Journal of Alloys and Compounds 293–295 (1999) 751–755

Effect of alakaline pretreatments (KOH, NaOH, LiOH) on electrochemical hydriding rate and work function of $LaNi_{2.5}Co_{2.5}$

H. Uchida[a,*], K. Yamashita[a], T. Tabata[a], H.H. Uchida[b], M. Iwase[c], Y. Katoh[c]

[a] *Department of Applied Physics, Tokai University 1117 Kita-Kaname, Hiratsuka, Kanagawa 259-1292, Japan*
[b] *Department of Resources & Environment, Tokai University 1117 Kita-Kaname, Hiratsuka, Kanagawa 259-1292, Japan*
[c] *Department of Electrical Engineering, Tokai University 1117 Kita-Kaname, Hiratsuka, Kanagawa 259-1292, Japan*

Abstract

The pretreatment of $LaNi_{2.5}Co_{2.5}$ with KOH, NaOH or LiOH solution induces the penetration of the alkaline atom of K, Na or Li, respectively. The presence of these alkaline atoms on the alloy surface reduces the work function for electrons of the alloy over 1.1 eV with K atoms. The electrochemical hydriding rate can be enhanced by decreasing the work function for electrons of the alloy.

Keywords: Alkaline atom; Work function; Activation; Hydriding rate; $LaNi_{2.5}Co_{2.5}$

1. Introduction

In previous studies [1–3], we reported the remarkable enhancement of the initial activation rate of the $LaNi_5$ and $LaNi_{2.5}Co_{2.5}$ alloys both in the H_2 gas phase and in alkaline electrochemical process by the pretreatment of the surfaces of these alloys with the alkaline hydroxide solutions such as KOH, NaOH and LiOH. Surface analyses of the alloys using Auger electron spectroscopy (AES) revealed that the alkaline atoms penetrate into the surface of the alloys, in which the alkaline atoms were distributed mainly in the surface oxide layers of the $LaNi_5$-based alloys. A similar penetration of Li atoms into the Pd surface by a pretreatment with a LiOH solution was also reported elsewhere [4]. According to the results of the reduction of work function for electrons of metals [5–7], we pointed out the possibility of the reduction of the work function for the electrons of the alloys by the presence of alkaline atoms on the surface, and the according ready transport of electrons from the alloy surface to the H_2 or H_2O molecules, resulting in the ready H_2 dissociation [3].

The aims of this work are to examine whether or not the reduction of the work function for electrons of the $LaNi_5$-based alloys takes place, and to elucidate the relation between the change in the work function and the enhancement of the initial activation of the electrochemical hydriding process. The enhancement of the initial activation in the H_2 gas process by the alkaline pretreatment was reported elsewhere [1–3].

2. Experimental procedures

$LaNi_{2.5}Co_{2.5}$ samples were prepared by arc melting, and subsequently annealed at 1073 K for 8 h in a vacuum of 10^{-4} Pa. The structure and composition were identified with X-ray diffraction (XRD) and induction coupled plasma induced photoemission spectroscopy (ICP), respectively. The prepared block sample was pulverized into particles less than 38 μm by the cyclic hydriding and dehydriding. The powder sample was mixed with Cu powders in a ratio, $Cu/LaNi_{2.5}Co_{2.5}=3$ in weight, and then pressed at a pressure of 3.78 tons cm^{-2} for 1 min. This sample with a weight of 0.24 g was formed to a pellet with a thickness of 2 mm and a diameter of 13 mm. The pellet sample was soaked in 3 M, 6 M or 8 M KOH, NaOH and LiOH solutions at 373 K for 30–180 min respectively as the alkaline pretreatment. In order to reduce the hydroxide layers formed by the pretreatment, the surface of the pretreated samples was rinsed in fresh distilled water at room temperature. The pellet sample was used as the negative electrode in the measurement of the initial activation rate of electrochemical hydriding process. $Ni(OH)_2$ plate and Hg/HgO electrode were used as the counter and reference electrode, respectively, in an open cell. The electrolyte of 6 M KOH was used for all rate

---

*Corresponding author.

