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Comparison of pretreatments by alkaline (Li, Na, K) hydroxides with NH_3–H_2O in the work function and hydriding kinetics of $LaNi_{2.5}Co_{2.5}$

H. Uchida[b,]*, K. Yamashita[a], M. Goto[a]

[a]Department of Applied Physics, School of Engineering, Tokai University, 1117 Kita-Kaname, Hiratsuka, Kanagawa 259-1292, Japan
[b]Department of Human Development, School of Humanity and Culture, Tokai University, 1117 Kita-Kaname, Hiratsuka, Kanagawa 259-1292, Japan

Abstract

The electrochemical hydriding rate of $LaNi_{2.5}Co_{2.5}$ with and without surface modifications by alkaline solutions of LiOH, NaOH, KOH and NH_3–H_2O was measured at temperatures between 298 and 318 K. The treatment with LiOH, NaOH and KOH enhanced the concentration of Li, Na and K atoms in the surface region. The increase in the K surface concentration was found to drastically decrease the work function of electrons at the alloy surface. This may accelerate the rate of the H_2O dissociation, resulting in the enhancement of the hydriding rate. The NH_3–H_2O treatment induced similar surface modifications to those of LiOH, NaOH or KOH, but without the penetration of alkaline metal atoms into the surface, and this treatment lowered the rate and raised the work function. The measured relationship between the activation energy and the work function suggests a shift in the rate controlling step from the H_2O dissociation to another partial step like the H_2O transport from the solution to the alloy electrode surface. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Metal hydride; Work function; $LaNi_{2.5}Co_{2.5}$; Electrochemical hydriding; Rate controlling step; Alkaline treatment

1. Introduction

At the initial stage of hydriding reaction of a hydrogen storage alloy in a H_2 gas or in an electrochemical process, the dissociation of the H_2 or H_2O molecules on the alloy surface usually becomes rate controlling [1,2]. The surface contamination of the alloy by oxidation or hydroxidation strongly inhibits the rate of the dissociation, resulting in a drastic lowering of kinetics. Details of such surface processes for rare earth based hydrogen storage alloys have been described in connection with the mechanisms of the initial activation [1–4], hydriding reaction [1,2,4,5] and heat conductivity effect on kinetics [6]. Our recent studies revealed that the alkaline treatment of the surface of hydrogen storage alloys with LiOH, NaOH or KOH induces a marked enhancement of the hydriding rate both in H_2 gas phase and in electrochemical processes. This treatment was found to decrease the work function of electrons of the alloy surface by the penetration of the alkaline atoms of Li, Na or K into the surface region [7,8].

In this study, an alkaline treatment with NH_3–H_2O solutions was examined in connection with the surface modification and the hydriding rate of the $LaNi_{2.5}Co_{2.5}$ alloy in order to compare results with those obtained for the LiOH, NaOH or KOH treatment. Through this comparison, we aimed to clarify the mechanisms of the enhancement of the hydriding rate by the presence of the alkaline atoms of Li, Na or K in the surface region.

2. Experimental

A block sample of $LaNi_{2.5}Co_{2.5}$ was prepared by arc melting and was heated at 1073 K in Ar for 8 h. The sample was pulverized by cyclic hydriding and dehydriding reactions to obtain a powder sample with particle sizes <38 μm. The structure of the alloy sample was examined using X-ray diffraction (XRD) and identified with the standard data of $LaNi_{2.5}Co_{2.5}$. The composition of the alloy was examined by energy dispersive X-ray (EDX) and found to be $LaNi_{2.5}Co_{2.5}$. For alkaline treatments, the powder sample was soaked in 3 M, 6 M or 8 M KOH, NaOH, LiOH or NH_3–H_2O solutions at 373 K for 30–180 min. The surface of the treated powders was rinsed in fresh distilled water at 298 K to remove the hydroxide layers formed during the treatments. This alloy powder was mixed with a Cu powder in a ratio of $LaNi_{2.5}Co_{2.5}$:Cu=1:3 in weight. The mixed powder was pressed at 3.78

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*Corresponding author.

