], Alain Galerie[b,*], Yves Wouters[b]

[a] School of Chemical Engineering, Faculty of Engineering, King Mongkut's Institute of Technology Ladkrabang, 1 Soi Chalongkrung 1, Ladkrabang, Bangkok 10520, Thailand
[b] Univ. Grenoble Alpes, SIMaP, 1130 rue de la piscine, BP 75, Saint Martin d'Hères cedex F-38402 France
[c] Department of Materials and Production Technology Engineering, Faculty of Engineering, King Mongkut's University of Technology North Bangkok, 1581 Pibulsongkram Road, Bangsue, Bangkok 10800, Thailand

ARTICLE INFO

Article history:
Received 2 October 2015
Received in revised form 1 February 2016
Accepted 2 February 2016
Available online 8 February 2016

Keywords:
A. Stainless steel
C. High temperature corrosion
C. Kinetic parameters

1. Introduction

Solid oxide fuel cell (SOFC) is an electrochemical device converting chemical energy to electrical energy via electrochemical reactions [1]. Conventionally, it must be operated at temperatures higher than 1000 °C. Since the moulding process of the electrolyte has been improved, its ohmic resistance was reduced, so, the operating temperature of SOFC can be now reduced to intermediate temperature around 800 °C. Thus metallic materials, especially ferritic stainless steels, have been tried to be used as interconnectors [2–4] due to their high electrical conductivity, their thermal expansion matching with the other cell components and their lower cost. A technical and economic discussion is developing to decide whether it is better to use specially designed steels (Crofer 22APU from ThyssenKrupp, for example), well adapted to the technology but very expensive, or multi-purpose steels (K41X from APERAM, for example) less performing but of reasonable cost. Unfortunately, Cr from all these alloys is volatilised in the cathodic conditions of SOFCs which use O_2 and H_2O as oxidising gases. The main volatilised products are chromium trioxide CrO_3 and above all chromium(VI) oxi-hydroxide $CrO_2(OH)_2$ [5–8]. These volatile species are the cause of many problems in SOFCs such as degradation of interconnect materials and Cr-poisoning leading to cathode material destruction, shorter lifetime of device, etc. [3,9–11]. The same problem arises in the reverse devices which produce hydrogen by High Temperature Electrolysis (HTE) of water vapour. In such devices, where electric energy is consumed to electrolyse H_2O on similar electrodes connected to similar stainless steel interconnectors, temperature and gas compositions are comparable to those used in SOFCs, with the same Cr-volatilisation problems in the anodic chamber of electrolysers. In the recent decades, researchers have tried to suppress Cr volatilisation from stainless steels by various methods such as developing special alloys [10] or finding interconnector protective coatings [12–14]. However, no method can be applied economically at the moment.

Preoxidation of metals and alloys in low oxygen pressure atmospheres is a method known to generate smart oxidised surfaces on alloys, different in terms of composition and morphology from

---

* Corresponding author. Fax: +33 476826767.
E-mail address: alain.galerie@laposte.net (A. Galerie).

http://dx.doi.org/10.1016/j.corsci.2016.02.002

those generated in the normal conditions. Well-adapted preoxidation was shown to strongly affect the behaviour of metallic materials in high temperature service. In the case of alumina-forming materials, for example, Matsumoto et al. [15] investigated preoxidation of a CoNiCrAlY alloy in the oxygen partial pressure range 0.2–10^{-17} bar and showed that life time in servic – after being covered by a thermal barrier coating – depended on the preoxidation conditions. Their conclusions confirmed the results of Nijddam et al. obtained on a $\gamma - \beta$ alumina-forming bond coat [16]. It is also admitted that low oxygen pressure preoxidation strongly reduces the sensitivity of alloys to carburisation or metal dusting [17,18]. Other service properties may also be improved, like in the work by Stack et al. who used preoxidation of the chromia-forming alloy 800H to reduce its rate of erosion–corrosion and demonstrated that a low-oxygen partial pressure H_2O/H_2 atmosphere was the most efficient [19]. In terms of scale chemistry, low oxygen pressures suppress the formation of higher valence oxides. For example, Latu-Romain et al. recently showed that a 25Cr-NiFe alloy, pre-oxidized at 1050 °C for 20 min in a very low oxygen potential atmosphere, formed an oxide scale where iron(III) and Ni(II) were absent from [20].

