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Chemical deposition of cerium oxide thin films on nickel substrate from aqueous solution

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Abstract

A golden yellow-colored cerium dioxide film has been deposited by immersion of an electroplated-nickel substrate into an aqueous solution containing 0.02 mol L^{-1} cerium nitrate at temperatures ranging between 303 and 343 K. The deposition rate of the film increased with an increase in solution temperature. The films exhibited good adhesion to nickel substrate. The films were characterized by X-ray diffraction (XRD), atomic force microscope (AFM), and X-ray photoelectron spectroscopy (XPS). XRD analysis revealed that the crystalline CeO_2 thin films with a fluorite structure were formed directly on the nickel substrate. XPS analysis suggested that the films mainly consisted of cerium(IV) oxide, while the surface was covered with hydroxide.

Keywords: Thin films; Chemical synthesis; Electrochemical reactions; Photoelectron spectroscopy

1. Introduction

Cerium oxide is an attractive material in various applications, including a solid oxide fuel cell electrolyte and automotive catalyst. Recently, cerium oxide films are shown to have significant effects on corrosion inhibition [1–9] and high-temperature oxidation resistance [10,11] of numerous metals and alloys. In industries such effects are of importance. Several techniques have been applied for the preparation of CeO_2 films, i.e. reactive sputtering, chemical vapor deposition, sol–gel, and spin coating, while these are costly processes. Thus, the development of the low cost coating method making cerium oxide films is required.

Electrochemical methods of cerium containing films from an aqueous solution, such as electrodeposition [12–15] and conversion coating [2–9], have received considerable attention in recent years. Cerium conversion coating process has been widely investigated to form a corrosion protection film alternative to chromate film, which is inexpensive and applicable at low temperature. In recent years, several authors have studied the cerium-based conversion coatings for corrosion protection on aluminium [2–5], magnesium [6], zinc [7,8] and these alloys, and stainless steels [9], while little attention has been made on nickel substrate. The cerium-based films were formed on the metal surface by immersing in an aqueous solution containing cerium ions. The films have a complicated nature composed of a mixture of Ce^{3+} and Ce^{4+} oxide/hydroxide compounds with amorphous structure [3,5,7,8]. In this paper, we reported, for the first time, the chemical deposition of crystalline CeO_2 thin films onto nickel metal substrate from an aqueous cerium nitrate solution by conversion coating method.

2. Experimental

An electroplated bright nickel film on a copper sheet was used as a substrate, because the bright nickel film has smooth surface. The nickel films were deposited galvanostatically at a current density of 20 mA cm^{-2} from conventional Watt-type bath that the commercial brightening agents were added. The thickness of the nickel film was 20 μm. After electrode-

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position, the specimens were rinsed in distilled water for subsequent use.

The chemical deposition of CeO_2 films on nickel substrate was performed by immersion of the nickel substrate into an aqueous solution containing 0.02 mol L^{-1} cerium nitrate, $Ce(NO_3)_3 \cdot 6H_2O$, at 303–343 K without stirring. The solution was prepared with distilled water (18 MΩ cm) and the reagent grade chemicals. No pH adjustment was carried out and the pH of solution was about 4.5. After immersion, the deposits were rinsed in distilled water and then dried in air at room temperature.

The content of cerium in deposits was determined by X-ray fluorescent spectrometer (XRF, Rigaku RIX-3100). The crystal structure of the deposited films was identified by X-ray diffraction (XRD, Rigaku RINT-2500) analysis with Cu Kα radiation, which was carried out by 2θ scanning mode with the incident angle fixed at 0.5°. The surface morphology of the films was observed using a tapping-mode atomic force microscope (AFM, Digital Instruments, NanoScope IIIa and Dimension 3000). Electron spectra measurements were performed by X-ray photoelectron spectroscopy (XPS, PHI ESCA5700). The X-ray source was monochromatized to use Al Kα (1486.6 eV). The binding energies were referenced to C 1s at 284.8 eV. An argon ion gun was used for depth profiling. The sputtering rate was approximately 3.5 nm min^{-1}. The atomic composition was calculated by area intensity of Ce 3d, Ni 2p, and O 1s spectra. The sensitivity coefficients of Ce and O were calibrated on the basis of area intensities of CeO_2 standard powder.

