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Coatings for improvement of high temperature corrosion resistance of porous alloys

S. Molin[a,*], M. Gazda[b], P. Jasinski[a]

[a] Gdansk University of Technology, Faculty of Electronics, Telecommunications and Informatics, Narutowicza 11/12, 80-233 Gdansk, Poland
[b] Gdansk University of Technology, Faculty of Applied Physics and Mathematics, Narutowicza 11/12, 80-233 Gdansk, Poland

Abstract

Porous alloys are proposed as supports for the next generation solid oxide fuel cells. Their application lowers the price of the fuel cells, which will result in faster commercialization. However, they are prone to high temperature corrosion. So far, there is lack of methods, which can improve high temperature properties of porous alloys for SOFC applications. A method for improving corrosion resistance of porous alloys has been proposed and investigated here. In this work protective coatings are prepared by the infiltration of precursor solutions that contain Y cations. High temperature oxidation properties of the modified alloys are compared with non-modified samples by cyclic thermogravimetry, electron microscopy and X-ray diffractometry measurements. The infiltration of Y precursor into the porous alloy decreases the high temperature corrosion rate. This method can be used to improve long term properties of porous alloys applied for fuel cells supports.

Keywords: B. Composites; C. Corrosion; D. Y_2O_3; E. Fuel cells

1. Introduction

Porous alloys are materials of choice for the next generation of solid oxide fuel cells (SOFCs).[1,2] For that application they must withstand thousands of hours at ~800 °C without severe degradation. Other possible applications of the porous alloys include medical implants, air filters, flow restrictors, sound attenuators and other. In the case of the high temperature exposure (>500 °C), which takes place in both anode and cathode SOFC compartments, an oxide scale forms. This can cause changes in porosity and in mechanical properties, which might result in restricted gas flow and in a mechanical failure.

In SOFCs the porous steel is used as a substrate for the deposition of ceramic components. In this case the alloy needs to provide appropriate mechanical strength of the fuel cell and easy access of gas to the electrodes. Typical porosity of the supports is approximately ~30 %. The high porosity results in a high specific surface area subjected to an oxidation and a growth of oxide scale. The formation of the oxides results in a decrease of porosity and an increase of interfacial electrical resistance. For example, it was shown that a breakaway oxidation of Fe22Cr stainless steel occurs at operating conditions of SOFCs, which results in rapid degradation of cell performance caused by blocked gas conducts in the support.[3]

The corrosion rate of porous alloys is very high, resulting in significant mass gain in a relatively short time.[4–7] The number of alloy materials available in powder form is limited. Main requirement for alloy is to be a chromia scale former, since chromia provides good electrical conductivity level and acts as a protective scale. Unfortunately, the chromium content in alloy composition, that is sufficient for dense steels, seems insufficient for porous alloys. Large area available for chromium scale formation causes problems with breakaway oxidation. For long term stability of metal supported fuel cell, the corrosion resistance plays a vital role and must be enhanced.

The degradation issues of dense stainless metallic plates are often solved by applying protective coatings on the surface.[8,9] It diminishes the rate of the oxide scale formation and lowers interfacial electrical resistance. Numerous properties of coatings on dense steels were investigated and reported in the literature.[9–12] However, to the best of our knowledge, the improvement of corrosion resistance of the porous alloys for SOFC applications by the introduction of coatings has not been reported before.

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* Corresponding author.
E-mail address: molin@biomed.eti.pg.gda.pl (S. Molin).

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2. Experimental

The porous supports were prepared using PI600 alloy powder (Ametek, USA), which is designed to work at elevated temperatures.[7] It is an austenitic Ni based alloy (∼74 wt.%) rich in Cr (∼16 wt.%) and Fe (9 wt.%). Powders were weighted (∼1.2 g) and uniaxially pressed (200 MPa) in a steel die (16 mm diameter). Afterwards samples were sintered at 1200 °C for 30 min in dry hydrogen atmosphere. Before switching on hydrogen flow, tube was flushed with Ar. The initial porosity of the porous supports was around 25%. Solution for the infiltration was prepared by dissolving yttrium chloride (Aldrich, USA) in ethanol. The substrates were then placed in a petri-dish and a few drops of solutions were added, which penetrated the pellets due to capillary forces. The pellets remained in a dish for 10 min followed by drying at 50 °C for 15 min. Then the pellets were heated up to 400 °C to decompose organics. This soaking/calcinations procedure was repeated several times to achieve the desired mass change (up to 2 wt.%). Modified and non-modified samples were then subjected to cyclic oxidation tests at 800 °C. Each cycle lasted 150 h at dwell temperature with 3 h heating and cooling times. Before and after each cycle the samples were weighted. Between the cycles also porosity was checked by Archimedes method using dedicated balance setup (Radwag, Poland) and vacuum assisted kerosene soaking of samples to ensure filling of pores. The measurement procedure included recording of weight of dry sample, sample soaked with kerosene and sample immersed in kerosene, what allows calculation of total, open and close porosity. Total number of cycles was 7, what resulted in the total oxidation time of 1050 h. Analysis of sample properties was then performed by scanning electron microscopy (Philips XL30 ESEM) and X-ray diffractometry (Philips X'Pert Pro) of the surface. X-ray diffractometry (XRD) measurements were collected with CuKα radiation at room temperature at a standard 2θ configuration.