PII: S0925-8388(99)00457-0

measurements. From the measured current in charging at a constant potential of −0.93 V, the H concentration absorbed by the negative electrode was calculated. In all reactions measured, no bubbles were observed during the hydriding. For point AES (PHI 15-155, 3 kV, 10 μA) analyses and for the measurement of work function for electrons of samples, block samples of the $LaNi_{2.5}Co_{2.5}$ with or without pretreatment were used. The work function of the samples was measured at room temperature in air directly after the alkaline pretreatment by the Kelvin method [8] where an Au electrode with a work function of 5.10 eV [9] was used as the reference material.

3. Results and discussion

3.1. Initial activation

Typical electrochemical hydriding curves, A, B, C, D and E measured at 298 K as the increase of the H concentration $[H]/[LaNi_{2.5}Co_{2.5}]$ as a function of time for the $LaNi_{2.5}Co_{2.5}$ with and without KOH pretreatments are shown in Fig. 1(a) for the initial stage at reaction time $0<t<150$ min and Fig. 1(b) for $0<t<350$ min, respectively. The sample surfaces were pretreated using 6 M KOH or 8 M KOH at 373 K for 30 min or 180 min. As can be seen from Fig. 1(a,b), the curves A, B, C and D of the pretreated samples exhibit higher hydriding rates than the curve E of the untreated sample. The rate becomes higher in the order for samples with pretreatments, 6 M KOH for 30 min (curve D), 8 M KOH 30 min (curve C), 6 M KOH for 180 min (curve B) and 8 M KOH for 180 min (curve A). These results qualitatively demonstrate that the initial rate increased as the pretreatment time or the KOH concentration is increased. Further discussion is made with respect to the change in work function at Section 3.3.

3.2. AES depth profiles

Fig. 2(a,b) shows the depth profiles of the $LaNi_{2.5}Co_{2.5}$ surfaces with the pretreatments of 8 M KOH at 373 K for 180 min and 30 min, respectively. These results demonstrate that the concentration of K becomes decreased with the depth. These decreasing profiles in the K concentrations are similar to those for the O atoms with the depth. This suggests that K atoms are distributed mainly in the surface oxide layers. The concentration of K is about 40% in relative amount (r.a.) for the sample pretreated for 180 min, and about 20% in r.a. for the sample pretreated for 30 min. The concentration of K atom in the surface is increased with increasing pretreatment time. The samples with the longer (180 min) and shorter (30 min) pretreatments exhibit the ratio of concentrations of K/Ni=3.3 and 1 in r.a., respectively. However, the penetration of K atoms seems to be saturated at a depth of 100–200 nm, judging from a sputter rate of 1–2 nm/min using 3 keV Ar^+. For both samples, the concentration of Ni at the surfaces is enriched, about 15–20% in r.a. compared with the other alloy elements. However, the measured rate for the sample with higher K concentrations (curve A in Fig. 1) is much higher than that with lower K concentrations (curve C in Fig. 1). This result is interesting when the conventional argument that the presence of the Ni at the surface is crucial for the initial activation both in the H_2 gas and electrochemical processes is taken into account. In fact, it is well known that the presence of increasing amount of fresh Ni sites on the surface is very effective for the enhancement of the dissociation of H_2 or H_2O molecules

