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ЭЛЕКТРОХИМИЧЕСКИЙ СИНТЕЗ И ХАРАКТЕРИСТИКАТОНКИХ ПЛЕНОК CeO_2–Gd_2O_3

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ELECTROCHEMICAL SYNTHESIS AND CHARACTERIZATION OF CeO_2–Gd_2O_3THIN FILMS

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Тонкие пленки CeO_2иGd_2O_3былиполученыметодомэлектроосаждения из водных растворов с различнойконцентрациейнитратовCe(III) иGd(III), при различном времени осажденияи комнатной температуре. Комбинируя условия синтеза обоих одиночных оксидов, Gd-допированные пленки церия были получены на подложках из нержавеющей стали. Структура и морфология электроосажденных пленок были изучены методами рентгенофазового анализа, сканирующей электронной микроскопии и спектроскопией комбинационного рассеивания.

Cerium oxide (CeO_2) is a material of special interest due to its wide applications as a promoter or support in three-way catalysts (TWCs) [1], gas sensors [2], optical coatings [3], etc. In the recent past years ceria doped with rare-earth oxides are intensively investigated for application as a solid electrolyte in solid oxide fuel cells (SOFC) [4] because of their much higher ionic conductivity at lower temperatures compared to the conventional electrolyte material of yttria-stabilized zirconia (YSZ), that allows to use cheaper SOFC components or to overcome fast ageing for instance [5]. It was shown that one of the best dopant is gadolinium, due to its optimum atomic radius and the resulting higher ionic conductivity [6]. Many research articles in literature are dedicated to prepare the doped ceria by variety of methods such as atomic layer deposition [7], laser beam evaporation ion [8], sol–gel processing [9], etc. Among these numerous deposition techniques, which are relatively complex, expensive and require high temperature, long heat treatment, etc., electrochemical deposition is a less onerous one, already used in industry and research, owing to its simplicity, easy scale–up (large area substrate) and high quality film. This work deals with the electrodeposition of CeO_2–Gd_2O_3 films and the influence of synthesis parameters on their morphology, thickness and composition.

Ceria, gadolinia and gadolinium–doped cerium oxide films were prepared using a classical three-electrode set–up for the electrodeposition: stainless steel disc as working electrode, saturated calomel electrode as reference, and platinum wire as counter–electrode. The substrate (stainless steel 316L) was cleaned in ethanol before deposition. The electrolyte was composed by $Ce(NO_3)_3{\cdot}6H_2O$ (0,01 M–0,001 M) with or without addition of $Gd(NO_3)_3{\cdot}5H_2O$ (0,005 M–0,0001 M) and with 0,1 M $NaNO_3$ as supporting electrolyte. For the fabrication of pure gadolinium films, the electrolytic solution contained $Gd(NO_3)_3{\cdot}5H_2O$ (0,01 M–0,001 M) in addition to the same supporting electrolyte. The solutions were saturated with molecular oxygen for 30 min before starting the experiment, and a slight O_2 bubbling in the reactor was maintained during the growth process. Films were deposited applying a −0,7 V/SCE to –0,9 V/SCE potential. Deposition time ranged from 5 min to 30 min. After deposition, samples were rinsed in deionized water. Thermal annealing was done at 600 °C for 1 h, in air, with a heating rate of 2 °C per minute.

The films were characterized by different methods. The structural characterization was performed using X-ray diffraction (XRD) and Raman spectroscopy. XRD was performed using Siemens D5000 instrument with Cu Kα radiation. Micro-Raman spectra were measured at room temperature with a Horiba Jobin system (HR800 UV) using line 632,8 nm of He–Ne laser. The morphology of the films was studied by scanning electron microscopy (SEM). Images were made with a high resolution Ultra 55 Zeiss FEG scanning electron microscope.