The easiest way to apply low O_2 potential to a metallic surface is to use either argon or a CO_2/CO mixture. Argon is a very popular gas used for preoxidation when O_2, present as an impurity, is required in very low amount (in the ppm order). In flowing argon the oxygen potential is not buffered and oxidation kinetics of metals is generally limited by the transfer of O_2 molecules from the gas or by adsorption onto the formed oxide. It was observed that surface composition of ferritic steels did not significantly change after preoxidation in Ar compared to pure O_2 or air, with the formation of Cr_2O_3, $MnCr_2O_4$ spinel and TiO_2 [21]. Recently, Magdefrau et al. [22] confirmed that preoxidation of Crofer 22 APU in Ar at 1050 °C did not change the chemistry of the scale, but modified the nucleation rate of Cr_2O_3 and $MnCr_2O_4$ spinel, increasing the thickness of the spinel layer and improving the oxidation resistance. Unfortunately, these authors did not investigate chromium volatilisation. On another hand, preoxidation in CO_2/CO mixtures imposes much lower oxygen partial pressures than argon, with a buffering effect which makes it stable. Gulsoy and Was exposed Alloy 617 (22% Cr, Ni-based) at 750–850 °C to CO_2/CO mixtures with $P(O_2)$ in the range 10^{-26}–10^{-21} bar [23]. They confirmed that, in such conditions, the formed chromia scale exhibited *n*-type conduction only, contrary to what is observed at O_2 pressures closer to the atmospheric pressure. As a side-effect, preoxidation in CO_2/CO mixtures may induce carburisation and metal carbides could form in the inner part of the oxide layer or in the metal subsurface [5,24].

For studying the influence of preoxidation on chromium volatilisation, these two atmospheres (Ar and CO_2/CO) were chosen in order to produce a surface oxide different from that forming in service conditions. Two temperatures were studied, 850 and 250 °C. At the temperature of 850 °C, in the same range as service conditions, thermodynamic equilibriums are thought to be achieved and diffusion phenomena in solids are rapid. At the lower temperature of 250 °C, the opposite situation is observed, where kinetic phenomena take over thermodynamics and mass transport in solids is extremely slow.

In this paper, thin preoxidation films on AISI 441, the commercial ferritic stainless steel stabilised by Ti + Nb, were grown in the conditions described above. Bare AISI 441 samples and preoxidised samples were subsequently oxidised at 800 °C in O_2-5%H_2O (SOFC cathode or HTE anode atmosphere) in order to measure Cr volatilisation. Comparison was made between preoxidised or bare steel and the effect of preoxidation was assessed and discussed.

2. Experimental

2.1. Specimen preparation and preoxidation

AISI 441 sheet (K41X commercial denomination) supplied by APERAM (Isbergues, France) in the 2B finish (cold rolled, annealed, pickled, skin-passed) has the chemical composition shown in Table 1. Samples were cut into dimensions of about $12 \times 12 \times 1\ mm^3$.

The cut specimens were ground on SiC papers up to 1200 grit. Several non-ground samples (as-received) were also tested and it was observed that abrasion slightly reduced the chromium volatilisation rate by a maximum of 5%, possibly due to roughness decrease. In the following, all results concern grounded samples. The specimens were preoxidised in 4 different conditions as discussed in the introduction section. Details are shown in Table 2. The preoxidation furnace was fed by high purity Ar (flow rate 13.7 L h^{-1} at room temperature) or by the CO_2/CO mixture (11 L h^{-1} with equimolar ratio CO_2:CO = 1:1). The oxygen partial pressures imposed by these atmospheres are reported in Table 2. The specimens were preoxidised in each condition for 3 h after a temperature ramp increase of 20 °C min^{-1}. After cooling, they were subsequently characterised and used for volatilisation testing.

2.2. High temperature volatilisation experiments

High temperature experiments were performed in order to observe Cr volatilisation from the bare and preoxidised specimens. Fig. 1 shows the experimental setup used for that purpose. The samples were hung inside the quartz tube sitting in the vertical electrical furnace held at 800 °C. A humidifier set was used in order to adjust humidity in the gas stream (5%H_2O in O_2) before flowing to the samples. The linear velocity of the gas was varied in the range 1–10 cm s^{-1} (actual velocity in the hot tube furnace). The duration of the experiments was 96 h. At the outlet of the furnace, a water-containing condenser was installed. It was controlled at 7 °C by a thermo-cryostat in order to condense all Cr volatile species. The gas was further flowed to a second bubbler for making sure that there was no Cr remaining in the outlet gas stream. After the experiment, the quartz tube and the condenser were cleaned by 0.1 mol L^{-1} hydrochloric acid and the collected solution was added to the condenser solution which was analysed by inductively coupled plasma (ICP) to measure the amount of volatilised chromium. A majority of the experiments was repeated in identical conditions and the experimental error on the volatilised mass was determined to be ±10%. The results are presented in the following as the mean chromium volatilisation rate over the duration of 96 h. No measurements were made at intermediate durations which could assess instantaneous volatilisation rate evolution with time. It is known from our experience, also shown for example by Stanislowski et al. [10], that the instantaneous volatilisation rate from bare stainless steel decreases with increasing time, predominantly in the first 100 h of oxidation. However, to get a simple comparative view, the choice was made in the present paper to measure the total amount volatilised from bare and preoxidised materials over the duration of 96 h only, without attempting to determine instantaneous values.

2.3. Characterisation of the preoxidised samples

The preoxidised specimens were observed by surface optical and scanning electron microscopy. They were characterised for phase determination by Raman spectroscopy (Ar^+ laser, 10 locations on each specimen) and X-ray diffraction (Cu Kα radiation). X-ray photoelectron spectroscopy (XPS) was also used to deter-