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Effect of HF pretreatment on H_2 reactivity with $LaNi_5$ and $LaNi_{4.7}Al_{0.3}$

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Abstract

The effect of fluorination of $LaNi_5$ and $LaNi_{4.7}Al_{0.3}$ surfaces on the initial activation of hydrogen absorption was examined at 298 K by the measurement of H_2 reaction probability under ultra high vacuum and low vacua conditions, and by the measurement of the initial rate of hydrogen absorption at pressures over 10^6 Pa. The HF pretreated $LaNi_{4.7}Al_{0.3}$ and $LaNi_5$ alloys degassed up to ultra high vacuum, and no improvement or even a marked reduction in the H_2 reaction rate was observed. However, the HF pretreated $LaNi_{4.7}Al_{0.3}$ degassed at low vacuum exhibited a much higher reactivity than the sample degassed in ultra high vacuum. The results obtained show the importance of alumina present in the fluorination, and a possible enhancement of catalytic properties by the oxidation of fluorinated $LaNi_{4.7}Al_{0.3}$.

Keywords: $LaNi_5$; $LaNi_{4.7}Al_{0.3}$; HF treatment; Reactivity

1. Introduction

During the initial activation of $LaNi_5$ [1] and $LaNi_{5-x}(Al,Mn,Co)_x$ alloys [2], the surface conditions markedly affect the rate controlling step of the H_2 absorption. The $LaNi_5$ with a clean surface exhibits the highest reaction probability, $r=1$, even at room temperature. However, r is decreased by several orders of magnitude as the surface becomes contaminated by degassing at lower vacuum [1]. The H_2 dissociation is a result of the interaction between the H_2 antibonding orbitals and the lobe shaped orbitals of the d electrons of the transition metal surface [3]. The electron transfer between the surface and H_2 is decisive for the H_2 dissociation [4]. Recently, intensive studies have been made by Suda and his co-workers [5] on the marked effect of fluorination of the surfaces of H storage alloys on the hydriding rate. However, the role of the fluorinated layers in the H_2 absorption is not clear. This study investigated the effect of fluorination of $LaNi_5$ and $LaNi_{4.7}Al_{0.3}$ surfaces on the initial activation in order to give additional information on this fluorination effect.

2. Experimental procedure

Massive and powder samples of $LaNi_5$ and $LaNi_{4.7}Al_{0.3}$ alloys were prepared by crushing their ingots produced by arc melting in Ar atmosphere. The structure and chemical composition of these samples were controlled by using inductively coupled plasma emission spectroscopy and X-ray diffraction, respectively. The fluorination treatment was made by soaking the samples into a 100% HF solution(12 N purity) for 3 h at 293 K, and then drying them in a 10^5 Pa N_2 gas flow at 393 K for 3 h. Auger electron spectroscopy of the formed fluorinated layers indicated a thickness of about 50 nm.

The volumetric Wagener's method was used to measure number of adsorbed or absorbed H_2 molecules per square cm, N, and the reaction probability, r, defined as the ratio of the rate of reacted H_2 molecules to the impinging rate of H_2 molecules on the metal surface. Details of this measurement method are described elsewhere [6]. A 0.2 g massive sample of $LaNi_5$ or $LaNi_{4.7}Al_{0.3}$ with a surface area of 1 cm^{-2} was used for the measurements of r and N at 298 K. Before hydrogenation, the whole pyrex glass system and the samples were degassed to a pressure of $5\cdot10^{-6}$ to $5\cdot10^{-8}$ Pa at temperatures up to 850 K. During the measurements,

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partial pressures of the system were monitored by mass spectrometry.

The initial rate of activation was measured using a Sieverts' type apparatus in the hydrogen solid solution regions where no pulverization, i.e., no marked changes in the surface layers took place. An intentional evacuation of the apparatus was made down to only 5–10 Pa in order to examine the contamination effect of the HF pretreated samples on the reaction rate. The effect of vacua on the initial rate, details of the measurement method and the effect of the sample mass, cell materials and thermal conductivity on the rate are reported elsewhere [7].

