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Experimental and theoretical investigation of the cycle durability against CO and degradation mechanism of the $LaNi_5$ hydrogen storage alloy

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Abstract

From both the experimental and theoretical aspects we have investigated the cycle durability against CO and degradation mechanism of the $LaNi_5$ hydrogen storage alloy with CO-containing H_2. Temperature-programmed desorption (TPD) measurements on the pristine alloy and the corresponding one after hydrogen absorption–desorption cycles exhibit that: (1) the molecular CO can be adsorbed on the clean alloy surface, and thus decrease the hydrogen storage ability of the alloy; (2) with the increase of the cycle number the partial decomposition of the CO and the subsequent adsorption of C atom and O atom on the surface is deleterious to the hydrogen storage competence of alloy. From the results of first-principle calculations, it is found that the adsorption of the molecular CO prefers the on-top and bridging sites on the Ni atoms. Moreover, the latter one is more stable than the former one.

Keywords: Hydrogen storage materials; Cycle durability; Carbon monoxide; Temperature-programmed desorption; First-principal calculation

1. Introduction

Hydrogen, as an ideal energy carrier, is of great interest to meet the challenge of environmental pollution and the upcoming energy crisis. On the way to hydrogen energy society, a safe, effective, and low-cost hydrogen-storage system is crucial for hydrogen economy of the future. Among different hydrogen storage systems, hydrogen storage alloys are important and widely used hydrogen storage materials. Form the viewpoint of practical application, hydrogen storage alloys should hold the property of long-term cyclic stability, that is to say, they must resist to deterioration originated from inevitably accompanied impurities, such as carbon monoxide (CO) involved in hydrogen produced by steam reforming.

Sandrock et al. [1] reported their works on hydrogen absorbing–desorbing cycle durability by using H_2 with 300 ppm O_2, H_2O or CO, and the results reveal that CO has the severest damage to the hydrogen storage ability. Tanaka et al. [2,3] systematically investigated the cyclic durability of Ca–Mg–Ni and Ti–V alloys in pure H_2 and in CO impurity-containing H_2. It is found that the alloys decrease hydrogen storage capacity seriously with increasing CO concentration. Surprisingly, crystal structures of bulk alloys before and after absorbing–desorbing cycles are kept almost unchanged. It is proposed that the devitalisation of alloy surface is responsible for the deterioration of hydrogen storage ability of the alloys. It is important to shed light on the degradation mechanism on the basis of both experimental results and theoretical calculations.

In this paper, we investigated the cyclic stability of the widely used $LaNi_5$ alloy in hydrogen containing the most possible impurity, CO. Both experimental and theoretical results are provided to elucidate the degradation mechanism of hydrogen storage ability.

2. Experimental details

The $LaNi_{4.9}Al_{0.1}$ alloy granules (JSW, The Japan Steel Works) were ground into powders with particle sizes between 100 and 500 μm using a stainless mortar in glove box under an argon atmosphere. The absorbing–desorbing cycle test were carried out with pure H_2 (99.99999%) or with H_2 containing 1000 ppm CO.

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The gas desorption properties were evaluated by temperature-programmed desorption (TPD) analysis using a home-made instrument connecting to a multi-channel quadrupole mass spectrometer (Q-Mass; Prizma, Balzers Instruments), which is capable for concurrent detecting of ^{12}CO (mass/charge ratio = 28), ^{13}CO (mass/charge ratio = 29), H_2 (mass/charge ratio = 2), CH_4 (mass/charge ratio = 16) and H_2O (mass/charge ratio = 18). In TPD experiments, the chamber was evacuated up to 1×10^{-8} Torr and the alloy surface were heated at a rate of 2 K/s.

The absorption–desorption cyclic durability was tested using a Sievert's type apparatus (JSW) [4]. For every absorption–desorption cycle, hydrogen was absorbed under the pressure of 2.0 MPa for 30 min and then desorbed under dynamic vacuum using a rotary vacuum pump.

