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A comparative study on the hydrogen absorption of thin films at room temperature deposited on non-porous glass substrate and nano-porous anodic aluminum oxide (AAO) template

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ABSTRACT

The influence of different morphology of the thin films deposited on the non-porous glass and nano-porous anodic aluminum oxide (AAO) substrates on the hydrogen absorption at room temperature was studied. A well-known sandwich-like Pd/Mg/Pd film was investigated. It is observed that the film deposited on the porous AAO template demonstrates a better hydrogen absorption in the H₂ pressure range 10–600 mbar with respect to the same film supported by the non-porous glass substrate. Moreover, the layer grown on the AAO, owing to its specific morphology inherited from the nano-porous substrate, has revealed its resistance toward stress accumulation caused by the lattice expansion, showing no buckle-to-crack network formation upon the hydrogen uptake. This interesting feature is expected to improve the cycling properties and structural stability of the system, and may help to investigate better the interaction of the H₂ with metal.

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1. Introduction

Thin film processing is a method that offers the opportunity to synthesize nanostructured materials in specific compositions, well-defined microstructures and dimensions. Moreover, cooperative phenomena can be introduced through the synthesis of multilayer films and kinetic limitations can be minimized, leading to novel materials with unique properties, such as switchable mirror behavior which is reflective in a transformation from a metallic reflecting to a transparent state upon the hydrogen absorption [1,2].

Hydrogen uptake by Pd-capped Mg thin films can occur at room temperature due to the high H₂ dissociation rate and high hydrogen diffusivity in the Pd outerlayer [3]. The

absorption process can be further enhanced by an electric current [2] or annealing the film prior to hydrogenation which optimizes the morphology and structure of the film [4]. The absorption kinetics of Mg thin films coated with Pd under mild conditions were previously studied [5]. It was demonstrated that the thinner Mg layer the better the hydrogen uptake rate and the higher hydrogen content at the beginning of the process. The Mg layer of 20 nm thickness has shown the best absorption kinetics with saturated hydrogen content of 5.5 wt% at 298 K and 0.7 bar H₂. The phenomenon was explained in terms of shorter diffusion length of hydrogen and larger Pd–Mg interface enhancing the interaction of catalyst (Pd) with metal (Mg). The better hydriding-dehydriding properties of Pd/Mg thin films were also associated with a low

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degree of crystallization: the most amorphous Mg in Pd/Mg films absorbed 5.6 wt% of hydrogen at 373 K under 1 bar H₂ and desorbed H₂ at a temperature lower than 463 K in vacuum of 7.0×10^{-1} Pa [6]. A relatively low saturation level of hydrogen in the Mg film is attributed to the formation of a magnesium hydride layer at the Mg/Pd interface that blocks further hydrogen uptake due to slow hydrogen diffusion in the β -MgH₂ phase [7]. This kinetic limitation can be, however, circumvented by working at low H₂ pressure (ca. 0.04–40 mbar) and relatively low temperature (ca. 260–400 K) [8,9]. The H content in the Mg film decreases with increasing H₂ pressure and temperature [10].

Frequently, the hydrogen absorption is related to a volume change, which can lead to considerable mechanical stresses causing property deterioration. Clamping to the substrate creates severe in-plane stresses in thin films during hydrogen uptake, which may change the equilibrium pressure plateaus of metal hydride films as compared to the bulk materials [11,12]. These stresses are released by the formation of buckle-to-crack network, changing the structure of the thin films [13,14]. This feature impedes the systematic studies of the interaction of the hydrogen with a metal. Moreover, the mechanical deformations and a lack of the structural stability of the films causes substantial problems in the application of thin films as a hydrogen sensors, since it results in hysteresis behavior in electrical resistance [15–19].

The effect of the clamping to the surface might be overcome by the use of the porous substrates, which, by the presence of the pores, can provide additional space where the film can expand freely in all three dimensions. Anodic porous alumina (AAO) is a well-known template material for nanofabrication [20]. The template material is usually obtained by self-organized two-step anodization. Structural features of the honeycomb-like nano-porous arrays are fully controlled by conditions of the anodization, like type of the applied electrolyte, anodizing potential, temperature and duration of the process. The AAO template was used to grow nano-porous palladium thin films, which have demonstrated better than traditional Pd hydrogen sensors sensitivity and very short response time [21,22]. It provides more surface area which is beneficial for rapid absorption/desorption and fast hydrogen gas diffusion.

