INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 41 (2016) 3465–3469

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Short Communication

Enhanced hydrogen capacity and absorption rate of $LaNi_{4.25}Al_{0.75}$ alloy in impure hydrogen by a combined approach of fluorination and palladium deposition

Botao Zhao[*], *Lifei Liu*, *Yiming Ye*, *Shilin Hu*, *Dong Wu*, *Pingzhu Zhang*[**]

China Institute of Atomic Energy, Fangshan District, Beijing 102413, China

ARTICLE INFO

Article history:
Received 15 September 2015
Received in revised form
25 December 2015
Accepted 26 December 2015
Available online 15 January 2016

Keywords:
AB_5-type alloy
Surface treatment
Palladium deposition
Fluorination

ABSTRACT

In this study, a new surface structure named 'net mosaic' is found to enhance the resistance against poisoning of compound alloy. The structure is composed of palladium nanospheres and fluorinated layer. Hydrogen capacity and characteristics absorption rate of F-0.5%Pd-$LaNi_{4.25}Al_{0.75}$ alloy are 1.147wt% and 0.062wt%/s in impure hydrogen containing O_2 and N_2 both of 0.1 at% under initial pressure of 0.71 MPa at 30 °C, respectively, which is remarkably raised by 10% and 68% than that of $LaNi_{4.25}Al_{0.75}$ alloy. Synergistic effect from fluorination and palladium deposition is proposed to illustrate the excellent performance of F-0.5%Pd-$LaNi_{4.25}Al_{0.75}$ alloy.

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Introduction

AB_5 type alloys have become a typical representative of hydrogen storage alloys due to its characteristics of easy activation, rapid absorption kinetics, moderate hydrogen capacity and platform pressure [1–3]. However, with air impurities such as O_2 and N_2 in hydrogen, the dynamic performance and hydrogen capacity of the AB_5 alloy are decreased significantly. The main reason is the occupation of active sites of molecular hydrogen into atomic state by impurity gases, resulting in diffusion obstruction of H atoms in the formation of oxide layer [4,5]. Therefore, high catalytic activity and good corrosion resistance of the alloy surface are required.

Palladium (Pd) deposition is mostly introduced in the treatment of the material surface because Pd can act as a catalyst in dissociation of H_2, which speeds up the rate of hydrogen uptake and release process [6–8]. Deposition of Pd can be achieved by means of chemical deposition, mechanical grinding, physical vapor deposition and ion beam sputtering et al. It was reported that $LaNi_{4.7}Al_{0.3}$ alloy treated by chemical

* *Corresponding author.*
** *Corresponding author.*
E-mail address: 18518705396@163.com (B. Zhao).
http://dx.doi.org/10.1016/j.ijhydene.2015.12.167
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deposition of Pd maintains the good hydrogen absorption performance even when exposed in air for two years [6].

Introducing protective layer by fluorination is another kind of surface treatment. Surface fluorination treatment carried out by S. Suda [9] showed that fluorination could eliminate oxide layer on the surface of the alloy by forming a fluorinated layer with protective effect, which can effectively reduce the poisoning effect of H_2O or air on hydrogen capacity. Furthermore, the main component of the fluorinated layer is verified to be LaF_3 of porous structure by H.Y. Park et al. [10].

In this work, a combined surface treatment technique of $LaNi_{4.25}Al_{0.75}$ alloy based on fluorination and Pd deposition is presented to investigate the poisoning resistance performance. Surface morphology and chemical composition of the treated surface were analyzed. The absorption kinetics and hydrogen capacity in the impure hydrogen containing O_2 and N_2 was tested. In addition, a synergistic effect of the fluorination and palladium deposition in enhancing the hydrogen capacity and absorption rate is discussed.

Experiment

$LaNi_{4.25}Al_{0.75}$ alloy (Shenyang Institute of Metal Research of Chinese Academy of Science) particles were selected through a 125 mesh sieve, with a particle size of 100–150 μm after mechanical pulverization employed in the experiment.

The sample treated with fluorination and palladium deposition was named as F-0.5%Pd-$LaNi_{4.25}Al_{0.75}$ and prepared by the following procedure: (1) Fluorination. The $LaNi_{4.25}Al_{0.75}$ particles were immersed in fluorination solution containing 6 g/L KF and 0.6 mL/L HF [11] and reacted for 15 min at 30 °C. (2) Sensitization. The fresh sensitizing solution composed of 5 g/L $SnCl_2$ and 20 mL/L HCl was prepared to ensure Sn^{2+} to be adsorbed on the surface of the alloy particles. (3) Activation. Activation solution is composed of 0.25 g/L $PdCl_2$ and 2.5 mL/L HCl. In this process, Sn^{2+} was replaced by Pd, acting as nuclei for Pd deposition. (4) Pd deposition. Solution for electroless palladium plating consists of 2 g/L $PdCl_2$, 27 g/L NH_4Cl, 160 g/L $NH_3{\cdot}H_2O$ [12], with N_2H_4 as a reducing regent at 60 °C for 15 min.

