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Deposition of YSZ Thin Films Using Electron Beam Evaporation Technique

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Formation of YSZ (yttrium stabilized zirconium oxide) thin films using electron beam (e-beam) physical vapor deposition technique was studied. The influence of e-beam gun power on growth of YSZ thin film was analyzed. The YSZ thin films (1.5 – 2 μm thickness) were deposited on optical quartz (SiO_2). Tetragonal phase ZrO_2 stabilized by 8 mol% of Y_2O_3 (8YSZ) ceramic powder was used as evaporation material. The substrate temperature was changed in the range of 20 °C – 600 °C and its influence on the crystallinity of deposited YSZ thin films was analyzed. The surface of the YSZ thin films was investigated by scanning electron microscope (SEM) and optical microscope. It was found that the e-beam power has the influence on the crystal orientation and homogeneity of the formed YSZ thin films. The dominant orientation of YSZ thin films texture is tetragonal (101) and is kept the same at different gun powers. The crystallite size varied between 12 – 49 nm and increased linearly with the substrate temperature.
Keywords: YSZ thin films, fuel cells, solid oxide fuel cell (SOFC), e-beam deposition, PVD.

1.INTRODUCTION

Yttrium stabilized zirconia (YSZ) is very interesting material because of high chemical stability, electrical resistivity, magnetic permittivity, low thermal conductivity, etc. YSZ is the most popular electrolyte material for solid oxide fuel cells (SOFCs) because it conducts only oxygen ions over a wide range of oxygen partial pressures. It is conditioned by low YSZ electrolyte price, good thermal properties (caused by high operating temperature), and ionic conductivity. SOFCs based on bulk (200 – 500 μm thick) YSZ membranes are normally operated at temperatures above 800 °C to achieve sufficiently high oxygen ion conductivity. One of the ways for lowering the cost and increasing the performance of SOFC is to use as much as possible thinner electrolyte layers (that is lowering the working temperature of the SOFC and the costs of the other components of FC). Moreover, the electrolyte should be made not porous (with cubic crystal orientation giving better ionic conductivity) on the porous substrates [1]. The shortcut between anode and cathode is the second problem. That has the influence on the electrolyte thickness (by now it is 2 – 3 μm of range).

YSZ electrolyte can be fabricated in different ways: using pressing-heating technique [1], aques tape casting [2], chemical vapor deposition (CVD) [3], flame assisted vapor deposition [4], and physical vapor deposition (PVD) techniques, such as: arc discharge deposition, DC sputtering, and e-beam deposition [5 – 10].

Physical vapor deposition could be one of the best techniques for getting good quality YSZ thin films. It is easier to control thin film properties using PVD technology, as compared to other technique [11].

In the present study, YSZ electrolyte thin films were deposited using e-beam deposition technique on different types of substrates. Tetragonal phase YSZ powder was used. Deposition parameters were changed in order to understand the influence of crystal phase of evaporated YSZ powders and substrate types on the texture, crystallite size, and homogeneity of formed YSZ thin films.

2. EXPERIMENTAL

YSZ thin films were deposited with e-beam deposition technique from tetragonal phase ZrO_2 stabilized by 8 mol % of Y_2O_3 (8YSZ) ceramic powder (SIGMA-ALDRICH submicron powder, 99.9 % purity based on trace metal analysis, 1.68 μm micron average particle size). Before deposition YSZ powder was pressed to the pallets of 25 mm diameter and 2 mm of thickness. YSZ thin films (1.5 – 2 μm of thicknesses) were deposited on optical quartz (SiO_2) at different substrate temperatures and e-beam power (deposition rates). The samples were cleaned in the ultrasonic bath (acetone solution) before deposition. ОІНЭ-7-004 PVD (e-beam deposition technique) system was used. More details on the technical parameters and experimental equipment of the used technique are presented in [11]. Residual gas pressure in the vacuum chamber was 4×10^{-3} Pa. The distance between electron gun and substrate was fixed at 240 mm. The substrate was additionally heated by a heater to temperatures from 20 °C to 600 °C. The deposition rate was evaluated from the thin film thickness measurements.