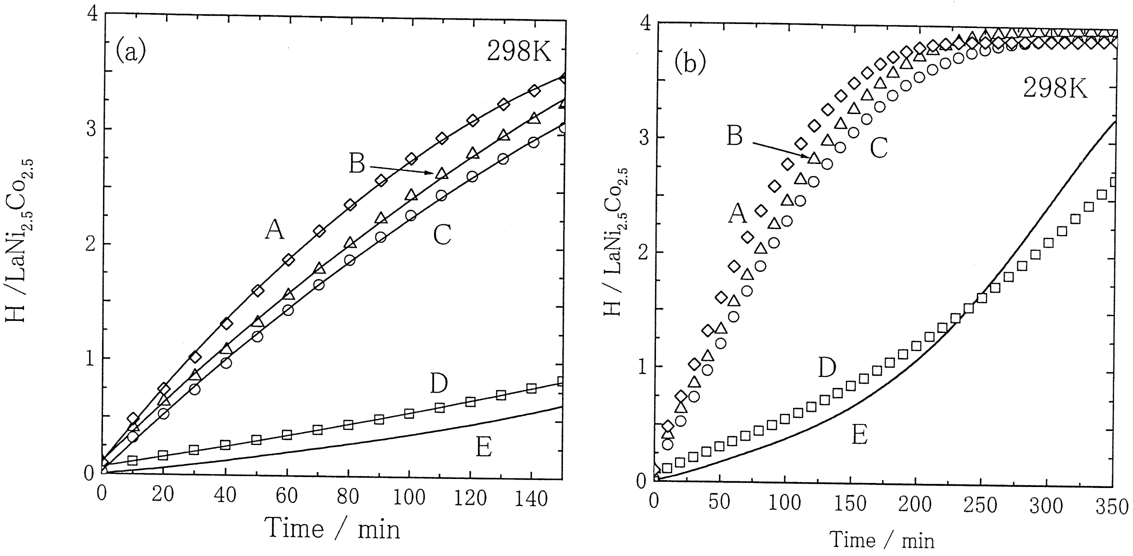

Fig. 1. Typical hydriding curves at 298 K for the $LaNi_{2.5}Co_{2.5}$ samples pretreated at 373 K with 8 M KOH for 180 min (curve A), 6 M KOH for 180 min (curve B), 8 M KOH for 30 min (curve C), 6 M KOH for 30 min (curve D) and without pretreatment (curve E), respectively; (a) for reaction time t, $0<t<150$ min, and for $0<t<350$ min, respectively.