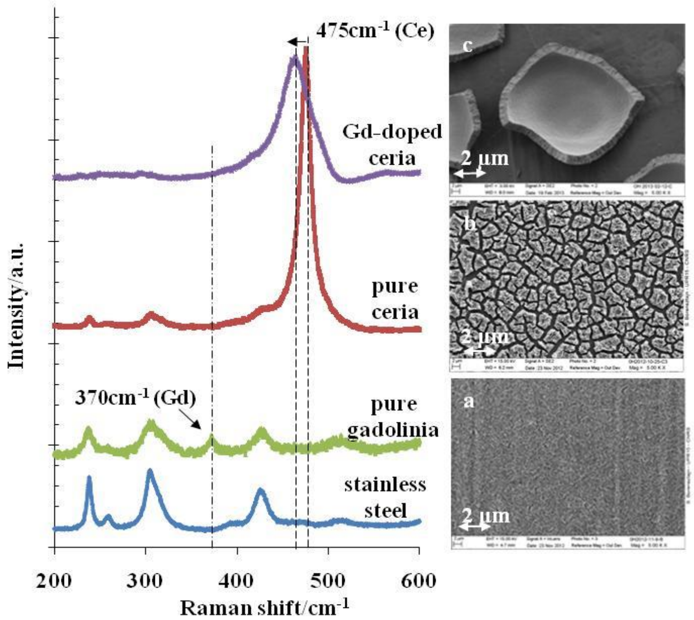

Fig. 1.Raman spectra of pure ceria, pure gadolinia and Gd–doped ceria after calcination at 600°C, 1h in air. Substrate spectrum is given as a reference. Inlets: SEM micrographs of a) pure gadolinia; b) pure ceria and c) Gd–doped ceria films.

The X-ray diffraction patterns confirm that the solid solutions of CeO_2−Gd_2O_3 were formed after calcination at 600°C the films which were deposited from electrolytic solutions containing $Gd(NO_3)_3{\cdot}5H_2O$ and $Ce(NO_3)_3{\cdot}6H_2O$ with different concentrations, regardless of the process time.

SEM showed observation that morphology and thickness of all as-grown films depends on composition of electrolytic solutions, time of deposition and annealing. At first sight, the films seem to fully cover the surface, as bare substrate is not visible, but on closer inspection there are cracks in the films. The cracks observed in the film are most likely due to shear stresses between oxide film and stainless steel substrate (during oxidation step or/and drying step) [4]. In comparison with the pure as-grown ceria or gadolinium films, the Gd−doped ceria shows much more compact and denser morphology (Inlets in Fig. 1.). During the work, it has been observed that the film's thickness increases with higher concentration of solutions and time of deposition, while it decreases after annealing because of sintering effect, thus higher compactness.

All CeO_2−Gd_2O_3 films deposited on stainless steel were investigated by Raman spectroscopy before and after calcinations. This highly sensitive and non-destructive technique is extremely powerful especially for fast analysis of the phase and relative thickness of samples, and also it can be used to study dopant incorporation. To confirm the formation of gadolinium-doped ceria solid solution, Raman spectra were obtained for pure gadolinium and pure ceria based films (Fig. 1a and Fig. 1b). There is a clear vibrational mode at 475cm^{-1}, which is typical of CeO_2 and corresponds to the F_{2g} symmetry, which confirms the formation of CeO_2 phase after heat treatment. The formation of a cubic structure of gadolinium films before calcination of samples wasn't further supported by Raman spectroscopy. The vibrational mode at 370cm^{-1} corresponding to Gd_2O_3 cubic phase was observed only after calcination of samples, but not anymore for the Gd–doped ceria film. The shift of the 475cm^{-1} peak to the lowest wave number and its shape confirm the solid solution [4].

The original result of this work is the fabrication from only one electrolytic solution of their Gd–doped ceria films by electrochemical technique. Raman spectroscopy and X-ray diffraction studies clearly shown that solid solution of Gd–doped ceria was obtained, in a cubic structure.

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