The film structure was analyzed by X-ray diffraction (XRD) (DRON-UM1 with standard Bragg-Brentan focusing geometry) with the 2Θ angle in the range of 10 – 80° using Cu K_α radiation in steps of 0.02°. Crystallite size d of YSZ thin films was estimated from the Scherrer's equation [11]:

$$d = 0.9\lambda/(\beta\cos\Theta), \quad (1)$$

neglecting the microstrain, where λ is the X-ray wavelength (0.154247 nm), Θ is the Bragg diffraction angle, and β is the full-width of peaks at half maximum intensity. The XRD results were quantified by defining a simple texture coefficient R [12] which is the ratio of the

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intensities of the (101) peak to the sum of the intensities of all peaks. As the spectra consisted of (101), (1100), (200), (211), (202) peaks, the coefficient becomes:

$$R_{101} = I_{101} / (I_{101} + I_{110} + I_{200} + I_{211} + I_{202}). \quad (2)$$

The value $R = 0.57$ corresponds to the random orientation, and $R = 1$ means preferred (101) orientation.

A Scanning Electron Microscope (SEM) JSM5600 and optical microscope OLYMPUS were used to investigate surface of the YSZ thin films.

3. RESULTS AND DISCUSSIONS

The XRD diffraction patterns of the pressed YSZ powder and optical quartz (SiO_2) are presented in Fig. 1. XRD diffraction patterns of YSZ powder shows that the positions of the Bragg peaks are typical for the tetragonal 8 % of YSZ.

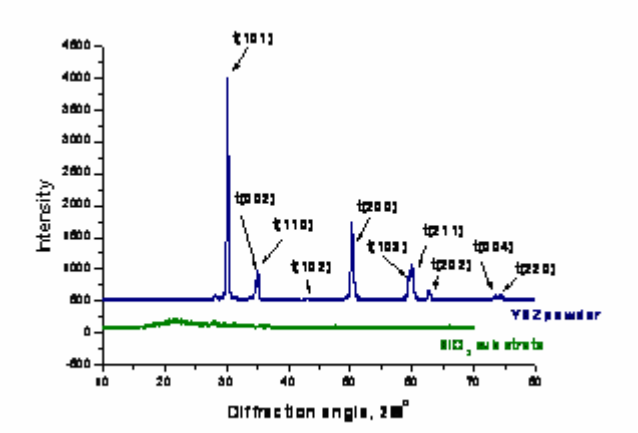

Fig. 1. XRD patterns of SiO_2 substrate and pressed ceramic powder of tetragonal phase ZrO_2 stabilized by 8 mol % Y_2O_3 (8YSZ). m – ZrO_2 monoclinic, t – YSZ tetragonal

The growth rate of the thin film during PVD has influence on the crystallite size of the deposited YSZ thin films. It is necessary to know growth rate dependence on the e-beam gun power for controlling the crystallite size. The growth rate dependence on the e-beam gun power [11] shows that increasing e-beam power the growth rate increases linearly. It could be changed in the range from 0.6 nm/s to 2.0 nm/s. The PVD deposited YSZ films have good adherence to substrate. Deposition starts to be not stable by increasing the rate and evaporates in big clusters. The films appear as uniform, shiny, and mirror-like (Fig. 3, a, b) for the lower rates (<1.5 nm/s and e-beam gun <1.0 kW). Deposition process is going to be unstable and the thin film starts to be nonhomogeneous with cracks (Fig. 3, c, d) and bad adhesion to the substrate (Fig. 4 – 5) at higher e-beam power, when the growing rate is higher than 1.5 nm/s.

Three types of materials: crystalline (Alloy 600, Fe-Ni-Cr), polycrystalline (Al_2O_3), and amorphous (optical quartz, SiO_2) substrates were chosen in order to understand the influence of substrate material on the crystal orientation of deposited YSZ thin film using e-beam deposition technique in the [11] work. It was found that the substrate has no influence on the crystal orientation of the YSZ thin film. The dominant YSZ thin films crystal orientation was cubic (111) and keeping the same for different types of substrate [11]. For that reason only one type substrate – optical quartz (SiO_2) was chosen in this work. To understand e-beam gun power influence on YSZ thin film formation when tetragonal phase YSZ ceramic powder is evaporated, thin films were deposited at different gun powers: 0.75, 0.9, 1.05, and 1.2 kW.

