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UV-Vis spectroscopical investigations of the YSZ thin films on corundum, silicon and silica substrates

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The preparation and characterization of the ZrO_2 stabilized with Y_2O_3 (YSZ) thin films on different substrates, which were produced by the so-called aqueous sol-gel synthesis, are reported. This sol-gel method is based on the complexation of the metal nitrate salts with 1,2-propanediol producing a final compound as thin layers on Al_2O_3, Si and SiO_2 substrates at relatively low temperatures compared with solid state reaction. Moreover, in this study we compared the optical properties of obtained films prepared by sol-gel synthesis using the dip-coating technique. All as-prepared YSZ thin layers on different substrates were dried at 400 °C temperature on a hot-plate and afterwards repeatedly calcined at 800 °C for 1 hour in air atmosphere after each coating procedure and characterized by X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM) and UV-Vis spectroscopy. XRD data exhibited that at 800 °C temperature a single crystalline $Y_{0.2}Zr_{0.8}O_2$ thin film with a cubic (Fm-3m) crystal structure was formed. The morphological features of the obtained coating investigated by SEM confirmed the nanosized surface of the YSZ coating. The optical reflection (UV-Vis) measurements of sol-gel derived specimens let us to conclude that both the preparation technique of the synthesized thin films and the amount of coating procedures significantly influence the optical properties of the as-prepared YSZ surfaces.

Key words: inorganic compounds, thin films, sol-gel growth, microstructure, optical properties

INTRODUCTION

Zirconium oxide (ZrO_2) is one of the industrially most important ceramic material [1] that finds wide applications in thermal barrier coating [2], clinical application [3], oxygen sensor [4], and electrolyte in a solid fuel cell (SOFC) [5–7]. Unfortunately, only a monoclinic phase of ZrO_2 is stable at room temperature, which is not suitable because of volume expansion during the transformation from a tetragonal to a monoclinic phase. The stabilization of ZrO_2 high-temperature phases: (1 170 °C) tetragonal and (2 300 °C) cubic, respectively, can be successfully performed by doping with

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different oxides including Y_2O_3, La_2O_3, Gd_2O_3, CeO_2, CaO, Sc_2O_3, In_2O_3, etc. Usually, stabilized zirconia has superior mechanical, thermal, and optical properties compared with the room-temperature stable monoclinic phase. Moreover, in order to achieve the best utilization of this kind of materials in the electrochemical devices, such as SOFCs and gas sensors, a strong demand for clarifying the source of the size dependence is emerging [8]. Nevertheless, that yttria-stabilized zirconia satisfied ionic conductivity only at very high temperature (about 1 000 °C), this electrolyte is the most commonly used in SOFCs in the past decade [9]. The reducing of the ZrO_2 stabilized with the Y_2O_3 (YSZ) operating temperature is related with the particle size of the synthesized material. As the grain size is reduced from a micrometer to a nanometer, the defect properties (defect formation, lattice defect and band structures) are considered to play an essential role in defining the ionic and electronic conduction in the nanometer regime [10].

The choice of an appropriate thin film deposition technique is influenced by the material to be deposited and desired film quality [11]. From this point of view, there are several techniques, which were applied for the manufacture of ceramic films (physical-vapour deposition, chemical-vapour deposition, sol-gel, etc.) [12]. However, the sol-gel synthesis is the most attractive method for the preparation of YSZ thin films on different substrates because of many following advantages. The sol-gel process is a wet chemical method that does not depend on high pH values or high sintering temperatures. The high surface area of dried gels results in high reactivity, which permits low process temperature. This method offers a molecular mixing precursor solution, which is capable of improving chemical homogeneity. Sol-gel technique also has superior advantage because of simplicity of the preparation and deposition of the solutions. Moreover, the cheapness of the equipment also plays substantial role in this case [13–18].

In this paper, we report on the synthesis and characterization of YSZ thin films on the corundum, silicon and silica substrates using the dip-coating technique. The sol-gel synthesis route was focused on the dissolution of simple salts in the 1.2-propanediol solution, which was used as both a solvent and a complexing agent.

