Surface processes of H₂ on rare earth based hydrogen storage alloys with various surface modifications

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Abstract

This paper reviews typical and significant results of the recent studies for the surface processes in H₂ absorption by rare earth based hydrogen storage alloys (RE–HSA). The kinematics of the hydrogen uptake by RE–HSA in the H₂ gas and electrochemical reactions can drastically be influenced by spontaneous and intentional modifications of the surface of RE–HSA. This paper deals with the following prototypical cases: The formation of the oxide layer on the surface of the alloys shifts the rate controlling step of the H₂ absorption from H₂ dissociation on the surface with thin oxide layers to the H permeation through the layer as the layer grows. Partial substitution of Ni with Al, Co or Mn for LaNi₅₋ₓ(Al,Mn,Co)ₓ results in the change in the surface H₂ processes, depending upon each substituent element. The penetration of alkaline atoms (Li, Na, K) into the surface of the alloys markedly enhances the initial activation in the H₂ gas and electrochemical reactions. The fluorination treatment of the alloy surfaces effectively protects the surface from the attack of contaminations in the H₂ gas. © 1999 International Association for Hydrogen Energy. Published by Elsevier Science Ltd. All rights reserved.

1. Introduction

In order to understand the mechanism of the H₂ surface process in the reaction of H₂ with metals, the following fundamental and essential issues are summarized.

1.1. Rate controlling steps in metal-H₂ reactions

In metal-H₂ reactions, the following partial steps should be considered as the rate controlling steps of the H uptake by metal [1]: For a metal with a clean surface, (1) the transport of H₂ molecules from gas phase to the metal surface; (2) the physisorption of H₂ molecules on the surface; (3) the H₂ dissociation into H atoms and the subsequent chemisorption of H atoms on the surface; (4) the surface penetration of H atoms into the metal; (5) the diffusion of H atoms in the metal; (6) the formation of H solid solution phase if an appreciable solubility limit would exist at low H concentrations (otherwise, step (7) would follow immediately after step (6)); and (7) the formation of a hydride phase. If the H concentration is not yet in an equilibrium state, additional partial steps are still active; (8) the hydride formation at the hydride/metal interface.

For a metal covered with surface layers such as oxide/hydroxide or metallic coatings, the following additional steps should be considered: (3a) the H₂ dissociation on the layer and (3b) the penetration of H into the surface layer and H permeation through the layer. The H₂ molecular permeation may take place for the layers with porous structures. Hydride phases tend to form at the layer/metal interface because of the preferential precipitation of hydride at incoherent sites such as misfits and dislocations [2]. Surface oxide and hydroxide layers become less effective with increasing temperature because these layers become thinner or
disintegrated by the diffusion of O atoms from the oxide layers into the metal, resulting in accelerated reaction rates of the H₂ absorption [3–5]. On the other hand, a metallic coating with Pd [6] or a fluorinated surface layer [7,8] effectively protects the metal surface from the attack of contaminations such as oxidation, hydroxidation and CO adsorption, leading to high H₂ reactivities.

1.2. Mechanism of the H₂ dissociation crucial for the initial activation

Recent surface studies confirmed that electron transfer between the surface and H₂ molecules is crucial for the occurrence of the H₂ dissociation [9]. The dissociation of covalent molecules such as H₂ and O₂ is a result of the interaction between the H₂ anti-bonding orbitals and the lobe-shaped orbitals of the d-electrons of metals. Thus, the ready dissociation of H₂ molecules on the metal surface is crucial for the initial activation of metals.

1.3. Measurement methods for the assessment of the H₂ surface process

Kinetic data for the H₂ surface process were obtained systematically by the volumetric measurements of the rate of H₂ absorption by metals in a wide range of the H₂ pressure from 10⁻⁸ to 10⁶ Pa.

1. The measurement of the reaction probability \( r \) under UHV: the volumetric Wagener method was used to measure the amount of gas molecules adsorbed and/or absorbed by the samples degassed under UHV condition and the reaction probability \( r \) which is defined as the ratio of rate of adsorption and/or absorption of gas molecules to impinging rate of gas molecules on the surface of the samples [10]. When all gas molecules impinging the surface react with a metal by the adsorption and/or absorption of gas molecules, the reactivity of this gas yields \( r = 1 \). With decreasing numbers of molecules reacting with a metal, \( r \) becomes lowered. \( r = 10⁻² \) means the reaction rate that only one of 100 molecules impinging the surface reacts with a metal. Thus, \( r \) gives a simple and useful quantitative assessment of the reactivity of a gas with a metal. Details of this method are described elsewhere [10]. In order to examine the surface effects on kinetics, the sample surfaces were intentionally modified by exposing the surfaces to O₂, H₂O or low vacua before H₂ exposure [11].