3. Results and discussion

3.1. Infiltration of the protective phase

Yttrium was chosen as an infiltration material due to its ability to improve high temperature properties of steels by the so called rare-earth effect. In the past, this precursor was successfully used to prepare coatings on dense steels also for SOFC applications.[10,13,14] In this study corrosion tests were carried out in air atmosphere, which resembles cathode compartment conditions of the fuel cells.

Mass gain of samples as a function of infiltrations number is presented in Fig. 1. After 20 infiltrations the mass gain was approximately 2% with a linear correlation between the mass gain and the infiltration number. Each infiltration resulted in about 0.1% mass change. The mass change of 2 wt.% corresponds to approximately 2.5 vol.% change. Using the proposed procedure a desired amount of protective phase can be introduced into the alloy support. Namely, the alloys with 1 and 2 wt.% of protective phase were prepared and investigated. The results were similar for both Y loadings and, therefore, only results on ∼1 wt.% infiltrated alloys (10 infiltrations) were presented here. The porosity difference between these samples was within the order of measurement accuracy (approximately 2%).

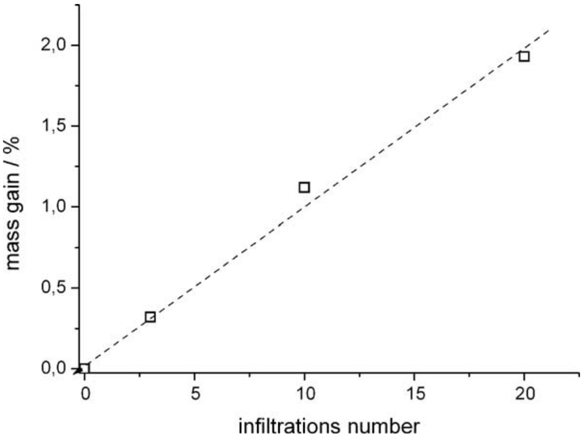

Fig. 1. Mass gain as a function of infiltration number for porous steels.

3.2. High temperature oxidation results

Kinetics of high temperature corrosion is usually expressed by mass gain per unit area of samples.[10] This corresponds to an oxide scale growth and resulting mass change of samples. However in case of the porous samples the situation is more complicated. The surface area is not known and is relatively hard to determine by experimental methods.[15] Therefore different approaches should be used. One possible way is to use percentage mass change with respect to the initial mass.[5,6] Sample mass after infiltration and after heat treatment at 500 °C is defined as initial mass. This parameter takes into account porosity level (higher porosity will cause higher mass gain). This approach is used in this study. The results of cyclic thermogravitometry of the studied samples are shown in Fig. 2. For non-modified sample after first 150 h a rapid mass increase is observed. The initial mass increases about 10%. Afterwards, the mass changes much slower and after 1050 h the total mass change of about 13% was observed. Such an initial mass change has also been shown before by Molin et al.[7] It is connected with the rapid

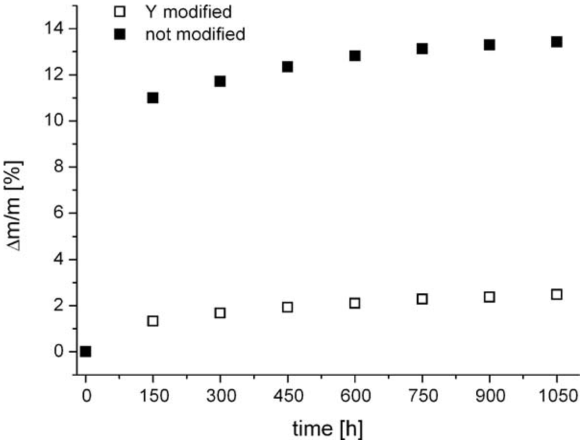

Fig. 2. Mass gain of samples subjected to cyclic oxidation at 800 °C.