EXPERIMENTAL

Samples preparation

Firstly, $ZrO(NO_3)_2 \cdot 2H_2O$ was dissolved in 50 ml of 1,2-propanediol at 60–75 °C under continuous stirring. Next, $Y(NO_3)_3 \cdot H_2O$ was added to the previous solution. The beaker with the solution was closed with a watch glass and left for 1 h with continuous stirring at 90–95 °C temperature. Finally, a yellow transparent Y-Zr-O nitrate-1.2-propanediolate sol was formed after all experimental procedures.

The obtained sol was used for the synthesis of thin films on corundum, silicon and silica substrates using the dip-coating technique. First, the Y-Zr-O sol solution was stirred in 50 mL beaker at room temperature for 10 h. The beaker was closed with watch glass and the mixture was repeatedly stirred for 5 h at 80–85 °C temperature. This procedure was extended before each dipping in a sonochemical bath for 30 min at room temperature.

YSZ thin films were deposited onto commercial corundum (1.5 × 1.5 cm) (Al_2O_3), silicon (1.0 × 1.0 cm) (Si) and silica (1.9 × 1.9 cm) (SiO_2) substrates by dip-coating technique from the Y-Zr-O nitrate sol stabilized with 1.2-propanediol. The films were deposited on the substrates by dip-coating procedure at the 5 mm/min immersion rate and were dried at room temperature for 24 h in air at ambient pressure in a horizontal position. Afterwards, the dried coated substrate was annealed at 800 °C temperature in air for 1 h. This process was repeated to build up the desired film thickness.

Characterization

X-ray diffraction analysis (XRD) of as-prepared samples was performed on a Bruker AXE D8 Focus diffractometer with a LynxEye detector using $CuK\alpha_1$ radiation. The measurements were recorded at the standard rate of 1.5 2θ/min. A scanning electron microscope (SEM) Hitachi TM3000 was used to study the surface morphology and microstructure of the obtained thin films. The reflection spectra were recorded at room temperature using a Perkin Elmer Lambda 35 UV/VIS spectrometer. A KSV D™ dip-coating apparatus, KSV Instruments Ltd., was used for coating preparation. The standard immersing (5 mm/min) and withdrawal rates (20 mm/min) for the dip-coating process were applied.

RESULTS AND DISCUSSION

X-ray diffraction

The XRD pattern of YSZ films obtained from Y-Zr-O nitrate solution in 1.2-propanediol using the dip-coating technique is shown in Fig. 1. This XRD pattern of the YSZ coating from Y-Zr-O nitrate-propanediolate sol, dried at 400 °C and annealed at 800 °C temperatures, presented in the top panel of Fig. 1, is matched with that of the standard ICSD card of $Zr_{0.8}Y_{0.2}O_{1.9}$ shown in the bottom. In addition, XRD results indicated that even at 800 °C a crystalline cubic (Fm-3m) $Zr_{0.8}Y_{0.2}O_{1.9}$ phase was formed. Moreover, the characteristic peaks of a YSZ crystal phase are relatively broad, which corresponds to either the nanosized particles that formed on the substrate or the amorphous character of the obtained coating.

SEM micrographs

As seen from SEM micrographs presented in Fig. 2, the surface of the obtained YSZ coating on the corundum substrate is relatively rough and composed of spherical particles the size of which varies from 100 to 300 nm. Moreover, Fig. 2 (a) clearly shows the formation of either holes or empty areas