In this work the AAO template was used to grow the Pd and Pd/Mg/Pd thin films. To compare its effect on the thin films morphology, the Pd and Pd/Mg/Pd layers were also deposited on the non-porous glass substrate using the same experimental conditions. The sorption properties of Pd/Mg/Pd layers at room temperature and pressures range 0.01–1 bar are studied. The sandwich-like structure film was selected since, due to the enhanced cooperative effect, it demonstrates superior hydrogen storage properties [23,24]. Particularly, the influence of different morphological features of the Pd/Mg/Pd thin films, which were deposited on morphologically dissimilar substrates: non-porous glass substrate and nano-porous anodized aluminum oxide (AAO), on the hydrogen absorption, is investigated. A preferential behavior of the film deposited on the nano-porous AAO template over the one supported by the non-porous glass substrate, with respect to structure stability of the film upon the hydrogen loading, is demonstrated.

2. Experimental

The AAO template with nanopores of approximately 63.7 ± 4.1 nm in diameter and the interpore distance of 93.3 ± 1.4 nm was fabricated using two-step anodization method. High purity 0.25 mm thick aluminum foil (99.9995%) was purchased from Alfa-Aesar. The foil was cut into specimens 2.0×3.5 cm. The specimens were degreased in acetone and ethanol. Samples were electropolished in a 1:4 mixture of 60% perchloric acid and ethanol at constant current density of 0.5 A cm^{-2} . Temperature was kept at 10 °C and duration of the electropolishing was 1 min. As prepared aluminum specimens were coated with acid-resistant dye to obtain 4 cm^2 of working surface per sample. Nano-porous alumina was formed by two-step self-organized anodization under 40.0 V cell voltage in a 0.3 M oxalic acid solution at 35 °C. To preserve constant temperature, the processes were carried out in double-walled electrochemical cell (0.5 dm^3) equipped with a circulator bath (Lauda 105). The solution was stirred during the anodization. Platinum grid with the surface area of 6 cm^2 was used as a counter electrode. Distance between the platinum grid and anodized aluminum was 30 mm. After the first step of anodization, formed alumina was removed by chemical etching in a vigorously stirred mixture of 6% wt H₃PO₄ and 1.8% wt H₂CrO₄ at 60 °C. After oxide removal the samples were re-anodized at the same conditions as presented in the first step of the process, but the duration of the second step was 7 h and 5 min to obtain 200 μm thick AAO template.

The Pd/Mg/Pd thin films were deposited onto glass and AAO substrate by vacuum evaporation at room temperature and under high vacuum of 5×10^{-6} torr. All evaporation processes were done using resistively heated tungsten crucibles.

The H₂ absorption/desorption isotherms of Pd/Mg/Pd thin films were measured by using the Micromeritics ASAP 2020 gas adsorption analyzer. Prior to the measurement the samples, loaded in 1/2 inch stem tube with a seal frit, were degassed on the preparation port to remove moisture and stray gases like CO₂ that might adsorb to the materials at ambient temperature and pressure. The preparation was performed at 373 K for 2 h at pressure of 3 μbar . The samples were backfilled with nitrogen. Second, the sample was degassed thoroughly on the sample port. Pressure composition absorption and desorption isotherms were measured in pressure range from 10 to 1000 mbar with the use of high purity hydrogen (99.999%) at room temperature. The isotherms were corrected for the background physisorption, measured in the second absorption/desorption cycle. It was found that the physisorption of H₂ was at the level of 10^{-4} – 10^{-5} wt% and, thus, introduced only a negligible error into the acquired data. The mass of H₂ was calculated taking into account the density of hydrogen at room temperature.

The mass of thin films was obtained from the difference between the weight of the film deposited on substrates and the weight of bare substrates; the entire mass of the film was 2.67 mg and 1.83 mg for the Pd/Mg/Pd film deposited on AAO template and on glass substrate, respectively.

The morphology and microstructure of the investigated samples were examined with a high resolution field emission

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