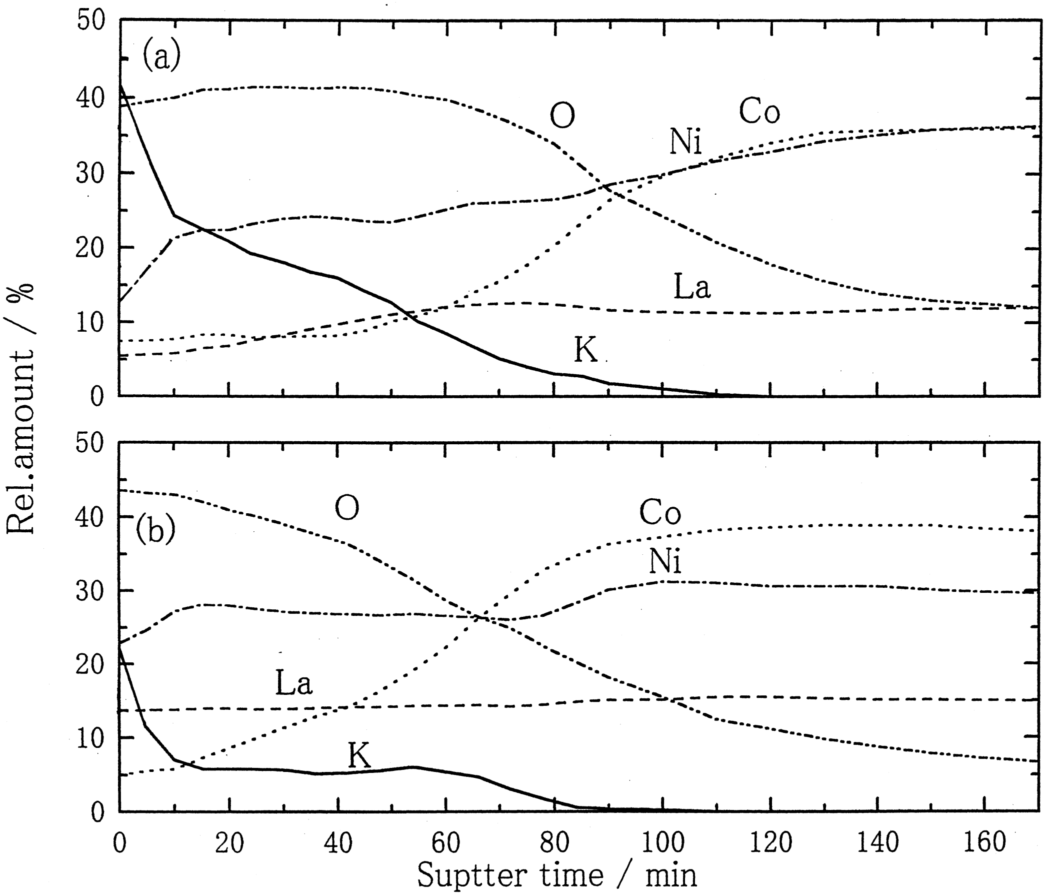

Fig. 2. AES depth profiles of the $LaNi_{2.5}Co_{2.5}$ pretreated at 373 K: (a) with an 8 M KOH for 180 min; and (b) with an 8 M KOH for 30 min, respectively. The sputter rate was about 1–2 nm min^{-1} at 3 keV Ar^{+}.

[10,11]. However, the results obtained here insist that in addition to the presence of Ni, the role of alkaline atoms at the surface should be considered in the mechanism of the enhancement of the initial activation in the electrochemical hydriding process.

3.3. Change in work function

Fig. 3 shows the changes in the initial hydriding rate in mol H_2 min^{-1} g^{-1} of the pretreated samples as a function of the change in the work function $\Delta\phi$ in eV. The pretreatment conditions shown in Fig. 3 exactly correspond to the conditions of the hydriding curves, A, B, C, D and E in Fig. 1. The reference value of the work function used in this study was that of the untreated sample with values from 4.95 eV. The change in the work function by the pretreatment was expressed as $\Delta\phi$ against the reference value of the untreated sample.

These results clearly show that the work function decreases with increasing KOH concentration, i.e., with increasing concentrations of K atoms at the surface and with extension of pretreatment time. The hydriding rate becomes increased markedly with the decreasing work function. Generally, the initial hydriding rate in electro-

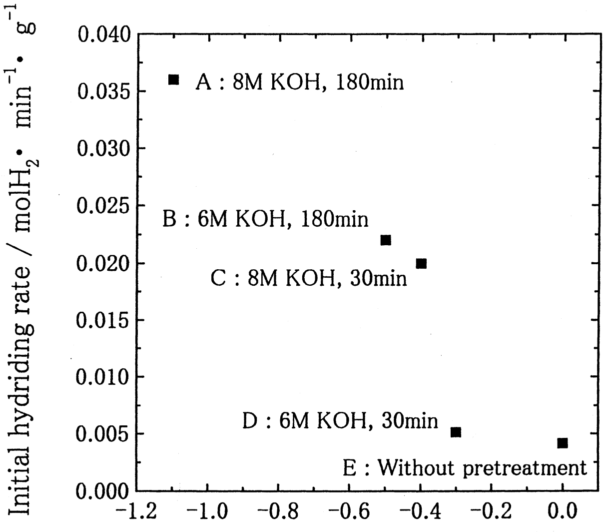

Fig. 3. The effect of the KOH pretreatment on the initial hydriding rate and on the change in the work function for electrons of the $LaNi_{2.5}Co_{2.5}$ samples. The pretreatment conditions, A, B, C, D and E corresponds to those in Fig. 1.

chemical process is controlled by the H_2O dissociation. Therefore, the presence of K atoms at the surface may facilitate the rate of H_2O dissociation, resulting in the increase of hydriding rate.