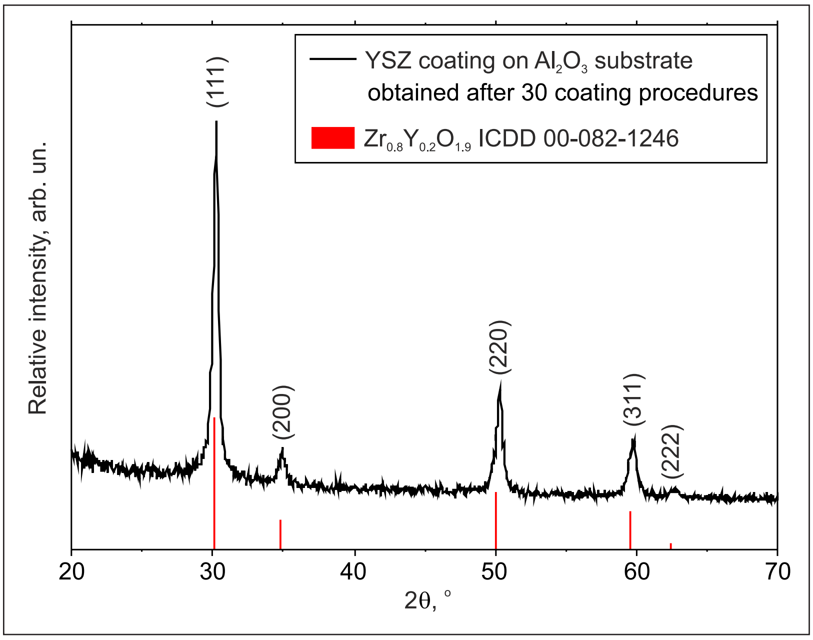

Fig. 1. Standard ICDD card of $Zr_{0.8}Y_{0.2}O_{1.9}$ and the XRD pattern of the YSZ coating annealed at 800 °C temperature

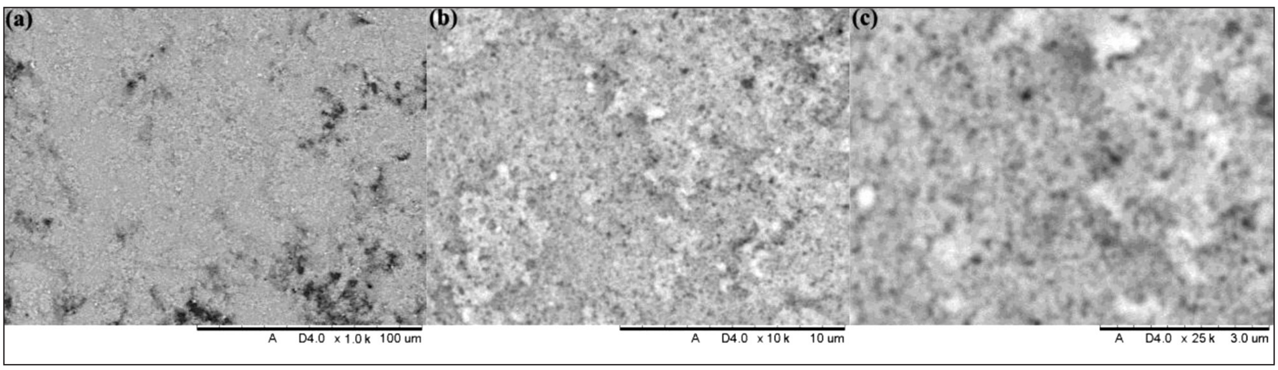

Fig. 2. SEM micrographs of the YSZ coating annealed at 800 °C temperature after 30 coating procedures on the corundum substrate

of the YSZ layer on the substrate in a size up to 20 μm. In addition, from Fig. 2 (b) and (c) it is clear that these particles agglomerate with each other by composing a net-like structure and tend to form irregular agglomerates with a size up to 1 μm. These obtained results are in a good agreement with XRD data, which also are related with a nano-metric nature of synthesized YSZ coatings.

UV-Vis measurements

The optical properties of the YSZ coatings precipitated on corundum, silicon and silica substrates were investigated. The UV-Vis reflectance spectra of YSZ thin layers prepared on different substrates and annealed at 800 °C of temperature are shown in Figs. 3, 4 and 5. As seen from Fig. 3, the nature of the reflectance spectra of YSZ coatings strongly depends on the layer thickness that is successfully controlled by amount of immersing procedures. From the UV-Vis spectra (Fig. 3) it is clear that the absorbance of the light in the range from 500 nm to 300 nm tends to decrease by increasing dipping and annealing procedures. Moreover, even after 10 coating procedures the reflectance of the YSZ coating in the range from 300 nm to 220 nm tends to increase by forming a wide band at 240 nm. By further increasing coating procedures up to 20 times the reflectance of the surface increased and the nature of the curve remained similar according to the case after 10 layers. It is also interesting to note that after both 25 and 30 immersing and annealing procedures the behaviour of the reflectance gradually increased. However, the shape of these reflectance bands in the range from 300 nm to 220 nm converged into several small peaks, which are attributed to both the enhanced roughness and the agglomeration of separate particles in the YSZ layer.