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t cm^{-2} for 1 min to form a pellet with a diameter 13 mm and a thickness 2 mm as an electrode for an electrochemical hydriding measurement The measurement of electrochemical hydriding rate was made in a 6 M KOH at 298, 308 and 318 K using a $Ni(OH)_2$ plate as a counter electrode and a Hg/HgO reference electrode. From the measured current in charging at a constant potential of −0.93 V, the H concentration absorbed by the alloy electrode was calculated. No bubbles were observed during the measurements. Block samples of the alloy were used for the depth profile analyses by point Auger electron spectroscopy (AES, PHI 15–155, 3 kV, 10 μA). The concentration of each alloy element (La, Ni, Co) dissolved from the alloy into the alkaline solutions during the treatment was measured using induction coupled plasma induced photoemission spectroscopy (ICP). The work function of the alloy samples was measured at 298 K directly after each alkaline treatment by the Kelvin method [9] where an Au electrode with a work function of 5.10 eV was used as the reference material. The measured work function of an alloy sample without pretreatment was 4.95 eV. Work function data measured for alkaline treated samples are denoted as deviations from this value in this study.

3. Results and discussion

3.1. Effects of KOH, NaOH, LiOH and NH_3–H_2O on electrochemical hydriding rate

Fig. 1 shows the first hydriding curves of $LaNi_{2.5}Co_{2.5}$ samples without and with surface pretreatments at 373 K for 60 min in 3 M KOH, 3 M NaOH, 3 M LiOH and 3 M NH_3–H_2O, in an electrochemical process at a constant potential −0.93 V vs. Hg/HgO at 298 K. The KOH, NaOH or LiOH pretreated samples exhibit much higher hydriding rates than an untreated sample. However, the hydriding rate of the sample pretreated with NH_3–H_2O is strongly reduced. As reported earlier, the rate can be enhanced with increasing concentration of alkaline solutions and treating time [8].

3.2. Surface concentration of K atoms and work function change

In this work, the relative change in the surface concentration of K atoms in the surface layer of the alloy samples was estimated from the AES depth profile data (see Fig. 2 in Ref. [8]). The relationship between the relative surface concentration of K atoms and the change in the work function $\Delta\phi$ is shown in Fig. 2. The samples were treated at 373 K under different conditions: (A) 8 M KOH for 180 min, (B) 6 M KOH for 180 min, (C) 8 M KOH for 30 min, (D) 6 M KOH for 30 min and (E) without surface treatment, respectively. As the surface concentration of K atoms is increased, the work function tends to decrease in an almost linear relation. The decrease in $\Delta\phi$ is more than 1.0 eV. This linear relation between the K concentration vs. $\Delta\phi$ is similar to the linear relation