2. The measurement of the rate of H₂ absorption under the high H₂ pressures: the rate of H₂ absorption by a metal was volumetrically measured using a Sierverts’ type system in the primary H solid solution region where no pulverization of sample takes place. This condition was essential to avoid dealing with marked surface changes and to confirm the effect of the surface and the mechanisms of the initial activation [12,13]. Details of the system used...
are reported elsewhere [12]. After vacuum degassing treatment, some samples were exposed to air or low vacua to modify the surface condition. The modified surfaces were analyzed using AES (Auger electron spectroscopy) and XPS (X-ray photoelectron spectroscopy) with respect to the surface composition.

1.4. Factors to be considered in kinetic measurements

The following experimental factors must strictly be considered in the kinetic measurements [14]: not only vacuum but vacuum leak rate of the system used change the surface conditions of samples, resulting in the marked changes in the rate of H₂ absorption and the mechanism of hydride precipitation [12,15,16]. Sample mass and heat conductivity of the cell materials affect the reaction rate and the rate controlling step [12]. The control of these factors is significant to measure intrinsic kinetic data. These facts are highly regarded in the establishment of JIS (Japanese Industrial Standard) for the assessment and measurement methods of HSA [17,18].

2. Effect of surface oxide layers on reaction kinetics of Ta and LaNi₅

The ready activation even at r.t. is a great feature of RE–HSA even after a long exposure of the alloys to air. Reactive transition metals such as Ti and Ta also absorb large amounts of H₂ and form stable hydrides; however, the H₂ absorption starts only at temperature higher than 500 K even after high vacuum degassing treatment of these metals. This section demonstrates the significant effect of surface oxides on the initial activation in contrast of Ta with LaNi₅.

2.1. Ta-H₂ system [3,4,19]

Fig. 1(a) summarizes the effect of a surface oxidation of the Ta surface on \( r_{H_2} \). Ta film and wire samples with clean surfaces prepared at 2500 K and \( 10^{-8} \) Pa exhibited high H₂ reactivities at the initial stage, \( r_{H_2} = 0.7 \) at 298 K and \( r_{H_2} = 1 \) even at 77 K, respectively. However, \( r_{H_2} \) became reduced with the increasing O₂ precoverage by several orders of magnitude. A sample exposed to O₂ at r.t. was precovered with O₂ layers in the range of the reaction probability of O₂ from \( r_{O_2} = 1 \) to \( 10^{-3} \), corresponding to a few monolayers of O₂ on the Ta surface. The subsequent H₂ exposure of this surface resulted in the reduction of \( r_{H_2} \) from 0.7 for a clean surface to \( 6 \times 10^{-2} \) for the O₂ precovered surfaces at 298 K. With increased O₂ precoverages at \( r_{O_2} < 10^{-1} \), \( r_{H_2} \) became strongly reduced to \( r_{H_2} = 2 \times 10^{-3} - 1 \times 10^{-5} \). Similar effects of surface oxides was observed also for the Ta wire samples degassed at a high vacuum of \( 10^{-6} \) Pa. A wire sample degassed at 2500 K exhibited a much higher reaction rate than another sample degassed at 2200 K. For a sample degassed up to 2500 K and then exposed to air for 24 h at r.t. before H₂ exposure, \( r_{H_2} \) became much lower even at 600 K. The marked reduction in the H₂ reactivity can be ascribed to the inhibited H₂ dissociation on surface oxide layers formed during the vacuum treatment or air exposure. The O concentration in Ta can be reduced only by volatilizing Ta oxides at temperatures higher than 2200 K. Therefore, the O concentration at the surface of Ta in vacuum degassing treatment is determined mainly by two competitive factors: volatilizing rate of Ta oxides and impinging rate of O atoms originated from residual gases in the vacuum used. Even while a sample is kept in a vacuum at r.t. after degassing, surface oxide layers can grow at a rate corresponding to partial pressures of residual O₂ or H₂O gas. At reaction temperatures lower than 500–600 K, the diffusivity of O atoms is still low, so that O atoms of the surface oxide layers cannot diffuse into the metal. In this case, the H₂ dissociation on stable surface oxide layers is strongly retarded. On the other hand, at reaction temperatures higher than 500 K, the diffusivity of O atoms becomes high, and the oxide layers become thinner or disintegrated. This results in the promotions of the H₂ dissociation, and accordingly the enhanced H₂ absorption rate as can be seen in the increasing \( r_{H_2} \) coming close to similar higher values (\( 10^{-6} - 10^{-2} \)) for the three Ta samples at temperatures over 700 K, independent of the pretreatments of the samples. In spite of the enhanced H₂ absorption rate, no H diffusion controlled kinetics could be measured even at these high temperatures. A H diffusion controlled rate estimated from the data measured for the Pd coated Ta samples [6] requires the \( r_{H_2} \) values of \( r_{H_2} > 0.1 - 1 \), which is higher by several orders of magnitude than the measured \( r_{H_2} \) for the Ta samples [4]. This means that even a very thin oxide layer of Ta strongly inhibits the H₂ dissociation.