The first-principle calculations have been performed using the Vienna ab initio simulation program (VASP) [5–8]. A nine-layer slab, separated by a vacuum layer of 14 Å, is used to model the $LaNi_5$ surface. The Monkhorst-Pack scheme [9] with $2 \times 2 \times 1$ k points ($7 \times 7 \times 7$ for bulk calculation) has been used for integration in the surface Brillouin zone for the $p(2 \times 2)$ supercell. Energy cut off for the plane waves is 800 eV. Fermi level is smeared by the Gaussian method [10] with a width of 0.2 eV. We used ultra soft Vanderbilt type pseudopotentials [11] as supplied by Kresse and Hafner [12]. The generalized gradient approximation by Perdew and Wang (PW91) [13] are used for the exchange-correlation energy. This set of parameters assures a total energy convergence of 2 meV per atom. In structural search, all the atoms are relaxed simultaneously. The search is stopped when forces on all atoms are less than 0.02 eV/Å.

3. Results and discussion

It is well known that TPD is a very useful method for studying surface adsorption. In the present work, we first studied the adsorption of CO on the $LaNi_5$ alloy surface. At room temperature, 10 Torr ^{13}CO were introduced into empty and alloy-containing sample tubes, respectively, for 10 min. The TPDs of ^{13}CO are shown in Fig. 1. No CO is desorbed from the clean sample tube (a), whereas a large amount of CO is desorbed from the $LaNi_5$ alloy surface with the maximum at the temperature of 400 K, indicating that the molecular CO can be easily absorbed on the alloy surface.

In order to study the influence of the adsorbed CO on the hydrogen storage ability, we first introduced pure hydrogen into clean alloy and ^{13}CO-covered alloy, respectively, at the pressure of 0.6 MPa for 10 min. After the system was evacuated to 10^{-6} Torr, we measured the TPDs of H_2 (Fig. 2). From the pristine alloy, a large amount of H_2 is desorbed with a maximum at 413 K, whereas no H_2 is desorbed from the CO pre-adsorbed alloy, indicating that the pre-adsorbed CO obviously prevents the H_2 absorption.

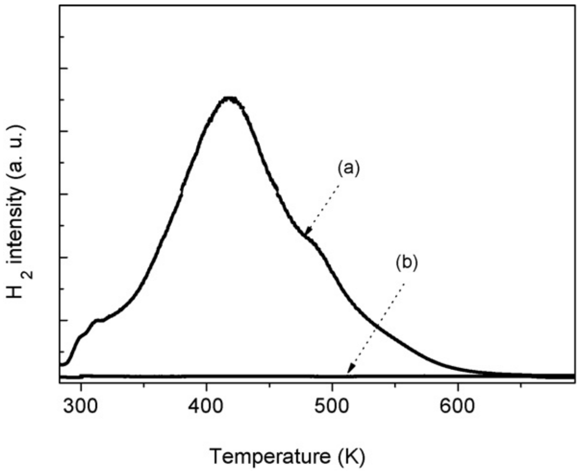

Fig. 2. TPDs of H_2 from (a) pristine and (b) CO pre-adsorbed alloy surfaces.

To give clearer picture of the effect of CO impurity on the hydrogen storage, hydrogen capacity was measured with pure H_2 and CO/H_2 (CO impurity-containing H_2) alternately used every 10 cycles at 293, 323 and 353 K, respectively (Fig. 3). After 10 cycles with pure hydrogen, the alloy is fully activated and its hydrogen storage capacity reaches 160 ml/g, corresponding to H/M = 1.17. However, the hydrogen storage capacity drastically decreases after changing the pure H_2 gas to CO/H_2 (1000 ppm CO). At 293 and 323 K, the hydrogen storage capacity decreases to H/M = 0.2 at one cycle, whereas at 353 K the decrease to the same level needs more than three cycles, indicating the strong temperature dependence of the hydrogen storage degradation. Moreover, the recovery of the hydrogen storage ability using pure hydrogen is much more difficult at 293 K than that at 323 and 353 K.

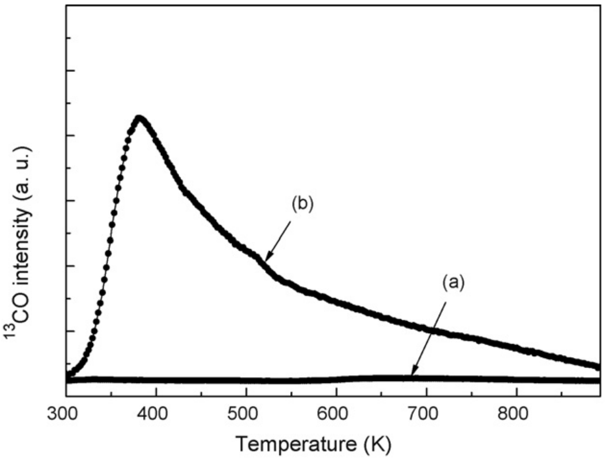

Fig. 1. TPDs of ^{13}CO from (a) clean sample tube and (b) ^{13}CO pre-adsorbed $LaNi_5$ alloy surface contained in the sample tube used for (a).