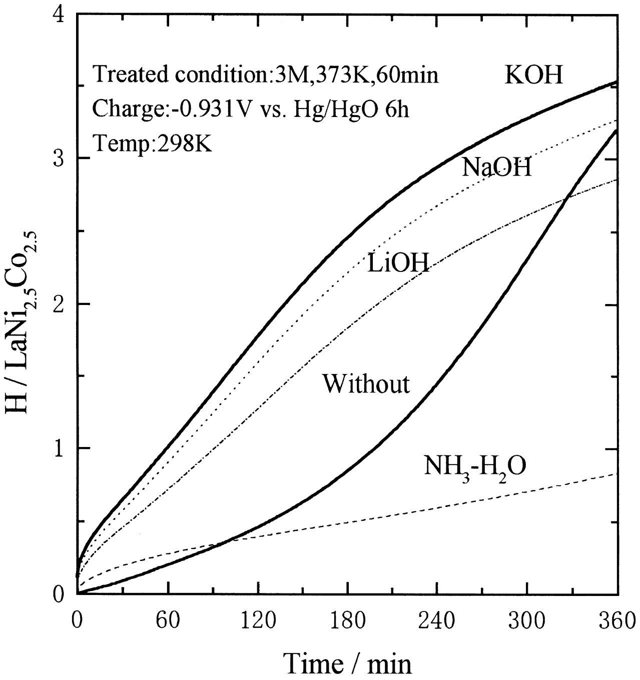

Fig. 1. Effect of pretreatments with 3 M LiOH, 3 M NaOH, 3 M KOH and 3 M NH_3–H_2O at 373 K for 60 min on the first hydriding rate of $LaNi_{2.5}Co_{2.5}$ at 298 K.

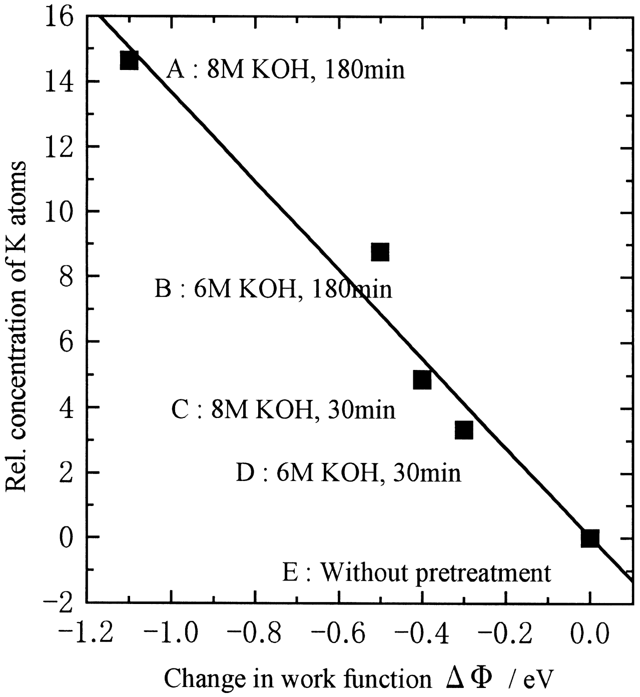

Fig. 2. Relation between the work function change and the relative concentration of K atom in the surfaces of the $LaNi_{2.5}Co_{2.5}$ samples pretreated with KOH under various conditions.

found between the initial hydriding rate and $\Delta\phi$ as reported previously [8]. These results demonstrate that the increase of the K surface concentration and the decrease of the work function enhance the hydriding rate.

The decrease in the work function of electrons of the alloy may aid in the dissociation of H_2O molecules since the electron exchange between the surface and H_2O molecules is required for the dissociation of covalent molecules like H_2O and H_2 [2,3]. This mechanism seems to be the reason that the alloy samples treated with higher KOH concentration or with longer treating time, which induces higher K concentrations in the surface, exhibit higher hydriding rates.

The NH_3–H_2O treatment induced a slight increase in the work function by 0.3 eV compared with that of an untreated sample. The lowered rate of the NH_3–H_2O treated sample may be attributed to this increase in the work function, resulting in a reduced dissociation rate.

3.3. AES depth profiles and ICP analyses

Fig. 3a and b shows the depth profiles of the surfaces treated in 3 M KOH and in 3 M NH_3–H_2 solutions, respectively. Both samples were treated at 373 K with these alkaline solutions for 60 min. The surface concentrations of La, Ni and Co atoms were found to decrease by 25, 35–40 and 60–75%, respectively, compared with those in the bulk, which indicates the dissolution of Ni if it is segregated in the subsurface layer.

