INFLUENCE OF HEAT TREATMENTS ON YSZ ELECTROLYTE FOR SOFC MANUFACTURED BY HVSFS

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High-velocity suspension flame spraying (HVSFS) is a promising technology to manufacture yttria stabilized zirconia (YSZ) as solid electrolyte for solid oxide fuel cells (SOFC). In this paper isothermal ageing and thermal cycling have been carried out in order to evaluate their microstructural and mechanical stability. X-ray diffraction (XRD), scanning electron microscopy (SEM) and focused ion beam (FIB) techniques have used to analyze the microstructure of YSZ electrolyte before and after ageing at high temperature. Elastic modulus has been monitored by nanoindentation, while scratch tests have been performed in order to estimate the influence of ageing on the interface electrolyte/anode adhesion.

INTRODUCTION

Hydrogen based energy systems represent one of the most promising ways to realize sustainable energy (EUR 20719 EN [1]). Compared with conventional systems, fuel cells provide a very efficient conversion device for converting hydrogen into electricity by electrochemical reaction. Moreover, with the use of hydrogen in fuel-cells systems, carbon emissions are very low and no emissions of harmful ambient air substances like nitrogen dioxide, sulphur dioxide or carbon monoxide (Xia et al [2]). SOFCs are an attractive option relative to other fuel cells because they exhibit greater fuel tolerance, higher efficiencies, and produce high-grade waste heat making them suitable for combined heat and power applications. Nevertheless, cost and stringent durability requirements at high operating temperatures have limited their entrance into main stream power markets (Stambouli and Traversa[3]). As a result, new electrolyte materials and production techniques for higher ion conductivity and reduced thickness are searched to reduce SOFCs operating temperatures (Will et al [4], Kim et al [5]). High velocity suspension flame spraying (HVSFS) is a technique which is able to create a dense electrolyte layer, i.e. Yttria Stabilized Zirconia (YSZ), by spraying nanosized oxide materials (Gadow et al [6]). In the present study, an evaluation of the microstructural and mechanical stability of YSZ electrolyte deposited by

HVSFS has been performed under conditions of isothermal ageing and thermal cycling experimental procedure.

Studied samples were provided by Institute for Manufacturing Technologies of Ceramic Components and Composites (IMTCCC) of the University of Stuttgart. The substrate material is a Crofer 22APU steel developed for SOFCs applications by ThyssenKrupp. The anode on the substrate is a Nickel-8YSZ (8 mol% yttria-stabilized zirconia) deposited by atmospheric plasma spraying (APS). On top of the anode 8YSZ electrolyte was finally deposited by HVSFS. In order to study the system, the initial circular cells with a diameter of 48 mm and 1.2 mm thickness were cut with a diamond disc to samples of 15 mm x 10 mm.

Samples were oxidized in ambient air at 800 ºC. Isothermal oxidation tests were performed holding this temperature during 300 and 400 hours and then cooling to room temperature. A lifting oven was used to carry out for the cyclic oxidation tests. Each cycle consisted of an isothermal holding at 800 ºC followed by cooling at room temperature during 15 minutes. The number of cycles applied was 300 and 400.

The effect of these high temperature exposures on the microstructure of 8YSZ electrolyte was analyzed by means of scanning electron microscopy (SEM), focused ion beam (FIB) and X-ray diffraction.

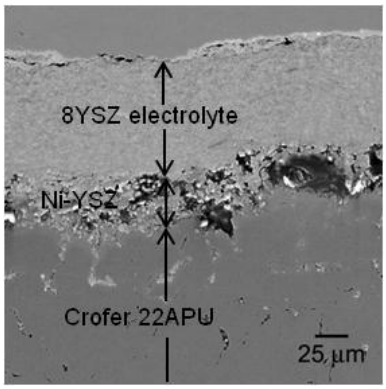
Nanoindentaion tests were carried out with a MTS nanoindenter XP instrument with a Berkovich indenter at constant deformation rate of 0.05 s^{-1} up to a depth of 2000 nm. Young's modulus was determined by a continuous stiffness module (CSM), which allows a dynamic determination of the Young's modulus during indentation. Values were obtained by the method developed by Oliver and Pharr [7]. In each experiment, 10 indentation measurements were made at the 8YSZ electrolyte on the cross section of the sample before and after high temperature exposure.

Scratch tests were performed under ambient conditions in a CSM-REVETEST automatic scratch tester using a Vickers indenter. The initial load applied at the surface was 1.5 N which was increased progressively up to 120 N along a distance of 12 mm at 10 mm/min.

