ELECTROPHORETIC AND ELECTROLYTIC DEPOSITION OF CeO₂ AND Ce₁₋ₓGdxO₂y FILMS

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ABSTRACT

CeO₂ and Ce₁₋ₓGdxO₂y films were prepared by electrodeposition. Thin films in the range of 0.1-2 μm were deposited via electrolytic deposition and deposits up to 200 μm were obtained by the electrophoretic method. The films were studied by X-ray diffraction, thermogravimetric analysis and scanning electron microscopy. The crystallization of electrolytic deposits begins at ~ 200°C. Morphologies of the films are dependent on the method of deposition, deposition parameters and additives. The amount of the deposited material can be controlled by variation of deposition time and current density.

INTRODUCTION

CeO₂ and doped ceria films are of considerable interest for applications in solid oxide fuel cells (SOFC) operating at reduced temperatures. These materials have significant potential for fabrication of electrodes and electrolytes as well as thin layers, preventing interfacial electrolyte-electrode reaction at elevated temperatures. Electrodeposition is a less common fabrication technique although several studies have recently been reported (1-4). The formation of ceramic films by electrophoretic deposition (EPD) and cathodic electrolytic deposition (CELD) offer important advantages such as low capital investment costs, rigid control of film thickness, uniformity of deposition rate as well as the possibility of formation of multilayer deposits of controlled thickness on substrates of complex shape (5-14). EPD requires the use of ceramic particles and as such deposit uniformity and minimal deposit thickness are limited by the particle size of the powders used for the EPD process (5,8). Owing to the use of ionic species instead of ceramic particles, the deposits obtained via CELD have lower particle sizes and exhibit higher sintering activity (5,13,14). CELD allows formation of coatings of atomic dimension and is now an important tool in deposition of nanostructured thin films (9,10). The deposition rate of the EPD process (5-8) is much faster than that of CELD (5,9,11,13), resulting in significantly higher deposit thickness. Therefore, EPD and CELD can be applied for formation of thick and thin ceramic films, respectively. This paper presents results of CELD and EPD of CeO₂ and doped ceria films.
EXPERIMENTAL PROCEDURES

The starting materials used were CeCl₃, Ce(NO₃)₃·6H₂O (Alfa Aesar), GdCl₃·6H₂O (Sigma), CeO₂ (Cerac), Ce₀.₈Gd₀.₂O₂.₉(NexTech Materials Ltd.), acetylacetone (Sigma), hydrogen peroxide H₂O₂ (30 wt% in water, BDH Inc.), polyvinyl butyral (PVB, Aldrich) and 4-Hydroxybenzoic acid (Alfa Aesar). A Ni/YSZ cermet (40 vol% Ni after reduction) was prepared by tape casting of NiO (Inco) and yttria-stabilized zirconia YSZ (TZ-8Y, Tosoh Corporation). Ni foil and Ni-YSZ cerments were used as substrates for electrodeposition. The electrochemical cell for deposition in a galvanostatic regime included the cathodic substrate and platinum anode. Cathodic deposits were obtained at constant current densities (c.d.) ranging from 0.1 to 2 mA/cm² for EPD and from 2 to 10 mA/cm² for CELD. 0.01M aqueous and mixed ethyl alcohol-water (5 vol.% water) solutions of CeCl₃, Ce(NO₃)₃·6H₂O and GdCl₃·6H₂O were prepared. CELD of ceria was performed from the solutions saturated with air or solutions containing 0.02M H₂O₂ additive. Ce₁₋ₓGdxOy deposits were obtained via CELD method from mixed CeCl₃ and GdCl₃ solutions, saturated with air. Laminated CELD deposits were fabricated by multiple deposition accompanied by hot plate drying. Suspensions for EPD were prepared by ball milling of CeO₂ or Ce₀.₈Gd₀.₂O₂.₉ powders in ethyl alcohol (40-100 g/L), followed by ultrasonic agitation. The deposition processes were quantified in experiments performed with Ni substrates, which were weighed before and after deposition followed by drying. The phase content of CELD deposits was determined by X-ray diffraction (XRD) with a diffractometer (Nicolet I2) using monochromatized Cu Kα radiation at a scanning speed of 0.5 deg/min. Thermogravimetric analysis (TG) was carried out in air between room temperature and 900°C at a heating rate of 10 °C/min using a thermoanalyzer (Netzsch STH-409). The microstructures of the deposited films were studied using a Philips 515 scanning electron microscope (SEM).

