Formation of a defect-free electrolyte film of solid oxide fuel cell by the method of reactive magnetron sputtering of a ZrY target[1]

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Abstract – The paper presents the results of investigations of the morphology, microstructure, phase composition and texture of yttria-stabilized zirconia (YSZ) thin films obtained by a reactive magnetron sputtering method. Experiments on the electrolyte film sputtering were carried out using two types of magnetron power sources: a DC power source and a bipolar pulsed power source. Sputtering of the coatings was realized in Ar/O_2 atmosphere onto the anode ceramic substrates (60 vol. % Ni + 40 vol. % $Zr_{0.9}Y_{0.1}O_{1.95}$) with porosity of 28 % and 45 % before and after reduction, respectively, heated up to the temperature of 300 °C. The thickness of the coatings was of 2–8 μm. It is shown that the magnetron sputtering combined with such method of surface modification as a preliminary ion implantation of a substrate allows not only changing the morphology, structural and mechanical properties of the obtained coatings and, as a result, obtaining dense, defect-free coatings with good adhesion but also allows essentially suppressing a columnar structure of the electrolyte film. The main crystal phase of the sputtered coatings is a cubic zirconia oxide (ZrO_2) oriented in the direction of (111).

1. Introduction

A necessary condition for transition to a wide application of solid oxide fuel cell (SOFC) is development of a reliable and economically sound technique for creation of a single fuel cell element (FCE). Exploitation characteristics of FCE are determined by the structure, stoichiometry and phase composition of an electrolyte film such as yttria- stabilized zirconia (YSZ) that, moreover, should be absolutely gas-tight. Most often, the reasons worsening gas impermeability of a YSZ film is availability of different defects in it such as cracks and exfoliations [1, 2] as well as its columnar structure [3, 4] due to the film growth mechanism inherent to the given material.

Different methods of electrode surface modification allowing eliminating defects of porous substrates, controlling dimensions of their pores that in its turn results in the growth of a thin-film electrolyte with a prescribed structure and also allows increasing catalytic reactivity of the functional layers composing FC are applied to control the above-indicated problems [5,6,7].

Other important problems restraining mass application of SOFC are their high operating temperatures (about 1000 °C) and insufficiently high specific characteristics. Electrolyte thickness decrease (usually, the thickness equals to tens of microns) to 2–8 μm allows decreasing the operating temperature to 650–800 °C [5, 8].

A promising method for SOFC structure formation is magnetron sputtering allowing obtaining coatings with prescribed structural and exploitation characteristics owing to control of the main parameters of the sputtering process.

This work is directed to obtaining a thin gas-tight electrolyte film without mechanical stresses and cracks by the reactive magnetron sputtering method. Influence of the porous substrate surface modification and namely, the preliminary substrate implantation on morphology, structure and phase composition of the obtained coatings is under study.

2. Experimental

The coatings were deposited on porous anode ceramic plates of 14-mm diameter and 2-mm thickness made of the powder mixtures (60 vol. % Ni+40 vol. % $Zr_{0.9}Y_{0.1}O_{1.95}$) that were annealed in the oxide state at the temperature of 1300 °C with the following one-hour air storage. Then their reduction was carried out at 900 °C with one-hour exposure in the moistened hydrogen. Their open porosity after oxidation and reduction was 28 % and 45 %, respectively. The dimension of the grains composing the substrate changed from 1 to 3 μm and the dimension of pores changed from 1 to 2 μm. The experiments were carried out at a vacuum setup equipped with an unbalanced magnetron sputtering system with a disk cathode of 120-mm diameter and 8 mm thickness made of the $Zr_{0.86}Y_{0.14}$ alloy. A vacuum chamber of dimensions 600× 600×600 mm ^{3} was pumped out to the residual pressure of $6\cdot10^{-3}$ Pa by means of a turbomolecular pump. The experiments were carried out in the Ar/O_2 atmosphere. Consumption of operating gases (argon and oxygen) was controlled by means of

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electronic mass flow controller. Operating pressures were changing in the range of 0.2–0.25 Pa. Prior to coating deposition, the substrates were heated to the temperature of 300 °C by means of a nichrome heater placed behind the substrate. The heating temperature was controlled by means of a thermocouple.

Two types of magnetron power sources were used in the experiments on reactive magnetron sputtering, and namely: a DC power source equipped with the arc control system and a bipolar pulsed power source. The operating voltage and the current were changed in the ranges of 330–390 V and от 4.1–5.6 A, respectively, the magnetron power was of 1, 1.5 and 2 kW. The ion current density for the DC and pulsed operating modes of the magnetron sputtering system was equal to 1.2 mA/cm^2 and 0.3 mA/cm^2, respectively. The growth rate of approximately 3 μm/h was reached at the magnetron power of 2 kW.

Preliminary surface implantation of the porous anode substrate by titanium ions was carried out at the voltage of 40 kV during 10 minutes. The dose of the implanted ions was 10^{16} ion/cm^2.