Table 1 shows the results of the ICP analyses of 3 M LiOH, 3 M NaOH, 3 M KOH and 3 M NH_3–H_2O solutions after the treatment of samples at 373 K for 60 min. The concentration of each element dissolved from the alloy into the alkaline solutions was in the order Co>Ni>La. This result is consistent with the surface modifications indicated by the AES depth profiles shown in Fig. 3. Similar penetrations of Li and Na atoms and surface modifications by the LiOH and NaOH treatments are reported elsewhere [7].

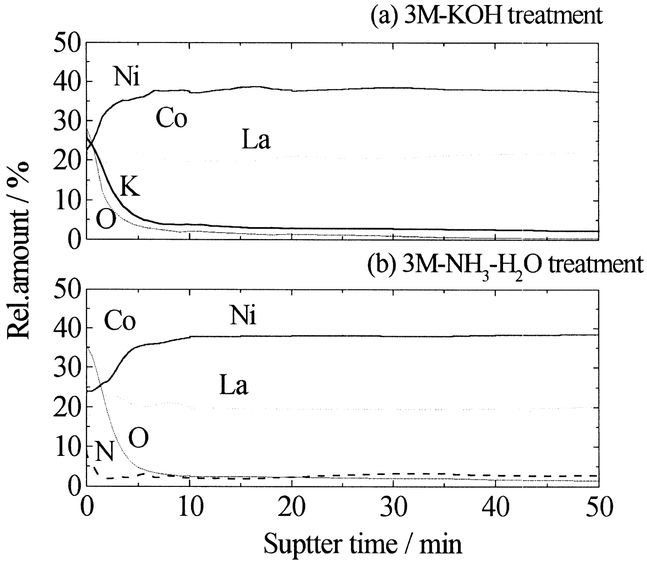

Fig. 3. AES depth profiles of the $LaNi_{2.5}Co_{2.5}$ pretreated at 373 K, (a) with 3 M KOH for 60 min and (b) with 3 M NH_3–H_2O for 60 min.

Table 1
ICP analyses of alloy elements in alkaline solutions of 3 M LiOH, 3 M NaOH, 3 M KOH and 3 M NH_3–H_2O in which $LaNi_{2.5}Co_{2.5}$ was heated at 373 K for 60 min

Element	LiOH (ppm)	NaOH (ppm)	KOH (ppm)	NH_3–H_2O (ppm)
La	1.312±0.002	2.410±0.024	3.058±0.073	1.044±0.015
Ni	1.256±0.008	2.906±0.022	3.454±0.153	1.432±0.025
Co	2.697±0.123	3.427±0.015	3.990±0.097	576±0.002

The surface composition modification by KOH and NH_3–H_2O was found to be similar, except for the presence of K atoms in the surface of the KOH treated samples. Most of the K atoms seem to be distributed in surface oxide layer. In spite of the surface oxide layer, the hydriding rate can be accelerated by the presence of K atoms in the surface. This effect is interesting since the dissociation of H_2 becomes markedly inhibited by the formation of a surface oxide layer, which results in a lowered hydriding rate or no reaction [1,3].

Traces of a very small amount of N atoms in the depth profile of the NH_3–H_2O treated sample may be caused by the uptake of N atoms by the alloy during the NH_3–H_2O treatment [10]. In Fig. 1, the NH_3–H_2O pretreated sample exhibits a higher initial hydriding rate than the untreated sample. This may be attributed to the presence of slightly higher surface concentrations of Ni and Co atoms on the sample surface as indicated in the AES depth profiles in Fig. 3. However, this effect is valid only for the initial stage of the reaction and for the first charging.

From the results indicated in Table 1, small amounts of Ni or Co dissolved in both LiOH and NH_3–H_2O solutions indicate that the possibility exists of Ni in the subsurface layer caused by the segregations. However, the reaction kinetics are measured differently which does not indicate the predominant effect of Ni segregated on the dissociative reaction kinetics.