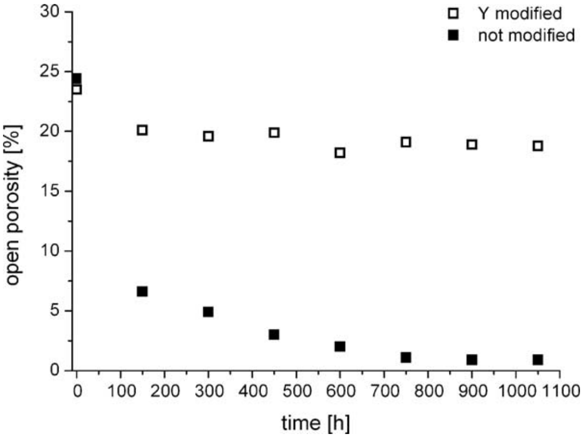

Fig. 3. Open porosity changes caused by oxidation at 800 °C.

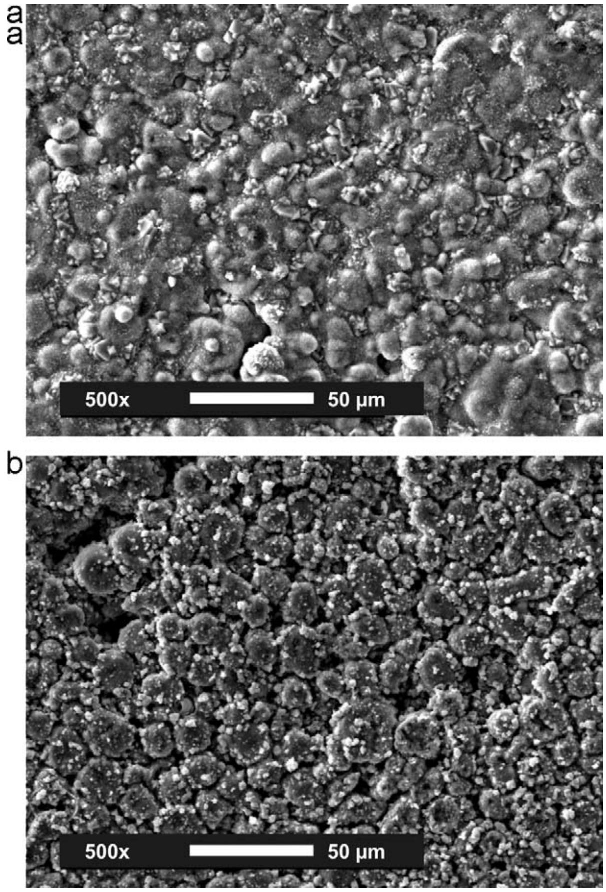

Fig. 4. SEM surface images of (a) not-modified and (b) Y-modified steels after total oxidation time of 1050 h at 800 °C.

formation of an oxide layer, followed by the slow oxide scale growth. Y-modified samples show much lower mass gain. After 150 h the mass change of less than 2% is measured and after 1050 h it increases up to 2.5 %. The first cycle is also responsible for the most of the mass gain, but in this case the total mass gain is much lower. It can be concluded here that only 1 wt.% of Y-infiltration significantly suppress the oxide scale growth.

Porosity measurements were performed to check the influence of scale growth on porosity and its structure. The recorded results of the open porosity are presented in Fig. 3. For the non-modified samples open porosity decreases rapidly with the first oxidation cycle. This result is consistent with thermogravimetry data, which showed rapid initial mass gain. Porosity drops from 25% to only about 7%. Further oxidation causes porosity decrease almost to 0%. After only 1050 h open porosity no longer exists and for a fuel cell it would end up in a total failure of performance due to gas supply shortage. For the Y-modified samples, the open porosity decreases initially by about 7% to about 18% after the first 150 h of oxidation. Afterwards open porosity remains stable up to the end of experiment. These results confirmed the superior properties of Y-modified samples. It must be added that in both cases the open porosity decrease is counter balanced by the closed porosity increase, while the total porosities remain constant (results not presented here). The open porosity decrease is caused by filling of pores and pore ducts inside sample by the corrosion products, so that finally further oxidation is limited due to gas access.