The preparation of Pd-$LaNi_{4.25}Al_{0.75}$ and F-$LaNi_{4.25}Al_{0.75}$ samples was followed by the previous step 2–4 with 2wt% Pd deposition and step 1 with fluorination.

Surface morphology was performed by a Supra 55 scanning electron microscope (SEM) by German Zeiss Co., Ltd. Specific surface area was characterized by Autosorb IQ-type nitrogen adsorption instrument of Quantachrome Co., Ltd. X-ray photoelectron spectroscopy (XPS) test was conducted on PHI Quantera SXMTM of ULVCA-PHI Co., Ltd.

Results and discussion

Surface morphology and composition

Surface morphology of $LaNi_{4.25}Al_{0.75}$, 2%Pd-$LaNi_{4.25}Al_{0.75}$, F-$LaNi_{4.25}Al_{0.75}$, and F-0.5%Pd-$LaNi_{4.25}Al_{0.75}$ are shown in Fig. 1. $LaNi_{4.25}Al_{0.75}$ in Fig. 1a has a smooth surface along with a surface area of 0.11 m^2/g obtained from N_2 adsorption equilibrium measurement. The palladium coating is found to be discontinuous in nature in Fig. 1b, which is composed of Pd nanospheres with an average diameter of 55 nm, and the surface area is increased to 0.28 m^2/g. In Fig. 1c, a dense net structure is formed on the surface of alloy after fluorination, and the structure has an average surface pore diameter of 80 nm with a higher surface area of 0.49 m^2/g. The surface area could further increase to 3.9 m^2/g for 24 h at 70 °C with similar fluorinating solution [13]. F-0.5%Pd-$LaNi_{4.25}Al_{0.75}$ alloy is presented in Fig. 1d, 'net mosaic' structure forms on surface of the alloy with the Pd nanoparticles uniformly embedded in the fluorinated net structure. Pd nanoparticles here show no obvious difference compared to that in Fig. 1b in particle size, but the average pore diameter of net structure is increased from 80 nm to 200 nm. Additionally, the specific surface area is measured up to be 0.60 m^2/g, which is further increased in comparison to that of samples prepared by Pd-deposition or fluorination.

The surface composition of samples was further studied by x-ray photoelectron spectroscopy (XPS). $LaNi_{4.25}Al_{0.75}$ is shown in Fig.2a, and binding energy of $La3d^{2/5}$ is located at 834.6 eV and 838 eV, which declares the existence of La_2O_3 and LaH_3 [6]. $Ni2P^{3/2}$ is correlated with two peaks located at 855 eV and 862 eV, and these peaks correspond to that of Ni_2O_3 and metallic nickel, respectively. However, peak intensity at 862 eV is very weak, which suggests that Ni element on the surface is mainly in the oxide form. Thus, it is assumed that elements La and Ni on surface of $LaNi_{4.25}Al_{0.75}$ are mainly in the oxide state, in a good agreement with the results of a previous work [4].

As shown in Fig. 2b, the profiles of elements (La, Ni) were not changed significantly for the Pd-deposition alloy comparing to $LaNi_{4.25}Al_{0.75}$, which reveals that the Pd deposition will not affect the composition of surface. Besides, binding energies of $Pd3d^{5/2}$ and $Pd3d^{3/2}$ peaks are 340.5 eV and 335.2 eV, respectively, corresponding to metallic palladium. In Fig. 2c, $La3d^{2/5}$ of F-$LaNi_{4.25}Al_{0.75}$ has only one peak located at 836.8 eV, corresponding to LaF_3, and the weak peak at 851.4 eV of $La3d^{3/2}$ is due to La_2O_3, which further indicates that element La is mainly in the form of LaF_3. It is also found that the Ni/La ratio is 0.4, far below the internal value (4.25), indicating that the outer surface of F-$LaNi_{4.25}Al_{0.75}$ is mainly composed of LaF_3 [14].

The XPS spectrum of F-0.5%Pd-$LaNi_{4.25}Al_{0.75}$ is shown in Fig. 2d, and the spectrum is slightly changed as compared to Fig. 2c. La is still in the form of LaF_3, which indicates that Pd-deposition has little effect on chemical composition of the fluorinated layer of net structure. The surface has a Ni/La atomic ratio of 1.1, higher than that 0.4 in F-$LaNi_{4.25}Al_{0.75}$, aligning with an increased diameter of fluorinated net structure shown in Fig. 1d. Thus, it can be concluded that part of LaF_3 backbone collapses during the deposition of Pd and then a net structure with larger diameter with inserted Pd nanospheres is formed. Considering the existence of fluorinated layer, the deposition of Pd is greatly reduced to 0.5% compared with that of 2%Pd-$LaNi_{4.25}Al_{0.75}$, leading to the attenuation of the peak intensity of metallic palladium as shown in Fig. 2d. As a result, the 'net mosaic' structure was obtained, proving the feasibility of the combined approach of fluorination and palladium deposition.

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