3.4. Activation energy for hydriding rate

Fig. 4 shows the temperature dependence of the measured initial rate of hydriding, dC/dt, of the alloy samples with various alkaline pretreatments. The samples were treated at 373 K under different conditions: (A) 8 M KOH for 180 min, (B) 6 M KOH for 180 min, (C) 8 M KOH for 30 min, (D) 6 M KOH 30 min and (E) without surface treatment, respectively. The scattering of points from the straight line, especially for samples C, D and E may include some different reaction mechanisms.

The measured rates are plotted against inverse tempera-

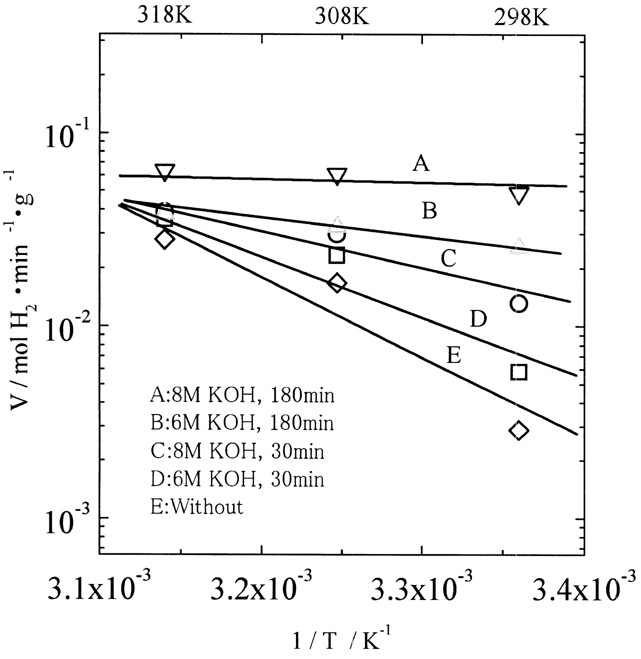

Fig. 4. Temperature dependence of the initial hydriding rate of the $LaNi_{2.5}Co_{2.5}$ samples without (E) and with different alkaline pretreatments (A–D).

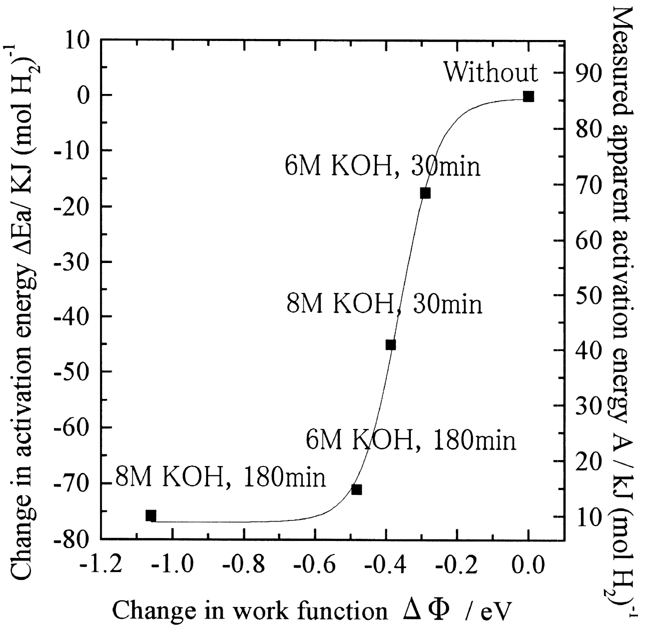

Fig. 5. Change in the activation energy ΔE_a, and the measured activation energy E_a as a function of work function $\Delta\phi$.

ture T^{-1}. From these relations, the apparent activation energy E_a was calculated using the following equation

$$dC/dt = A \exp(-E_a/RT)$$

where dC/dt is the initial hydriding rate in mol H_2 min^{-1} ($g\text{-}LaNi_{2.5}Co_{2.5}$)$^{-1}$, A is a proportional constant, E_a is apparent activation energy in kJ (mol H_2)$^{-1}$, R is the gas constant 8.315 and T is reaction temperature in K.