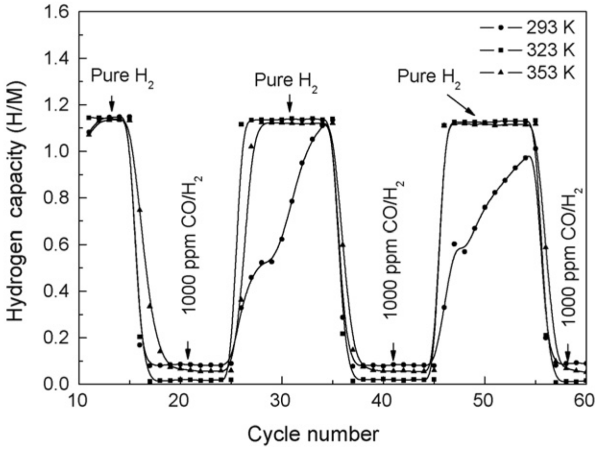

Fig. 3. Cyclic stability of hydrogen storage capacity with pure H_2 and CO/H_2 (1000 ppm) alternately used every 10 cycles at 293, 323 and 353 K, respectively.

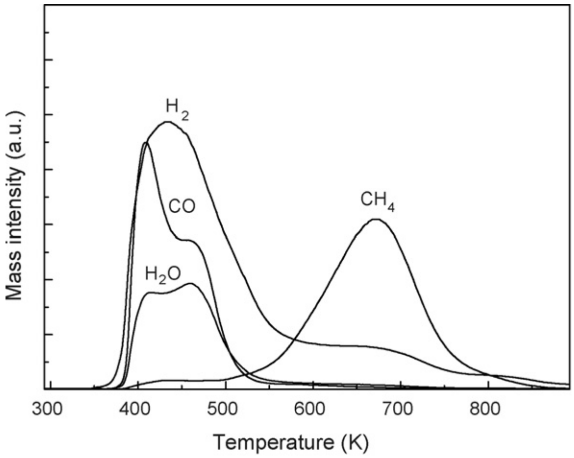

Fig. 4. TPDs of $LaNi_5$ alloy after 60 adsorbing–desorbing cycles alternately using H_2 and CO/H_2 (1000 ppm) at 353 K.

Fig. 4 is the TPD results for the sample after 60 cycles alternately using H_2 and CO/H_2 at 353 K. Interestingly, besides the CO desorption peaks at 413 and 453 K, there are two H_2O peaks at 413 and 473 K and one CH_4 peak at 663 K. In contrast, the TPD results for the sample after 60 cycles alternately using H_2 and CO/H_2 at 293 K show very small H_2O and CH_4 desorption peaks. It was proposed that the formation of CH_4 is derived from molecular CO and H_2 on $LaNi_5$ alloy surface [1,14]. In our TPD experiments, it is found that molecular CO is completely desorbed from the alloy surface before 550 K, suggesting that the resultant CH_4 comes from dissociated C species of CO. The dissociated O species gives the H_2O product. The present observations indicate the dissociation of CO on the alloy surface.

First-principle calculation method has been employed to clarify the adsorption states of CO on $LaNi_5$ alloy surface and their adsorption energies. After fully relaxing all six possible adsorption structures, we finally get three stable structures. The schematic model of the CO adsorption on $LaNi_5$ surface is shown in Fig. 5a and the charge distributions of CO adsorbed on different sites are shown in Fig. 5b, c and d, respectively. The calculated bond lengths of CO on the on-top site of La atom, the on-top site of Ni atom and the bridge site of two Ni atoms are 1.149, 1.179 and 1.205 Å, respectively. The C–M bond lengths (M = La, Ni) are 2.760, 1.734 and 1.885 Å, respectively. Previous theoretical calculations have reported that for CO adsorption on Ni (1 0 0) surfaces, the C–Ni bond length at the on-top site of Ni atom and at the bridge site of two Ni atoms are 1.73 and 1.89 Å [15], respectively, which is in agreement with our results, indicating that the adsorption of the molecular CO prefers the on-top and bridging sites on the Ni atoms, between which the latter is more stable than the former. The adsorption energies (E_{ads}) for CO on the on-top site of La atom, on-top site of Ni atom and bridge site of two Ni atoms are 0.462, 2.066 and 2.180 eV, respectively.