RESULTS AND DISCUSSION

Figure 1 shows cross section morphology of the as-received specimen where 8YSZ electrolyte, Ni-YSZ anode and stainless steel Crofer 22APU are clearly differentiated. The electrolyte has a thickness between 80-90 μm and has a dense and compact structure compared with the anode.

FIGURE 1: SEM micrograph of cross-section of an as-received specimen.



A detailed observation of the electrolyte by FIB showed the presence of some pores and little cracks mainly parallel to the surface see Figure 2. X-ray diffraction spectra of the electrolyte showed peaks corresponding to cubic phase with no evidence of any other crystalline structure.

FIGURE 2: FIB section through 8YSZ electrolyte

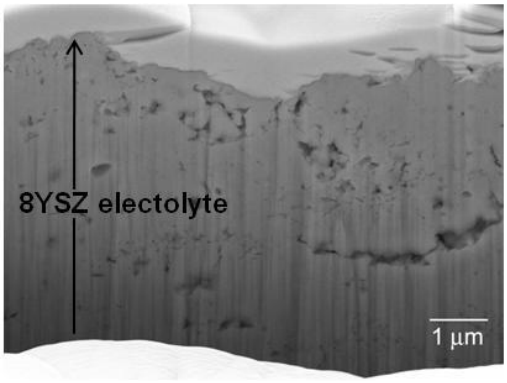
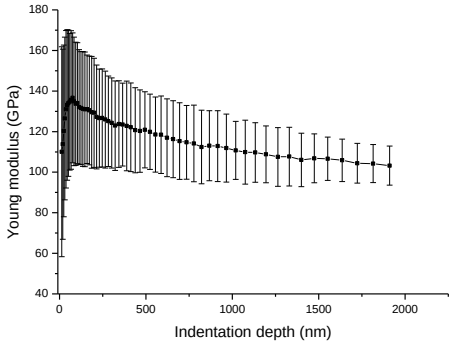


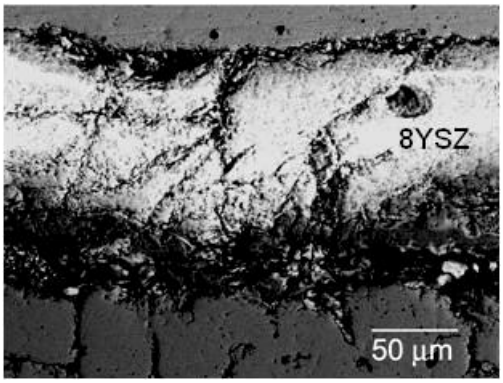
Figure 3 shows the evolution of the Young's modulus with penetration depth. It is interesting to note that the dispersion of values decreases and becomes homogeneous at depth of about 1000nm, with an average value of 105 GPa. This phenomenon can be attributed taking into account that indentations are initially performed in or near some pores or short cracks which leads to very low values. As the indentation depth is higher there is no dependence on the initial site of the indentation.

FIGURE 3: Evolution of the Young's modulus with the indentation depth.



Isothermal ageing and thermal cycling at 800 ºC induced the formation of cracks in the electrolyte. Specimen cross-sections were examined by SEM and revealed that cracks growth into the electrolyte to the anode and some of them parallel to the surface, Figure 4. However, the analysis by EDS (Energy Dispersive X-ray Spectroscopy) did not show any diffusion of Nickel to the surface. X-ray diffraction patterns taken after exposure at high temperature were similar to the as-received material, only the peaks corresponding to cubic phase were observed.

FIGURE 4: SEM micrograph of cross-section of a specimen aged at 800 ºC during 300 h.



Nanoindentations performed at the centre of the electrolyte after heat treatments showed no difference on average of Young modulus, probably because of the small size of indentation imprints (9 µm) and because all of them were located away from thermal defects.

Scratch results showed the detrimental effect of high temperature exposure. The adhesion to the anode decreased especially for samples subjected to thermal cyclic oxidation. In this case, 120N were enough to cause the delamination of 8YSZ electrolyte.

CONCLUSIONS

In this work, the influence of heat treatments on 8YSZ electrolyte for SOFC manufactured by HVSFS was studied. After isothermal ageing and thermal cyclic oxidation at 800 ºC, electrolyte showed microstructural stability and similar values of Young modulus.

However longitudinal and transversal cracks were induced in the electrolyte and anode adhesion decreased especially for samples subjected to cyclic oxidation.

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