Similar results, comparing with the previous case, of YSZ layers precipitated on the silicon substrate from Y-Zr-O nitrate-propandiolate sol in the UV-Vis reflectance spectra, shown in Fig. 4, were obtained. In this case, the reflectance of the YSZ coatings increased by decreasing the wavelength in the range from 500 nm to 220 nm. Moreover, as seen from Fig. 4, after 2 dipping and annealing procedures the band of reflectance at 240 nm did not appear, which concluded about the low concentration of YSZ on the surface of the silicon substrate. However, after 7 and 10 coating procedures, the characteristic band of the reflectance at 240 nm reappeared what consistent pattern is with the data presented in Fig. 3.

Finally, the UV-Vis spectra of the YSZ samples precipitated on the silica substrate from Y-Zr-O nitrate-propandiolate sol in Fig. 5 are presented. In this case, the reflectance of the YSZ coatings increased by decreasing the wavelength in the range from 1 100 nm to 220 nm. Moreover, the reflection band at 240 nm even after two coating procedures has appeared. This result is determined by enhanced roughness and a porous structure of the silica surface that is much suitable for the formation of YSZ coating even after 2 dipping and annealing procedures.

In conclusion, it should be noted that UV-Vis spectroscopy is a suitable method for the quick determination and fine controlling of the YSZ thin layers on the corundum, silicon and silica substrates.

CONCLUSIONS

The preparation and characterization of the YSZ thin films on the Al_2O_3, Si and SiO_2 substrates, which were produced by the so-called aqueous sol-gel synthesis, were reported. This sol-gel method was based on the complexation of the metal nitrate salts with 1,2-propanediol producing a final compound as thin layers on different substrates. XRD data exhibited that at 800 °C temperature a single crystalline $Y_{0.2}Zr_{0.8}O_2$ thin film with a cubic (Fm-3m) crystal structure was formed. According to XRD analysis data the Y-Zr-O nitrate-propandiolate synthesis route is suitable for the preparation of thin YSZ films on the Al_2O_3 substrate. The surface morphology of obtained YSZ thin films was almost identical independent of the used substrate. The morphological features of the obtained coating investigated by SEM confirmed the nanosized surface of YSZ layers. The quality of obtained coatings was successfully controlled by UV-Vis reflectance spectroscopy. It was concluded that reflection of the synthesized YSZ samples slightly depends on both the layer thickness and the nature of the substrate.

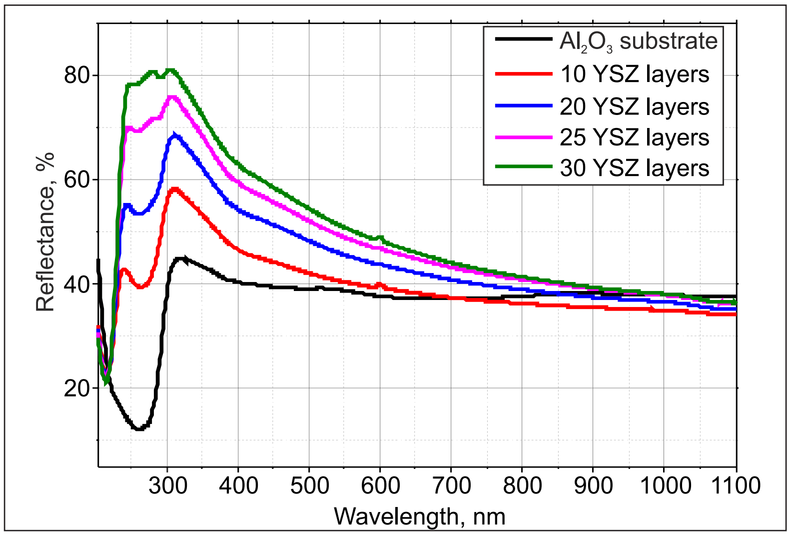

Fig. 3. UV-Vis reflectance spectra of the YSZ coatings on the corundum substrate obtained from the Y-Zr-O nitrate-propandiolate sol