3.4. Work functions of K, Na and Li atoms and hydriding rates

Fig. 4(a,b) shows additional evidence of the crucial role of alkaline atoms, K, Na and Li in the acceleration of the H_2O dissociation rate and according hydriding rate. $LaNi_{2.5}Co_{2.5}$ samples were pretreated with 3 M KOH, 3 M NaOH and 3 M LiOH at 373 K for 60 min, and then the hydriding rates of these samples were measured with respect to the change in the work function by the pretreatments with different alkaline atoms (Fig. 4(a)), and to the work function of the alkaline atoms (Fig. 4(b)). AES analyses confirmed that each alkaline treatment induced similar depth profiles for each alkaline atoms in the samples: the surface concentrations 8–10% in r.a. and depths of about 50–100 nm for K, Na and Li atoms, respectively.

Fig. 4(a) exhibits a linear relation between the measured hydriding rates and the decrease in the work function changes ($\Delta\phi$), of the samples. Fig. 4(b) shows a similar linear relation between the measured hydriding rates and the work functions (ϕ) of the alkaline metals: 2.90 eV for Li, 2.75 eV for Na and 2.30 eV for K, respectively. The work function of K atom is the lowest among these alkaline atoms (Fig. 4(b)), and the sample treated with KOH exhibits the highest rate (Fig. 4(a)). The rate becomes increased with the decrease of the work function of the alkaline atoms penetrated, and also with the decrease in the work function of the alloy samples. These results clearly give the evidence that the alkaline atoms strongly affect the surface process of the H_2O dissociation in electrochemical process where the H_2O dissociation may accelerated by the ready electron exchange due to the reduction of work function between the H_2O molecules and the alloy surface. The presence of alkaline atoms in the oxide layers seems to facilitate the transport of electrons from the alloy surface to the H_2O molecules, resulting in the ready dissociation of H_2O and the accelerated rate of hydriding. When the electron exchange is concerned only for the metal surface and covalent molecules, the mechanism may be explained by the arguments by Lang et al. [6] that the presence of alkaline atoms in the surface region strongly changes the local states of *d*-electrons, resulting in the occurrence of the ready exchange of electrons between metal surface and covalent molecules. However, in the case of the alkaline treatment, the ready electron exchange seems to proceed rather by the ready transport of electrons from the alloy surface to the H_2O molecules through surface oxides. With this respect, further investigation may be required to elucidate the role of the alkaline atoms in the oxide layers.

4. Conclusion

The alkaline pretreatment of $LaNi_{2.5}Co_{2.5}$ with alkaline hydroxide solutions such as KOH, NaOH and LiOH induces the penetration of the alkaline atoms (K, Na, Li) into $LaNi_{2.5}Co_{2.5}$. These atoms seem to be present mainly in the surface oxide layers. The presence of these alkaline atoms in the surface oxide layers markedly enhances the rate of the initial hydriding. The initial hydriding rate becomes higher as the work function of the alloy surface is decreased by the addition of the alkaline atoms. The enhancement effect becomes more marked in the order of