3. Results and discussion

3.1. The effect of the HF pretreatment on reaction probability

Fig. 1 shows the changes in r for $LaNi_5$ samples with and without the HF pretreatment. An untreated $LaNi_5$ sample degassed under ultra high vacuum 10^{-8} Pa, where no residual gas contaminated the surface before H_2 exposure, exhibits the highest rate, $r=1$ at the initial stage. That rate decreases for an untreated $LaNi_5$ which was degassed in a lower vacuum of 10^{-6} Pa where the main residual gas was H_2O with partial pressures ranging from 10^{-7} to 10^{-5} Pa during the measurement. For the HF pretreated $LaNi_5$ samples, the r values ranging between $r=10^{-2}$–10^{-3}. They are independent of the degassing conditions and are even lower than those for the untreated $LaNi_5$ sample degassed in 10^{-6} Pa. These results suggest that the fresh Ni layer induced under the outer LaF_3 layer by the fluorination [5] does not seem to be present in this case because even in the presence of large amounts of oxides, trace amounts of fresh Ni, on which the H_2 dissociation and the H spill over can be promoted, markedly increase the rate to values up to $r=1$ [8].

Fig. 2 shows the rate changes for $LaNi_{4.7}Al_{0.3}$ samples with and without the HF pretreatment. Untreated samples exhibit a decrease of r values from 10^{-2} to 10^{-4}, independent of the degassing conditions. An untreated sample degassed in 10^{-6} Pa exhibits slightly higher initial r values than the sample degassed in higher vacuum 10^{-8} Pa, which may be ascribed to the enhancement of r by the partial oxidation of Al [9]. For the HF pretreated samples, a sample degassed in a low vacuum 10^{-6} Pa exhibits r values lying between $r=1\times10^{-1}$ to 4×10^{-3} which are higher than for the other sample degassed in a ultra high vacuum 10^{-8} Pa. With increasing N, the pretreated sample degassed in 10^{-6} Pa tends toward a constant value of $r=4\times10^{-3}$ which is higher than the r values for the untreated samples. Compared to the results for the HF pretreated $LaNi_5$, it is interesting to note that the oxidation or hydroxidation of the fluorinated $LaNi_{4.7}Al_{0.3}$ surface, which can take place in the low vacuum degassing before H_2 exposure, seems to be crucial to induce a catalytic activity to promote the H_2 dissociation. This is in good agreement with many reports for the enhancement of catalytic reactivity surfaces by mixing alumina and AlF_4 [10] or the fluorination of alumina [11] where the O atoms near the alumina surface are replaced by F and OH,

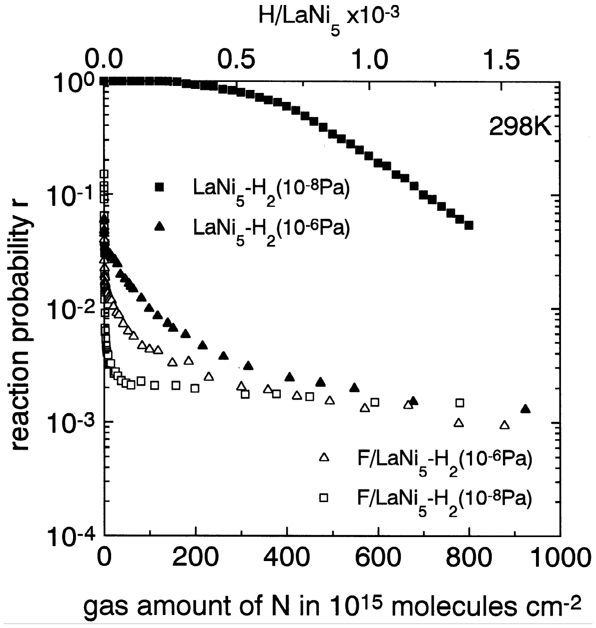

Fig. 1. Changes of the reaction probability, r, as a function of the H_2 amount absorbed by $LaNi_5$ samples with and without the HF pretreatment after vacuum degassing at 10^{-8}Pa=■, □ ; at 10^{-6}Pa=▲, △ respectively.