Investigations of the surface morphology and microstructure of the coating fracture were made by means of an optical microscope, scanning electron microscopy (Philips SEM-515) and atomic-force microscopy (AFM "Solver – P 47"). The X-ray structure analysis was made by means of the diffractometer XRD – 600 at CuK_α radiation. The thickness of the YSZ films was measured at the interferometer.

3. Results and Discussion

To investigate the influence of different parameters of the sputtering process on the film characteristics, the samples of electrolyte films were obtained at the porous substrates under the following conditions:

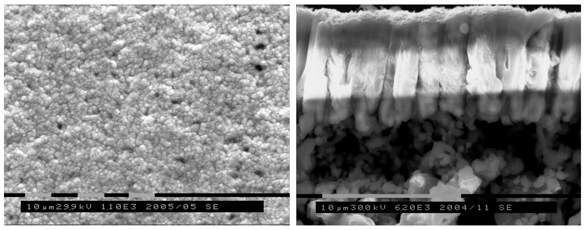
1. DC magnetron deposition (DC-mode).
2. Magnetron deposition of films onto the substrate preliminary implanted with titanium ions (DC-mode).

The analogous experiments were carried out at the magnetron power supply from a pulsed power source (pulse-DC mode).

The following results were obtained.

Fig. 1 presents the surface morphology and microstructure of the fractured cross-section of the YSZ electrolyte films obtained at the NiO-YSZ substrates by means of the DC magnetron sputtering. The surface morphology and microstructure of the fractured cross-section of the films deposited at a pulsed magnetron supply have the analogous view in all cases.

Investigations of the surface morphology (Fig. 1, *a*) have shown that the surfaces have a grain rough structure repeating the structure of the initial substrate for both sputtering modes. The grain dimension for the coatings obtained in the DC- and pulse-DC modes changes in the range of 1–2.7 μm and the roughness value (R_a) calculated for these samples equals to 120–160 nm. At the surface of some samples one could see pores that were closed not completely that testifies about insufficient thickness of the coating. In all experiments the thickness of the coatings for different samples changed from 2 to 8 μm.

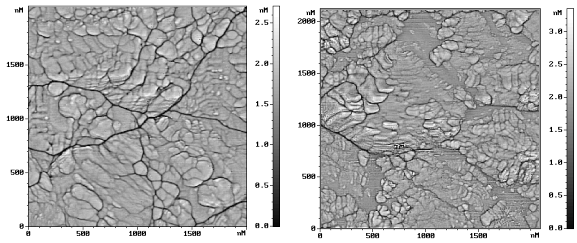


a b

Fig. 1. SEM micrographs of the surface (a) and fractured cross-section (b) of the YSZ electrolyte films obtained in the DC-mode

Investigations of the fracture surfaces of YSZ films detected the availability of a columnar structure (Fig. 1, *b*) both in the DC- and pulse-DC modes. Moreover, one can see a sufficiently well-defined border testifying about insufficient adhesion of the substrate-film system. It was noted as well that the film grows denser at the substrate parts consisting of more fine grains and it is presented by well-defined columns at the parts formed by coarse grains. This testifies to the fact that the structure of the substrate grains specifies the structure of the film grains.

In order to improve the structural characteristics of the deposited coatings, a series of the samples was obtained in the DC- and pulse-DC modes with application of the preliminary ion implantation of a porous anode substrate surface. Application of this method of the surface modification allowed obtaining the following results.

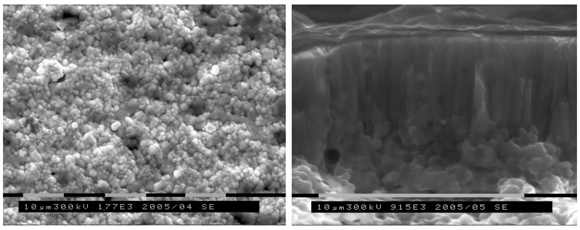


a b

Fig. 2. AFM-images: a) sputtering in the pulse-DC mode; b) sputtering in the pulse-DC mode onto the preliminary implanted substrate

Fig. 2 presents the AFM-images in the mode of boundary sharpening between the grains of the surface obtained at the magnetron supplying from a pulsed power source without implantation (Fig. 2, *a*) as well as in combination with a preliminary implantation (Fig. 2, *b*). Comparing the presented images one can see that while the surface of the coating obtained at the unimplanted substrate is presented by separate grains with sufficiently well-defined boundaries between them (Fig. 2, *a*), at the surface of the coating obtained at the implanted substrate (Fig. 2, *b*) the grain coalescence into a unified more dense structure is observed. Furthermore, the boundaries both between the fine grains and coarse elements of the structure practically disappear.

It was noted that this method of surface modification provided the electrolyte film formation with an essentially developed surface (Fig. 3, *a*).



a b

Fig. 3. SEM micrographs of the surface (a) and fractured cross-section (b) of the YSZ electrolyte deposited in the pulse-DC mode onto the implanted anode substrates

The grain dimension of the given samples changed from 50 to 1200 nm for the coatings obtained in the pulse-DC mode and from 60 to 1500 nm for the samples deposited in the DC-mode. The value R_a was approximately 200 nm for both sputtering modes. Cracks-free and surface exfoliations were found on the surface of the samples.