2.2. LaNi₅-H₂ system [9,11,12,15]

The surface of RE–HSA exposed to air or low vacuum is covered with a mixture of dense oxides and hydroxides of the alloy species. In contrast with Ta, the RE–HSA with surface oxide layers exhibit high reactivities with H₂ gas even at r.t. Fig. 1(b) summarizes the effect of surface contaminations on \( r_{H_2} \) with LaNi₅. A sample degassed at a vacuum of \( 10^{-8} \) Pa without appreciable residual gases exhibited the highest reactivity, \( r_{H_2} = 1 \), indicating that the H₂ dissociation easily takes place on a clean surface. However, samples
Degassed at vacuum of $10^{-7}$ and $10^{-6}$ Pa with main residual gases of CO and CO$_2$ exhibited lowered $r_H$ of $10^{-2}$–$10^{-3}$. The LaNi$_5$ samples degassed up to $10^{-8}$ Pa were precovered with O$_2$ and H$_2$O until the reactivities of O$_2$ and H$_2$O became $r_{O_2} = 10^{-3}$–$10^{-2}$ and $r_{H_2O} = 10^{-2}$–$10^{-1}$ respectively. In the subsequent H$_2$ exposures, these samples exhibited $r_H$ in the order of $10^{-2}$. A sample degassed up to 473 K at $10^{-2}$ Pa exhibited much lower reactivities, $r_H = 10^{-3}$ at 298 K. In that degassing treatment, the partial pressures of main residual gases were in the order of H$_2$O > H$_2$ > CO$_2$ > CO. In spite of extensive surface contaminations of the LaNi$_5$ surface at a low vacuum, $r_H$ was reduced only by an order of magnitude compared with the $r_H$ for the sample degassed at a higher vacuum and temperature. This result shows the high durability of the LaNi$_5$ surface against contaminations such as surface oxidation and hydroxidation, and which is quite different from that for Ta at 298 K in Fig. 1(a).

Even after the treatment of the RE–HSA in air after vacuum degassing, the alloys exhibit high H$_2$ absorption rates at H$_2$ gas pressures as high as 0.1–1 MPa. This is the main reason why the alloys can be used for various applications. Fig. 1(b) shows the temperature dependence of $r_H$ for the H$_2$ absorption by the LaNi$_5$ samples exposed to air before H$_2$ exposure. Although the apparent rates of H$_2$ absorption are still high, $r_H$ for such air exposed LaNi$_5$ samples is lying at $10^{-3}$–$10^{-5}$.

Fig. 2 shows the transition of the rate controlling step for the initial rate of H$_2$ absorption by the LaNi$_5$ air exposed for 15 h after vacuum degassing treatment [9]. The initial rate, $v$ was measured with respect to the pressure and temperature dependences using the following equation:

$$v = kp^n \exp(-Ae/RT)$$

where $k$ is the proportional constant, $n$ is the exponent of pressure, $R$ is the gas constant, $Ae$ is the apparent activation energy which can be calculated from the $v$ vs $1/T$ plot. For limiting case 1, $n$ becomes close to 0.5 (H permeation through the surface layers) with $Ae > 15$ kJ/mol H$_2$, which were measured for the heavily oxidized samples with grown oxide layers at temperatures lower than 300 K. For limiting case 2, $n$ becomes close to 1 (H$_2$ dissociation) with $Ae < 5$ kJ/mol H$_2$, which were measured for the samples with thin oxide layers at temperatures higher than 700 K. These results indicate the shift of the rate controlling step of the H$_2$ absorption rate between H permeation and H$_2$ dissociation, depending upon the surface conditions [9,12,20]. This is in good agreement with the results of a model calculation for the H$_2$ adsorption kinetics by oxide covered Ta [21].