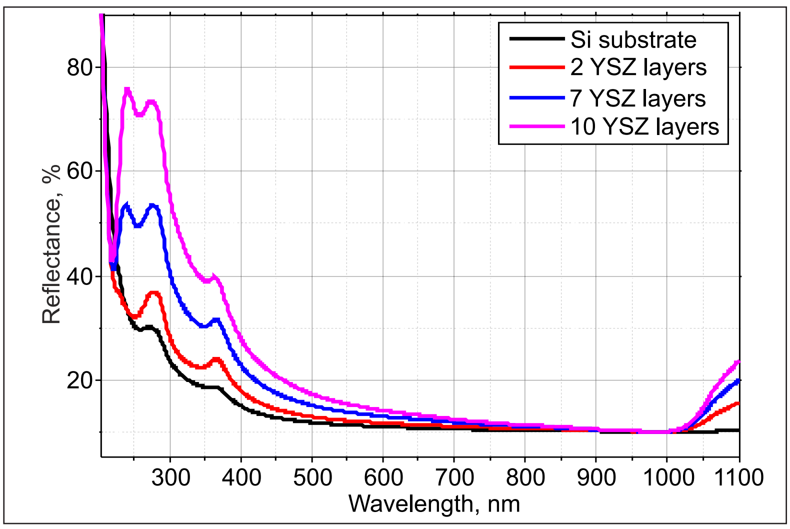

Fig. 4. UV-Vis reflectance spectra of the YSZ coatings on the silicon substrate obtained from Y-Zr-O nitrate-propandiolate sol

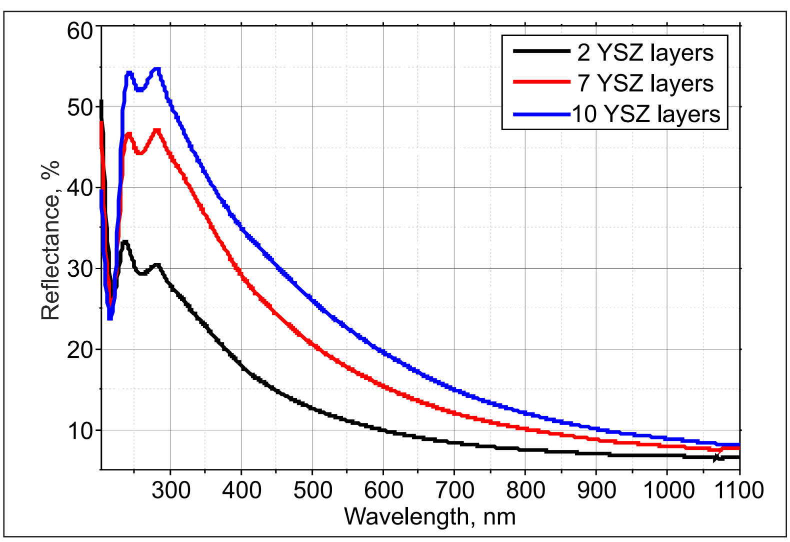

Fig. 5. UV-Vis reflectance spectra of the YSZ coatings on the silica substrate obtained from Y-Zr-O nitrate-propandiolate sol

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YSZ PLONŲ SLUOKSNIŲ ANT KORUNDO, SILICIO IR SILICIO OKSIDO PADĖKLŲ UV-Vis SPEKTROSKOPINIAI TYRIMAI

Santrauka

Darbe YSZ ploni sluoksniai nusodinti ant korundo, silicio ir silicio oksido padėklų iš pradinių druskų tirpalų 1,2-propandiolyje panaudojant merkimo technologiją. Gautosios dangos po kiekvienos merkimo procedūros papildomai kaitintos 800 °C temperatūroje (1 val. ore). Pagaminti sluoksniai buvo tirti Rentgeno spindulių difrakcijos (XRD), skenuojančiosios elektroninės mikroskopijos (SEM) ir ultravioletinės bei regimosios šviesos spektroskopijos (UV-Vis) metodais. Atlikus iškaitintų dangų XRD analizę matyti, jog 800 °C temperatūroje susiformuoja kubinė $Y_{0.2}Zr_{0.8}O_2$ (Fm-3m) junginio kristalinė struktūra. SEM analizė atskleidė, jog gautieji paviršiai yra sudaryti iš 100–300 nm dydžio netaisyklingos sferos formos dalelių, kurios linkusios jungtis tarpusavyje. Remiantis UV-Vis tyrimo metodu, galima daryti išvadą, jog susintezuotų YSZ plonų sluoksnių atspindžio spektrams turi įtakos merkimo bei kaitinimo procedūrų skaičius ir skirtingas padėklų paviršius.