RESULTS AND DISCUSSION

CELD is achieved via hydrolysis of metal ions or complexes by electrogenerated base to form deposits on cathodic substrates (9-16). The following reactions are used to generate base at an electrode surface:

\[ 2H₂O + 2e^- \rightleftharpoons H₂ + 2OH^- \]  \[ \text{[1]} \]
\[ NO₃^- + H₂O + 2e^- \rightleftharpoons NO_2^- + 2OH^- \]  \[ \text{[2]} \]
\[ O₂ + 2H₂O + 4e^- \rightleftharpoons 4OH^- \]  \[ \text{[3]} \]

CELD experiments revealed the formation of deposits from cerium, and gadolinium salt solutions in aqueous and mixed solvents. More adherent and uniform deposits were obtained from chloride baths. Mixed (1-x)CeCl₃-xGdCl₃ (x=0.1, 0.2, total concentration 0.01M) were used for co-deposition experiments. At this point, it is important to note that the valence state of cerium can be changed in alkaline solutions containing H₂O₂ or saturated with air, and formation of Ce(OH)³⁺ species can be expected (17,18). Following the scheme proposed in (17), it can be assumed that cerium species Ce(OH)³⁺ are hydrolyzed by electrogenerated base to form the cathodic deposit. Figs. 1 and 2 show
Figure 1. Deposit weight versus charge passed in CELD: for deposits obtained from 0.01M CeCl₃ solution saturated with air in mixed ethyl alcohol-water (95:5 volume ratio) solvent (a) and for deposits obtained from aqueous 0.01M CeCl₃ +0.02 M H₂O₂ solution (b).

Figure 2. Deposit weight versus charge passed in CELD process for deposits obtained from 0.01M GdCl₃ solution in mixed ethyl alcohol-water solvent (95:5 volume ratio).

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deposit weight versus charge passed for deposits obtained from 0.01M CeCl₃ and 0.01M GdCl₃. The curves were found to follow nearly linear time dependence. In this regard, according to Faraday's law, the deposit weight is proportional to the charge passed.

The X-ray diffractograms of fresh ceria deposits and those thermally treated at 200 and 400°C are shown in Fig.3. As prepared deposits contained a significant amount of amorphous phase. On heating the deposits to 200°C, the XRD pattern displayed peaks of CeO₂, which are broadened due to the fine size of the crystallites. These reflexes become clear and sharp at higher temperatures and can be attributed to a cubic CeO₂ structure (JCPDS Index Card 34-394). It is important to mention that CeO₂ powders obtained by cathodic electrosynthesis (16) exhibited well defined crystalline structure and no thermal treatment was used to induce crystallinity. The difference in crystallinity of fresh films obtained in this work and powders in (16) can be attributed to different experimental conditions such as temperature and current density.

TG data presented in Fig. 4 show that most of the weight loss occurs below 200°C. Additional rapid decline in weight was recorded in the region 520-580°C, then the weight fell gradually. The total weight loss of ~11% up to 900°C can be attributed to dehydration of the deposits and decomposition of surface carbonates.

Thin CELD deposits (0.1 –0.3 μm) were crack free and adhered well to the substrates. However, significant cracking was observed after air drying when deposit thickness exceeded ~0.3-0.4 μm. Multiple deposition accompanied by hot plate drying was performed in order to prevent cracking. Maximal film thickness of CELD deposits evaluated by scanning electron microscopy reached ~2 microns.

As pointed out above, the CELD process is based on base generation in electrode reactions and neutralization of ionic species to form deposits. During the deposition process an insulating layer forms, which prevents OH⁻ generation. Coating resistivity is a major limiting factor of the electrodeposition method for development of thick coatings. In contrast, particle/electrode reactions are not involved in EPD and ceramic particles do not lose their charge on being deposited. Therefore thick coatings can be deposited by the EPD method.