3. Results and discussion

A transparent golden yellow-colored film was deposited onto the electroplated-nickel substrate by immersion into $Ce(NO_3)_3$ aqueous solution. Fig. 1 shows the amount of cerium deposited in the films as a function of immersion time at different solution temperatures between 303 and 343 K. The film thickness shown in Fig. 1, was estimated from the amount of cerium and the density of cerium dioxide, 7.215 g cm^{-3} [16]. The deposition rate of the cerium-containing films greatly increased with increasing solution temperature, and was found to be 0.25, 6.7, and 22 nm min^{-1} at 303, 323, and 343 K, respectively. The film up to 30 nm exhibited a good adhesiveness to the nickel substrate (examined with tape adhesion test). However, the increase of the film thickness above 30 nm caused the deposited films peel.

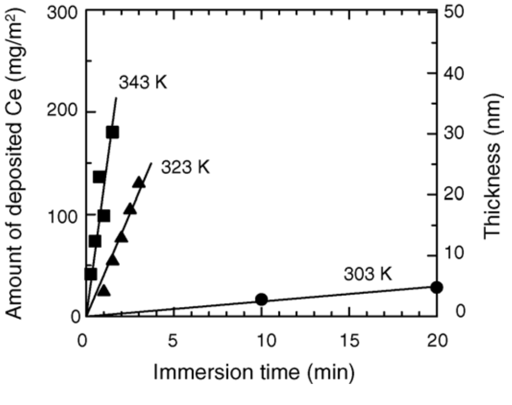

Fig. 1. Amount of deposited cerium and film thickness as a function of immersion time of the nickel substrate into 0.02 mol L^{-1} $Ce(NO_3)_3$ solution at 303, 323, and 343 K.

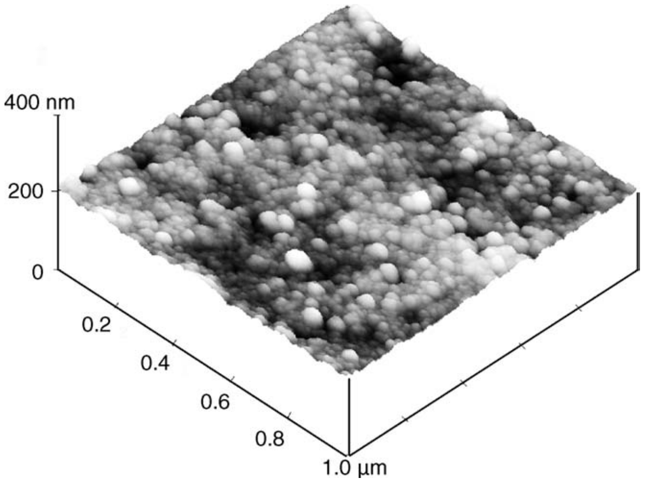

Fig. 2. AFM image of the film deposited on nickel substrate by immersion into 0.02 mol L^{-1} $Ce(NO_3)_3$ solution for 3 min at 323 K.

Fig. 2 shows AFM image of the surface morphology of the film on the nickel substrate prepared by immersion for 3 min at 323 K. The surface morphology of the film was smooth and crack-free. The substrate was completely covered with a large number of small grains, of which diameters were ranging between 20 and 60 nm. The root mean square roughness, evaluated from the AFM image, was about 7.5 nm. The surface morphology of the deposited films was not affected by the solution temperature.