The calculated activation energy for various pretreatments was 10.1 kJ (mol H_2)$^{-1}$ for condition (A), 14.8 kJ (mol H_2)$^{-1}$ for (B), 40.9 kJ (mol H_2)$^{-1}$ for (C), 68.4 kJ (mol H_2)$^{-1}$ for (D) and 85.8 kJ (mol H_2)$^{-1}$ for (E). The apparent activation energy markedly decreased with increasing KOH concentration or treatment time, namely, with the increasing surface concentration of K atoms. This shows that the presence of K atoms in the surface accelerates the rate of H_2O dissociation. This mechanism may also be applied to the effect of the enhancement of the hydriding rate of the alloy in a H_2 gas phase where the alloy was pretreated with LiOH, NaOH and KOH [7,8].

3.5. Activation energy and work function

In Fig. 5, the change in the activation energy ΔE_a is plotted as a function of the work function change $\Delta\phi$. ΔE_a decreases as $\Delta\phi$ is reduced from 0 to -0.5 eV (where $\Delta\phi$ is measured versus $\phi=4.95$ eV of the untreated $LaNi_{2.5}Co_{2.5}$ surface). Then, at $\Delta\phi < -0.5$ eV, ΔE_a becomes almost constant, independently of $\Delta\phi$ although $\Delta\phi$ becomes much more negative and that the alloy surface becomes covered with much higher concentrations of K atom.

According to experimental and theoretical surface studies for the change in the work function induced by the surface coverage of alkaline atoms [11–14], the work function ϕ dramatically decreases with increasing coverage of K. This effect is explained by the change in distribution of valence electrons of the metallic surface, which is induced by the hybridization of valence electrons of the metallic surface and alkaline atoms [14].

Based on this mechanism, the sharp drop in ΔE_a with decreasing $\Delta\phi$ (Fig. 5) suggests modifications in surface electronic structure with increasing K concentration. As AES data show, the alkaline pretreated alloy surfaces are covered with oxides, and K atoms seem to be mainly in surface oxides. Our previous study revealed the crucial roles of La surface oxides and/or La oxides–Ni interfaces for the H_2 dissociation on the oxidized $LaNi_5$ surface [3]. The drastic decrease in the activation energy with increasing K concentration in the surface layers means that the presence of K atoms decreases the work function of electrons of surface oxide and/or the alloy to accelerate the rate of H_2O dissociation, leading to more ready electron exchange between the surface and the H_2O molecules. These mechanisms seem to yield the sharp drop of the activation energy with decreasing work function at -0.5 eV$<\Delta\phi<0$ eV.

At $\Delta\phi<-0.5$, since the dissociation rate becomes much higher, and the H_2O dissociation may be no more rate controlling. Instead, another partial step like the transport of H_2O molecules from solutions to the alloy electrode surface may become rate controlling.

4. Conclusion

Alkaline treatment of $LaNi_{2.5}Co_{2.5}$ alloy with LiOH, NaOH and KOH induces the penetration of alkaline atoms, Li, Na and K, respectively, into the surface region of the alloy. The alkaline atoms are distributed mainly in the surface oxide layers of the alloy. The work function of electrons of the surface treated by NH_3–H_2O slightly increased and the hydriding rate was strongly reduced. With increasing surface concentration of K atoms, the work function of the alloy surface becomes markedly reduced over 1.0 eV. This lowers the apparent activation energy of the hydriding reaction and accelerates the rates of the H_2O dissociation and the hydriding of the alloy. With a further increase in the surface coverage of the K atom, the apparent activation energy becomes almost constant, independent of the work function decrease. This suggests a shift of the rate controlling step from the dissociation of H_2O molecules on the surface to another partial step like the H_2O transport from solution to the electrode surface. An additional study may be necessary to clarify the precise rate controlling mechanisms.

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