It is well known that the hydrogen storage process consists of the hydrogen adsorption and dissociation on alloy surface and thereafter the hydrogen atoms diffuse toward alloy bulk. Wallace et al. proposed a model for such process and, especially, emphasized that the existence of Ni atom on the alloy surface is very important due to its catalysis effect for the initial steps of hydrogen storage—hydrogen adsorption and dissociation [16].

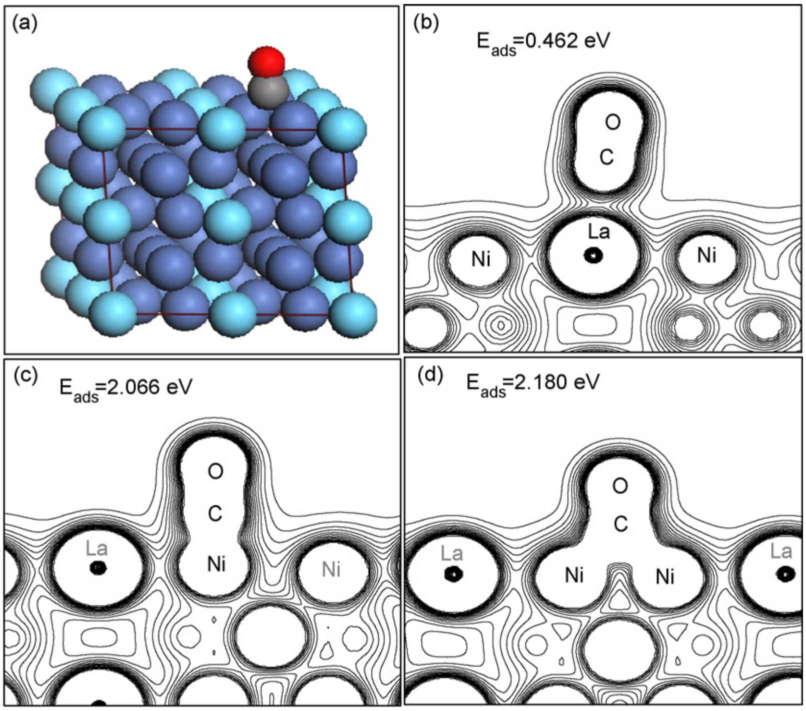

Fig. 5. (a) Schematic model of CO adsorption on $LaNi_5$ alloy surface and electron density distributions when CO adsorbed on (b) on-top site of La atom, (c) on-top site of Ni atom, and (d) bridge site of two Ni atoms. Insets are their adsorption energies.

The results from both of the present experimental and theoretical studies show that CO can easily adsorb on Ni atoms of the alloy surface, which were proposed to be the active sites for H_2 adsorption and dissociation, and consequently prevent the absorption of H_2 to the alloy. That is to say, the activation sites of alloy surface, Ni atoms, is easily to be occupied by CO and therefore hinder the adsorption of H_2 on the alloy surface, which inevitable degrade the alloy hydrogen storage ability.

4. Conclusions

The present experimental results reveal that, at room temperature, molecular CO can be easily adsorbed on $LaNi_5$ alloy surface and degrade the hydrogen storage ability of the alloy. Through theoretical calculations it is found that, comparing with the adsorption on La atom, CO prefers the adsorption on the on-top and bridging sites on the Ni atoms, and the latter is more stable than the former. CO adsorption on Ni atoms of the alloy surface, which were proposed to be the active sites for H_2 adsorption and dissociation, may consequently prevent the absorption of H_2 to the alloy. In addition, the observation of CH_4 in the TPD experiments from the alloy after enduring absorbing/desorbing cycles with CO impurity-containing in H_2 indicates that adsorbed CO can dissociate into C and O atoms on the alloy surface, which may further depress the alloy hydrogen storage ability.

Acknowledgements

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