Fig. 3 shows XRD patterns of the film deposited on the electroplated-nickel substrate by immersion in 0.02 mol L^{-1} $Ce(NO_3)_3$ aqueous solution for 3 min at 323 K, and the

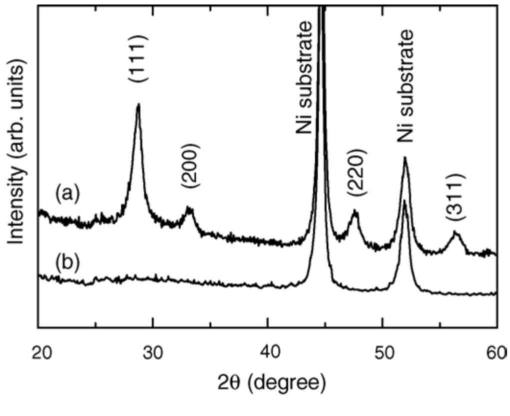

Fig. 3. Low incident X-ray diffraction patterns for (a) the film deposited on the nickel substrate for 3 min at 323 K and (b) the nickel substrate.

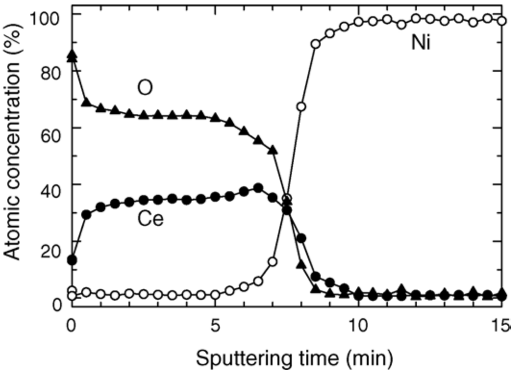

Fig. 4. XPS depth profiles of the film on nickel substrate prepared by immersion into 0.02 mol L^{-1} Ce(NO$_3$)$_3$ solution for 3 min at 323 K.

electroplated-nickel substrate. Similar XRD patterns were obtained for the films prepared at different solution temperatures between 303 and 343 K. Several peaks were observed in addition to nickel substrate peaks, and were assigned to those of CeO$_2$ phase with a cubic fluorite structure [16]. Peak broadening of diffracted X-ray line was caused by the fine grain size of the crystallites, which were observed by AFM. The lattice parameter of the CeO$_2$ film, calculated from peak angles measured by $2\theta/\theta$ method, was 0.5415 nm, which agreed with that of the ICDD card of CeO$_2$ (0.5411 nm) [16]. This result indicates that direct deposition of crystalline CeO$_2$ with fluorite structure occurs by immersion of the nickel metal in a simple aqueous solution containing cerium(III) nitrate without subsequent heat treatment of the films.

Fig. 4 shows the depth profiles of Ce, Ni, and O for the film prepared by immersion of the nickel substrate for 3 min at 323 K. Only peaks identified as Ce and O could be observed throughout the deposited film, while no signal of Ni was detected. At the surface, the oxygen content was higher than that in the bulk, and the atomic ratio of oxygen to cerium (O/Ce) was 6.5. In contrast, the composition of the bulk phase of the film was almost constant and the O/Ce ratio was about 1.9, suggesting that cerium dioxide, CeO$_2$, was the main component of the film. The interface between the CeO$_2$ film and the nickel substrate appeared around 7.5 min of sputtering, where the Ce and O signals decreased and the Ni signal increased significantly. These results suggested that the nickel substrate was covered with the uniform CeO$_2$ film.