Investigations of fractured cross-section microstructure have shown that the preliminary implantation allowed increasing the contact area between the substrate and the film and, as a result, obtaining a coating with good adhesion. Moreover, it was discovered that in the samples deposited at the magnetron supplying from the pulsed power source, the electrolyte film structure presents coalesced columns without apparent boundaries and cracks between them forming a unified dense structure testified as well by the results of surface investigation using a AFM method (Fig. 2, *b*). Thus, we managed to suppress essentially the columnar structure of the YSZ electrolyte films (Fig. 3, *b*).

The diffraction patterns of the YSZ films obtained at the above-indicated operation modes of the magnetron sputtering system are presented in Fig. 4. The diffraction patterns of the YSZ films showed the lines of cubic zirconia oxide (ZrO_2) oriented in the direction of (111) are mainly present and only a minor fraction of ZrO_2 monoclinic phase of (111) orientation is present in the YSZ films obtained at the DC and pulse-DC sputtering as well as at the sputtering in the DC-mode onto the preliminary implanted anode substrate. Moreover, lines of metallic Ni were fixed. The lines of ZrO_2 and Ni are given by the film and reduced substrate, respectively. It is seen from the diffraction patterns presented in Fig. 4 that all films are polycrystalline. Alongside with the pre-

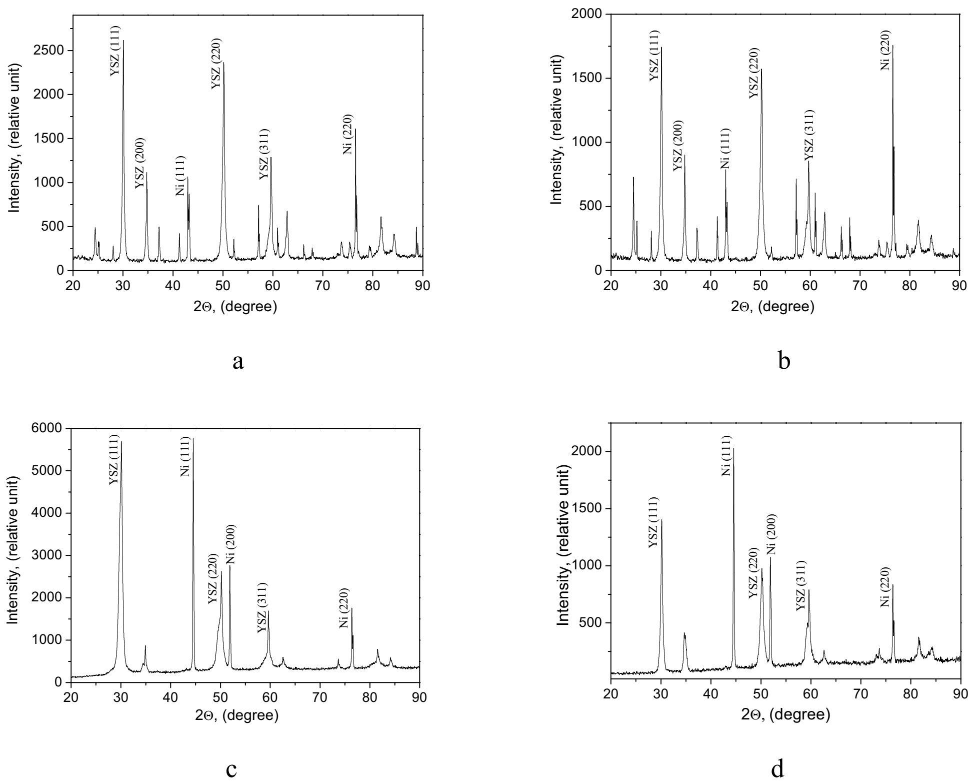


Fig. 4. Diffraction patterns of the films: a) DC-mode; b) pulse-DC mode; c) DC-mode of sputtering onto the implanted substrate; d) pulse-DC mode of sputtering onto the implanted substrate

ferred orientation of (111) the growth of coatings in the directions of (220), (311) and (200) is observed. The most perfect texture was obtained at the DC-mode sputtering onto the preliminary implanted substrate (Fig. 4, *c*).

4. Conclusions

It is shown that the magnetron sputtering method is promising for formation of dense and defect-free electrolyte films.

The main conclusions arising from the results obtained during fulfillment of the present work are the following:

– the structure of the substrate grains specifies the structure of the film grains. In order to obtain more dense and uniform electrolyte films of less thickness it is necessary to use the substrates having the pores of less diameter (it is desirable to have a nanostructured substrate);
– application of the preliminary ion implantation of a porous substrate allows changing the structural and mechanical properties of the obtained coatings, increasing the adhesion and the contact area of the substrate-film system and during deposition in the pulsed operation mode allows essentially suppressing the columnar structure;
– magnetron sputtering both in the DC and pulse-DC modes provides formation of the electrolyte films with a cubic crystal structure and preferable orientation in the direction of (111) that corresponds to a maximally dense atomic packing at the surface. Availability of such texture facilitates ion motion through the film improving the electrolyte characteristics.

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