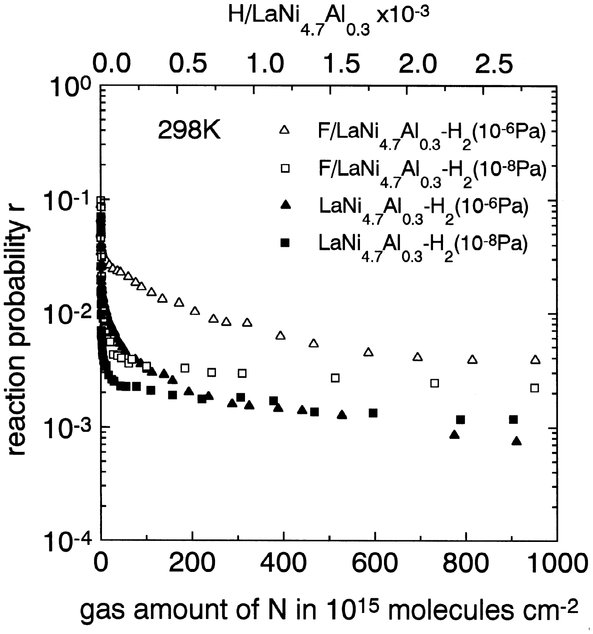

Fig. 2. Changes of r as a function of the H_2 amount absorbed by $LaNi_{4.7}Al_{0.3}$ samples with and without the HF pretreatment after vacuum degassing at 10^{-8}Pa=□, ■, and at 10^{-6}Pa=△, ▲ respectively.

resulting in a HO-AlF_4 bonding on the fluorinated alumina surface. This localized OH with large electronic strains [12] is assumed to act as catalysis for the decomposition of the covalently bonded gases.

3.2. The effect of the HF pretreatment on initial activation

The powder samples of the HF pretreated $LaNi_5$ and $LaNi_{4.7}Al_{0.3}$ with a 500 μm diameter were exposed to H_2 at 298 K immediately after the pressure of the system had attained 5 to 10 Pa by 5 min evacuation at 298 K. At these low vacua conditions, the partial pressures of residual gases in the cell were in the order $H_2O > H_2 > CO_2 >$ CO. After the 6 months air exposure of untreated $LaNi_5$ and $LaNi_{4.7}Al_{0.3}$, no significant activation was seen at 298 K within 2000 s. However, in spite of such a long exposure to air after the HF pretreatment, the HF treated $LaNi_5$ and $LaNi_{4.7}Al_{0.3}$ could be activated at a H_2 pressure 10^6 Pa and 298 K as shown in Fig. 3. Under these experimental conditions, the treated $LaNi_{4.7}Al_{0.3}$ tended to exhibit higher activation rates than the treated $LaNi_5$. However, further investigations are needed by changing the experimental conditions to confirm the H_2 processes. In the light of the results the fluorinated layers on $LaNi_5$ seems to act simply as protective layers to contaminations rather than as catalytic layers.

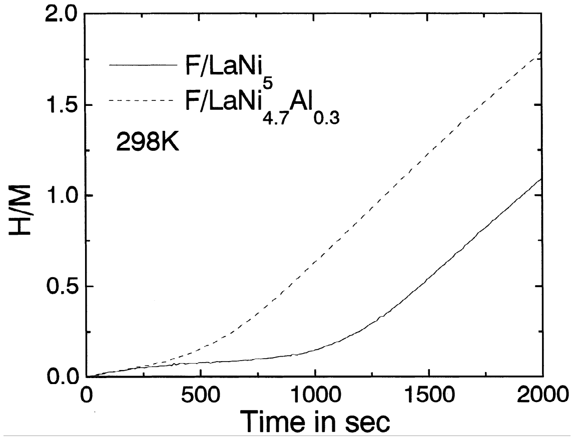

Fig. 3. The initial activation of the HF pretreated $LaNi_5$ and $LaNi_{4.7}Al_{0.3}$ exposed to air for 6 months, at a H_2 pressure of 10_6 Pa at 298 K. (M=$LaNi_5$, $LaNi_{4.7}Al_{0.3}$)

4. Conclusions

The formation of fluorinated surface layers appears to inhibit H_2 dissociation on a clean $LaNi_5$ surface at 298 K. In contaminative conditions like in low vacua or air, the fluorinated layers seem to act as protective layers to the contaminations on the $LaNi_5$ surface, rather than as catalytic layers on the $LaNi_{4.7}Al_{0.3}$ surface. For the fluorinated $LaNi_{4.7}Al_{0.3}$ surface, the enhancement of the H_2 reactivity by low vacuum degassing of the sample indicates a possible enhancement of the surface catalytic properties by the oxidation of the fluorinated $LaNi_{4.7}Al_{0.3}$ surface.

Acknowledgments

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