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K44M ferritic stainless steel as possible interconnect material for SOFC stack operating at 600 °C: Characterization of the oxidation behaviour at early working stages

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ABSTRACT

A commercial ferritic stainless steel (FSS) known as K44M (Type 444, according to ASTM A 240, DIN 1.4521 according to NF EN 10088-2) was aged in static air in two differing thicknesses (i.e. 1.5 and 0.4 mm) at a thermal cycle corresponding to the curing phase of an experimental glass used as sealing in solid oxide fuel cell (SOFC) stacks, and to an ageing process in air of 200 h at 600 °C.

The characterization performed on the aged samples after the complete treatment and at each step of the thermal cycle allowed to investigate the scale formed depending on the temperature and to the thickness of the samples.

Introduction

For more than one decade ferritic stainless steels (FSSs) are considered as the best candidates to manufacture interconnect for stacking solid oxide fuel cells working at intermediate temperature (600–800 °C, IT-SOFC) due to their CTE match with the ceramic components, excellent formability, and affordable cost [1,2]. Moreover the FSSs suitable as interconnects in SOFC stacks need to show an adequately low oxidation rate and to form of a protective and conductive scale, as is the case of chromia former steels with Cr content usually higher than 16 wt.%. Numerous studies [3–6] have been carried out with the aim to understand the behaviour

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of different steels used in air at high temperature with or without protective coatings. The attention is nowadays focused on commercial FSSs among other reasons to facilitate the breakthrough into the SOFC stack market [1–4,6–11].

This paper refers to the first results on a wider research program aimed to the investigation of the oxidation behaviour of commercial FSSs from the first starting process to each stage of operation of a stack. This is in order to point out the evolution of thermal grown oxide (TGO, which is the focus of this paper), the interaction among materials and the influence of environmental parameters (which will be discussed elsewhere). In the research achievements discussed hereafter the very first stages of a real stack are simulated as specific thermal treatments from the point of view of the metallic interconnect. As a matter of fact the first step corresponds to the sealing curing process, and to the first 200 h of operation at a working temperature of 600 °C. In the simulated thermal treatment the atmosphere was the steady laboratory air and no current or mechanical load were applied, as is the case for glass sealing process.

In order to investigate the natural oxidation of the selected FSS, namely K44M provided by Aperam in two different thicknesses (1.5 and 0.4 mm), no coatings were added. The temperature was selected on the basis of the recent advances in SOFC that showed the possibility to work with cells at 600 °C while keeping the efficiency high enough to remain in the interest of an industrial scale up [12–15] as is the case of the promising dual membrane cells [16].

In oxidizing atmospheres and at SOFC operating temperatures, volatile $Cr^{(VI)}$ species (e.g., CrO_3 and $Cr(OH)_2O_2$) are formed by reaction of the chromia scale, poisoning the cathode and the sealing; this results in a rapid degradation of the cell performance in terms of: reduction of the cathode catalytic activity and increase in the ion transport resistance at the cathode-electrolyte interface [17]; the sealing changes its mechanical properties and lowers the gas tightness. The application of a coating on the cathodic side of an interconnect represents a good solution to face the degradation of the aforesaid cell components [6]. Nevertheless not all the FSS components are coated (e.g. the anodic side of the interconnect and other structural parts of the stack as those in correspondence with the gases entrance and exit) and chromium base vapours can enter in to the stream. Stainless steels used for the manufacturing of different parts of a stack have different thicknesses depending on their purpose: the interconnect is usually thin, in order to allow an easier shaping, whereas structural parts are thick and not coated.

A study focused on the understanding of TGOs formation on stainless steel sheets with different thicknesses and during the very first stages of a stack turns out to be interesting both for the definition of the parameters for an adequate stack modelling and for encouraging the introduction of coatings in different areas of the stack.

Working at 600 °C opens other issues as the high risk of second phase precipitation (i.e. σ phase in the Fe–Cr equilibrium diagram) for Cr content higher than 20 wt.% [18,19]. This increases the attractiveness of commercial FSSs with concentration of chromium in the range 11–19 wt.% [20].

Experimental

Materials

One commercial FSS K44M (Aperam), also known as Type 444 (Eu designation X2CrMoTi18-2, DIN 1.4521) was selected for this study in order to evaluate its behaviour and suitability for further studies and applications in stacking of IT-SOFCs.

The nominal composition of the FSS is shown in Table 1.

This FSS is of particular interest by its suitability in applications where an excellent stability in critical environments such as high pressure water vapour is demanded: manufacturing of hot water tanks, boilers, fume ducts, heat exchangers. Moreover carbon and nitrogen are stabilized by the presence of niobium which inhibits chromium carbides precipitation thus avoiding, at high temperature, Cr depletion at grain boundaries. This would increase the sensitivity to oxidation of the ferritic matrix nearby the precipitates (i.e. grain boundary among the carbide and the metal) causing a decreased oxidation resistance.

The K44M matches all properties requested to an interconnect in SOFC stacks:

- it is a chromia former;
- it has a mean coefficient of thermal expansion (CTE, α) $11.9 \cdot 10^{-6}$/K between 20 and 800 °C;
- at high temperature, it exhibits a high oxidation resistance, particularly in cyclic oxidation, which allows its use up to 1050 °C.

The expansion coefficient of the K44M is closer to those from oxide layer which is developed, compared to austenitic grades. The thermal stresses are also much lower. Practically no scaling of the layer is observed. This results to a low material loss.

Rectangular coupon samples, 2 × 3 cm × cm sized, were mechanically cut from two set of the FSS differing in thickness (i.e. A = 1.5 mm, and B = 0.4 mm). A total of 120 specimens were prepared and divided into two groups called GA and GB respectively according to their thickness. Samples of group A were cut from a sheet cold rolled at the manufacturing site of the firm while those from group B where further cold rolled at the R&D facility of Aperam.

Ageing

The FSS specimens were introduced as-rolled in the muffle furnace after simple degreasing and rinsing. No further surface treatments were applied in order to preserve the surface state due to the industrial rolling process. The overall thermal cycle applied to age the FSS in air corresponds to the curing process of an experimental glass base powder used to seal the

Table 1 – K44M nominal composition according to Aperam.

Elements	C	Si	Mn	Cr	Mo	Nb	N	Fe
wt.%	0.015	0.4	0.3	19	1.9	0.6	0.015	Bal.