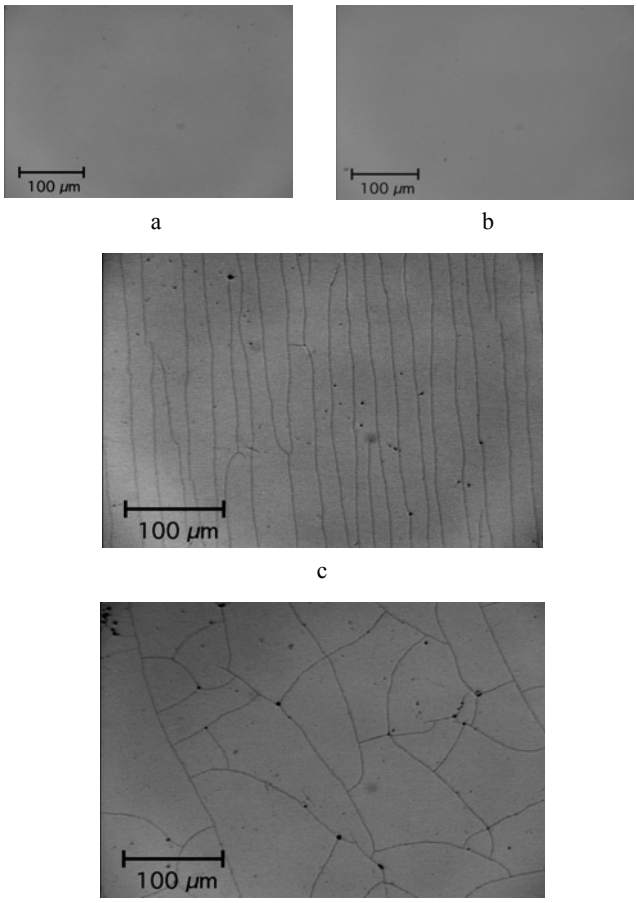

Fig. 3. The photographs of YSZ thin films deposited at different e-beam gun powers: a – 0.75 kW, b – 0.9 kW, c – 1.05 kW, and d – 1.2 kW

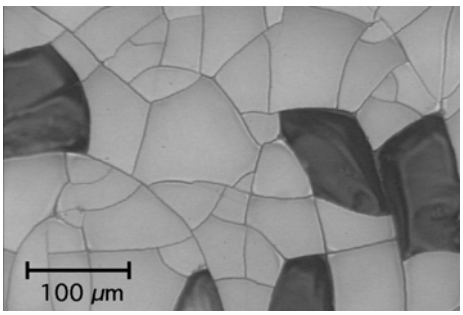

Fig. 4. Optical microscope image of the surface of YSZ thin film deposited at high e- beam gun power (1.2 kW)

The sharpness of (101) XRD peaks indicates high degree of homogeneity of YSZ thin films (Fig. 6). YSZ thin films exhibit minor (110), (200), (211) and (202) orientation also. Deposited YSZ thin films repeat the crystal orientation of the chosen evaporated material at low electron gun power.

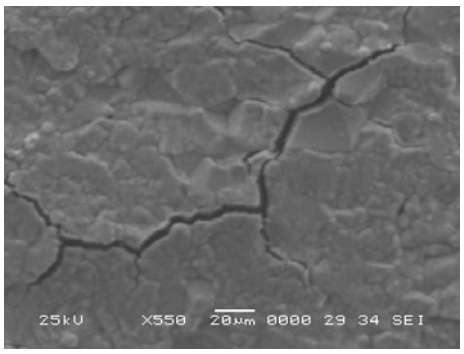

Fig. 5. SEM image of the surface of YSZ thin film deposited at high e- beam gun power (1.2 kW)

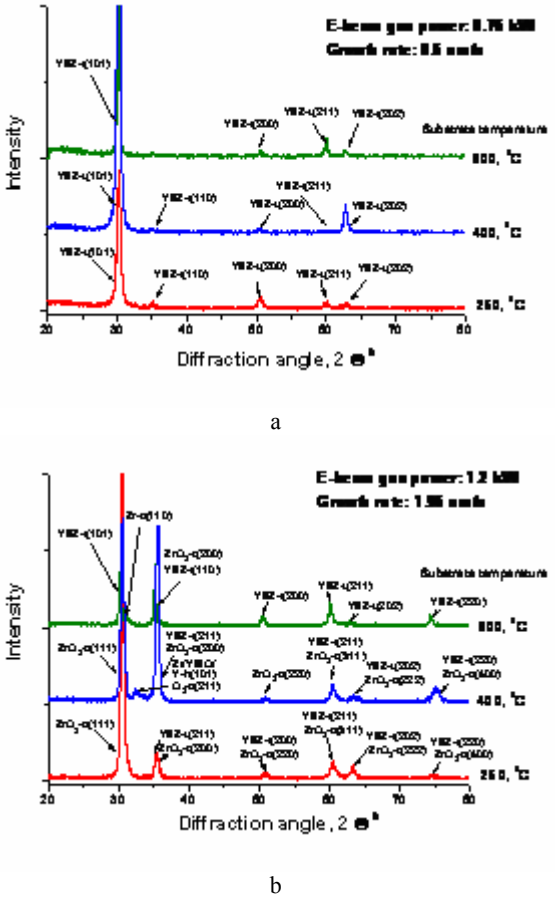

Fig. 6. XRD patterns of YSZ thin films deposited on SiO_2 substrates at different e- beam gun powers: a – 0.75 kW, b – 1.2 kW and substrate temperatures are 250 °C, 400 °C, 600 °C