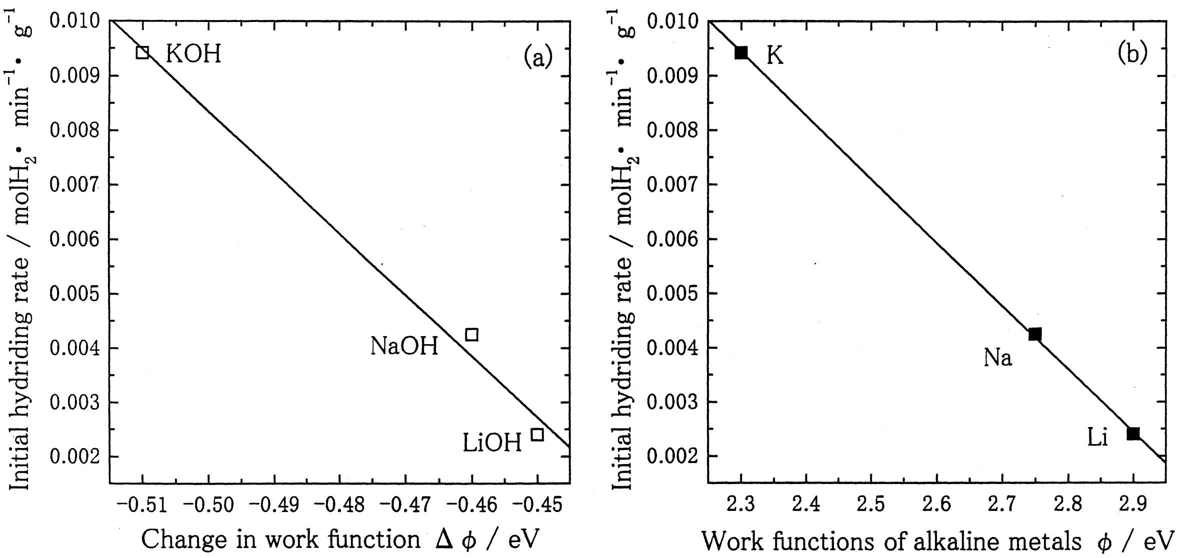

Fig. 4. (a) The effect of the pretreatments with 3 M KOH, 3 M NaOH and 3 M LiOH solutions on the initial hydriding rate of the $LaNi_{2.5}Co_{2.5}$, and (b) the relation between the measured initial hydriding rates and the work functions of Li, Na and K metals.

the alkaline atoms of Li, Na and K at the surface. The role of these alkaline atoms seems to decrease the work function for electrons of the alloy, which is crucial for the H_2O dissociation in electrochemical hydriding process. In conventional electrochemical hydriding processes, the role of alkaline atoms has been neglected. However, the occurrence of the penetration of alkaline atoms into the alloys and the alkaline atoms induced enhancement of the hydriding rate should be further examined. We believe that similar mechanisms may take place also in the hydriding process in the H_2 gas phase [1–3].

Acknowledgements

This study was supported by the Energy Materials Project of the General Research Organization, Tokai University.

References

[1] H. Uchida, M. Kawachi, K. Goto, Z. Phys. Chem. 183 (1994) 303.
[2] H.H. Uchida, Y. Watanabe, Y. Mathumura, H. Uchida, J. Alloys Compd. 231 (1995) 679.
[3] H.H. Uchida, K. Moriai, K. Aoyama, H. Kondo, H. Uchida, J. Alloys Compd. 253/254 (1997) 525.
[4] H. Uchida, M. Sato, W. Cui, T. Tabata, M. Kumagai, H. Takano, T. Kondo, Effect of the penetration of Li atoms into the Pd surface on the thermodynamic properties of the Pd-H system, J. Alloys Comp. 293–295 (1999) 30–33.
[5] J.B. Taylor, I. Langmuir, Phys. Rev. 44 (1933) 423.
[6] N.D. Lang, S. Holloway, J.K. Norskov, Surf. Sci. 150 (1985) 24.
[7] G. Ertl, S.B. Lee, M. Weiss, Surf. Sci. 114 (1982) 527.
[8] D. Baikie, E. Venderbosch, J.A. Meyer, J.Z. Estrup, Rev. Sci. Instrum. 62 (1991) 725.
[9] H.B. Michaelson, J. Appl. Phys. 48 (1977) 4729.
[10] T. Suziki, T. Kawahata, H. Uchida, Z. Phys. Chem. 181 (1993) 423.
[11] H. Uchida, E. Fromm, J. Less-Common Met. 95 (1983) 147.