The cerium oxidation state in the film formed by conversion coating process depends on the deposition processing conditions [4,17]. In order to investigate the chemical state of Ce and O in the film, the XP high-resolution spectra of Ce 3d and O 1s were measured. Fig. 5(a) shows the Ce 3d spectrum of the surface of the deposited film. The Ce 3d spectrum is complex owing to a satellite structure that results from the hybridization with O 2p orbitals and partial occupancy of the 4f levels. Burroughs et al. [18] indicated that the Ce 3d spectrum excites a number of components attributed to 3d$_{5/2}$ and 3d$_{3/2}$ photoelectrons and these satellite peaks of 'shake-down' type, which were indicated by the horizontal bars in Fig. 5(a). The measured peaks at the binding energy of 882.0 (v), 900.5 (u), 888.6 (v''), 907.3 (u''), 891.8 (v'''), and 916.4 eV (u''') were assigned to Ce 3d5/2 and 3d3/2 characteristic peaks corresponding to Ce^{4+} state, in good agreement with the reported spectra [3,5,15,18,19]. No characteristic peaks, v' and u', corresponding to Ce^{3+} state, were observed. These results indicate that Ce^{4+} was the dominant oxidation state in the film prepared chemically on nickel substrate.

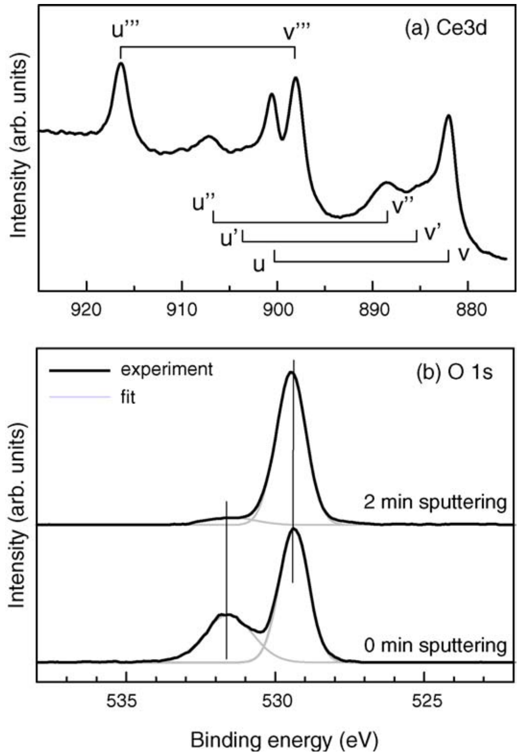

Fig. 5. (a) Ce 3d and (b) O 1s spectra of the film deposited by immersion into 0.02 mol L^{-1} Ce(NO$_3$)$_3$ solution for 3 min at 323 K. O 1s spectra were measured at different Ar$^+$ sputtering time, 0 min (without sputtering) and 2 min.

The O 1s spectrum of the surface layer shown in Fig. 5(b) was characterized by two different peaks. Praline et al. [19] reported that the O 1s binding energy in cerium oxide can vary depending on the oxidation state of cerium between 529.6 and 530.3 eV, corresponding to Ce^{4+}–O and Ce^{3+}–O bonds, respectively. Therefore, the lower peak at 529.4 eV could be assigned to the Ce^{4+}–O group. Another peak with binding energy of 531.6 eV was assigned to the Ce–OH group. This shows that the prepared film consisted of the mixture of cerium(IV) oxide and cerium(IV) hydroxide at the surface. In the bulk, the O 1s spectra were curve fitted to two peaks, shown in Fig. 5(b). The main peak at 529.4 eV and the weaker peak at 531.6 eV were assigned to Ce–O bond in tetravalent cerium oxide, CeO$_2$, and Ce–OH group, respectively. Consequently, it was clear that the major component of the film prepared chemically on nickel substrate was cerium(IV) dioxide, CeO$_2$.

4. Conclusion

The CeO_2 films were directly deposited onto an electroplated-nickel substrate from an aqueous solution containing cerium nitrate by an immersion method. The deposition rate of the film formation increased with the solution temperature from 303 to 343 K. The cerium oxide films were characterized by XRD, AFM and XPS. Immersing of nickel substrate in a cerium nitrate solution leads to the formation of the crystalline CeO_2 film with a fluorite phase. The films uniformly covered the nickel substrate and had the small grains whose diameters were between 20 and 60 nm. XPS results indicated that the films mainly consisted of cerium(IV) oxide, while the surface was covered with hydroxyl group.

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