The substrate temperature has no influence on orientation of the YSZ thin film (Fig. 6, a) at low e-beam gun powers (<0.9 kW) and thin film growing rates (<1.5 nm/s). Similar results were received using CVD technique [3]. The temperature does not influence the crystal orientation also at these points. XRD measurements start to show cubic ZrO_2 peaks (Fig. 6, b) when e-beam gun power is higher than 1.0 kW (growing rate >1.5 nm/s). One can suggest the assumption allows making the decision that at high e-beam gun power the thin films start to have two different phases: tetragonal YSZ and cubic ZrO_2. From that it is possible to conclude that the YSZ material at the high e-beam gun power from the evaporant start to evaporate in the different type of clusters.

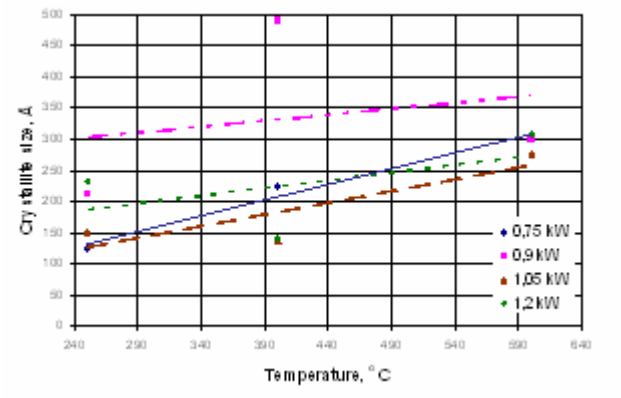

Fig. 7. Dependence of YSZ thin film crystallites size (calculated from XRD data) on SiO_2 substrates temperature at different e-beam gun power

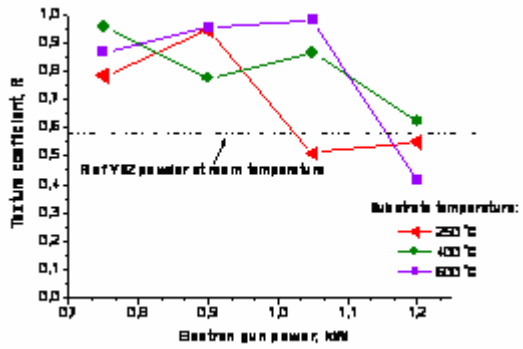

Fig. 8. Dependence of YSZ thin films texture coefficient *R* on the electron gun power at different substrate temperatures

Fig. 7 shows that the substrate temperature and e-beam gun power has the influence on the crystallite size of the YSZ thin film. Crystallite size is increased from 120 nm to 230 nm by changing the e-beam gun power at 250 °C substrate temperature. Crystallite size is decreased from 250 nm to 140 nm by increasing gun power at 400 °C substrate temperature and keeping the same at 600 °C substrate temperature. The lowest crystallite size is found to be equal to 250 °C for the substrate temperature.

The texture coefficient as a function of electron gun power at different substrate temperatures during the deposition of YSZ thin films is shown in Fig. 8. The films grow with preferred (101) orientation. The texture (101) dominates in the electron gun power region (0.75 – 0.9 kW) when the substrate temperature is 250 °C. The same texture (101) at higher temperatures (400 – 600 °C) dominates but it is registered in the wider electron gun power region (0.75 – 1.05 kW).

4. CONCLUSIONS

According to the obtained results it could be seen that the growth rate depends on the e- beam gun power. The films with good adherence to the substrate appear uniform, shiny and mirror like in the range less than 1.5 nm/s with e-beam gun power less than 1.0 kW. YSZ thin films crack (start to be nonhomogeneous) with bad adhesion to the substrate at higher e-beam gun powers. The structure of

deposited YSZ thin films corresponds to evaporating material and it is in tetragonal phase. The texture (101) dominates at lower e-beam gun powers. Also, XRD measurements show cubic ZrO_2 peaks at higher e-beam gun powers and thin films start to have two different phases: tetragonal YSZ and cubic ZrO_2. So, it is possible to conclude that the YSZ material at the high e-beam gun powers start to evaporate (from the evaporant) in the different type of clusters. That also allows changes in texture. The crystallite size increased linearly (from 12 to 49 nm) increasing the substrate temperature.

Acknowledgements

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