Scanning electron microscopy images of oxidized (1050 h, 800 °C) samples are shown in Fig. 4a and b. The surface of not modified sample is fully covered with corrosion products. Almost no porosity can be seen. This is in agreement with thermogravimetry and porosity data. The corrosion products filled all available space. For Y-modified samples, the surface is porous and much less corrosion products are visible. Alloy grains are still clearly visible. Corrosion products are visible as either some separated larger residues (few microns in diameter) on the surface or as a uniform corrosion scale product visible under higher magnifications.

The phases of corrosion products were evaluated using X-ray diffractometry analysis of oxidized alloy surfaces. XRD pattern of sample Y-modified and not subjected to any additional heat treatment is shown in Fig. 5. Only peaks corresponding to stainless steel phase are present. The same is for sample heat treated at 500 °C for 1 h. The impregnated Y phase is not detected by the X-ray diffractometry due to the low volume fraction of Y-containing phases and, possibly, due to their amorphous state after the deposition. The XRD patterns of oxidized samples are showing peaks originating from the alloy substrate and new peaks that can be attributed to corrosion products. The intensities of additional peaks for Y-modified sample are much lower than for non-modified, which corresponds to lower amount of corrosion products.

The oxide phases present in the patterns of not-modified steels are $NiO > NiFe_2O_4 > Cr_2O_3$ (written in accordance to relative peak intensity which is assumed to be connected to phase content). Probably, the NiO, which is present in a large amount, is responsible for the high mass gain. This oxide is not considered as a protective oxide for steel corrosion, while $NiFe_2O_4$ and Cr_2O_3 can be regarded as protective oxide scales.[9,11] In study by Molin et al. [7] similar phase composition was reported for this alloy oxidized in air in similar conditions. For Y-modified steels only $Cr_2O_3 > NiFe_2O_4$ phases are present. The predominance of the protective chromium oxide results in the low corrosion rate. In the patterns Y containing products have not been determined.

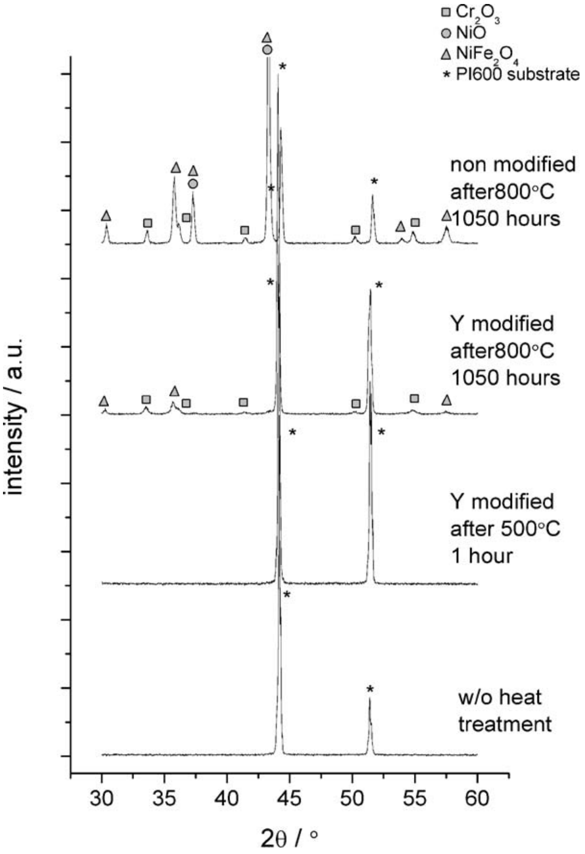

Fig. 5. XRD patterns of modified and not-modified stainless steel samples after different heat treatment procedures.

This is probably related to a very low amount of this phase that might be under the limit of measurement.

A lot of research must still be carried out in order to fully describe the protection mechanism of the infiltrated phase and their potential applicability to different fields, but initial results presented here provide the foundation for this purpose.

4. Conclusions

A new method for the improvement of high temperature corrosion properties of porous supports was reported. The infiltrated porous PI600 alloy with Y containing precursor showed reduced mass gain upon oxidation in air. The Y-modified samples remained porous while non-modified samples lost almost all of the open porosity. As revealed by SEM analysis, addition of Y inhibits formation of non-protective NiO oxide phase in the alloy. This initial study shows the opportunity of enhancing the lifetime of these porous materials, which can be suitable in many applications. Future research will focus on studying different coating materials, oxidation atmospheres and electrical conductivity.

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