The use of a mixed alcohol-acetylacetone solvent was demonstrated to be effective in achieving charging of CeO₂ particles. The mechanism of particle charging was attributed to adsorption of protons (19). EPD experiments revealed that CeO₂ particles were positively charged and moved toward the cathode under the applied field. Deposits of various thickness were obtained on Ni and Ni-YSZ cermet substrates. Electron microscopic investigations have shown that the microstructures of the deposits were influenced by powder characteristics, current density and Ce(NO₃)₃·6H₂O additive. Particle size was reduced by milling and presedimentation. It is known that low particle size offers advantages in fabricating of ceramic coatings with dense packing and good sinterability (7). The uniformity of electrophoretic deposits results from the insulating properties of the deposits and electric field dependence of the deposition rate. However, the uniformity is controlled by particle size (5,8). In order to achieve uniform deposition the size of particles should be significantly lower than the deposit thickness. Low current densities were found to be preferable in order to decrease microporosity. However, deposition rate decreased with decrease of current density. It is important to note that the

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Figure 3. X-ray data for deposits obtained by the CELD method from 0.01M CeCl₃ solution saturated with air in mixed ethyl alcohol-water solvent (95:5 volume ratio),

Figure 4. TG data for deposits obtained by the CELD method from 0.01M CeCl₃ solution saturated with air in mixed ethyl alcohol-water solvent (95:5 volume ratio),
use of low current densities results in a lower potential drop between electrodes as well as low electric field. On the other hand, the rate of EPD process is proportional to the electric field \((2,7)\). The effect of electrolytes on the deposition rate and deposit morphology was investigated. SEM observations at low magnifications indicate that deposit uniformity is improved by use of 0.1-0.2 mM cerium nitrate additive. Further increases in the electrolyte concentration resulted in particle aggregation and increased porosity of the deposits. Similar influence of electrolytes on the surface morphology has also been reported \((6)\). It was established that the use of the PVB additive provides a certain strength to the green deposits.

Cathodic electrophoretic deposition of \(\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_2\) was performed from suspensions in ethyl alcohol. PVB and 4-hydroxybenzoic acid were found to be effective binder materials. In Fig. 5 the deposit weights of \(\text{CeO}_2\) and \(\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_2\) obtained in EPD experiments are plotted against deposition time. Deposit weight was found to be a linear function of deposition time when the current is constant. One may recall that constant current EPD provides constant voltage drop in the electrophoretic bath, resulting in constant deposition rate. Therefore, coating thickness can be controlled by variation of deposition time at constant current density. It is seen that the amount of the deposited material in the EPD process is much higher (by 2 orders of magnitude) than that in CELD, resulting in significantly higher deposit thickness. Fig.6 shows SEM pictures of \(\text{CeO}_2\) and \(\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_2\) deposits obtained on Ni substrates.

**Figure 5.** Deposit weight vs deposition time in EPD:
(a) for deposits obtained from 40 g/L \(\text{CeO}_2\) suspension in mixed ethyl alcohol-acetylacetone (95:5 volume ratio) solvent, containing 0.5 g/L PVB and \(2 \times 10^{-4}\) mol./L \(\text{Ce(NO}_3)_3\) additives, c.d. 2 mA/cm²
(b) for deposits obtained from 100 g/L \(\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_2\) suspension in ethyl alcohol solvent, containing 1 g/L PVB additive, c.d. 0.1 mA/cm².
Figure 6. SEM photos of CeO$_2$ (a) and Ce$_{0.8}$Gd$_{0.2}$O$_2$$_9$ (b) deposits obtained via EPD
Scanning electron micrographs of green deposits (Fig.6) revealed a smooth morphology and dense packing of particles. The deposits included particles of various dimensions ranging up to ~ 1 μm. Observed microporosity is attributed to particle packing. EPD processing has been shown to be suitable for the deposition of CeO$_2$ and Ce$_{1-x}$Gd$_x$O$_y$ films of thickness 1-200 μm.

SUMMARY

This investigation has shown that CeO$_2$ and Ce$_{1-x}$Gd$_x$O$_y$ films of various thickness in the range 0.1-200 μm can be obtained via electrolytic or electrophoretic deposition. The films can be deposited as monolayers or multilayers and deposit thickness can be controlled by variation of deposition time or current density.

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