For the ready activation of the oxidized LaNi$_5$, several models are proposed [20]. A typical model for the air exposed LaNi$_5$ is the surface segregation model [22] where the H$_2$ process is assumed as a sequence of the H$_2$ molecules permeation through porous La oxides segregated at the surface and the subsequent H$_2$ dissociation at fresh Ni clusters lying under the oxide. In fact, the presence of very small amounts of Ni clusters on the oxidized La surface enhances $r_H$ by several orders of magnitude [23]. However, AES and XPS analyses show that no fresh Ni atoms exist on the air exposed LaNi$_5$ surface. The reduction of Ni oxides under high H$_2$ pressures is thermodynamically possible; however, the produced H$_2$O covers the reduced Ni surface at r.t. During the $r_H$ measurement of the oxidized LaNi$_5$, no H$_2$O production was observed at r.t. Such a reduction may proceed only at higher temperatures where the H$_2$O adsorption on Ni can be neglected. Our previous study [24] revealed that the oxidized La exhibits high $r_H$ in the order of $10^{-4}$. When the fact that the H$_2$ molecules dissociate on the oxidized LaNi$_5$ surface is taken into account, the La oxides on the air exposed LaNi$_5$ seem strongly responsible for the H$_2$ dissociation at the first stage of the initial activation. Our recent study revealed that Ce and Tb oxides as well as La oxides exhibit high reactivities with H$_2$ at r.t.

3. Necessity of standardization of measurement methods

The fact that the rate controlling step shifts accord-
The inconsistency among reported kinetic results for the \( \text{H}_2 \) absorption rate of RE–HSA. In fact, the \( \text{H}_2 \) absorption curve of the alloys changes its shape from sigmoidal to linear with reducing contamination effects of the surface \([15,16]\). Based on these facts, in Japan the standardization of the measurement and assessment methods for the reaction rate \([17]\) and cyclic life \([18]\) of HSA were established as JIS, where the control of experimental factors necessary for reproducible results \([14]\) was highly regarded.

4. Effect of partial substitution of Ni with Al, Co and Mn on surface kinetics

Cyclic hydriding and dehydriding reactions in \( \text{H}_2 \) gas phase and electrochemical conditions can be improved by partial substitution of Ni for RE–Ni\(_{5-x}\)(Al,Mn,Co)\(_{x}\) alloys. However, the role of each substituent elements such as Al, Co or Mn in the \( \text{H}_2 \) absorption kinetics of the alloys is not yet clear. Systematic studies have been conducted with respect to the effect of these elements on the \( \text{H}_2 \) surface process in the initial activation \([25,26]\). The measurement of the rate, \( v \) of \( \text{H}_2 \) absorption by the LaNi\(_{4.5}\)Al\(_0.5\), LaNi\(_{4.5}\)Co\(_0.5\) and LaNi\(_{4.5}\)Mn\(_0.5\) was made in \( \text{H}_2 \) solid solutions at 351 K. The compositions of these alloys were determined, so that the equilibrium pressures of \( \text{H}_2 \) are lying at similar levels. The particle sizes of these alloys were stabilized by 30 cycles of hydriding and dehydriding reactions. Using a \( \text{H}_2 \) gas with an ultra high purity (7N), marked reductions in the particle sizes of these alloys were not measured even after...
the 100 cyclic reactions. The significant effect of the purity of H₂ gas used on the pulverization is reported elsewhere [13]. In order to contrast the role of each element, the surface of each sample was modified by oxidation in air for 1–10 h at r.t. The modified surfaces were analyzed using XPS and AES. For the alloys exposed to air for 3 h, XPS analyses showed that the air exposure induces the formation of oxides at the topmost surface: Al₂O₃ (40 nm) for LaNi₄.₅Al₀.₅, Co₃O₄ and NiO (80 nm) for LaNi₂.₅Co₂.₅ and MnO₂ and Mn₃O₄ (more than 100 nm) for LaNi₄.₅Mn₀.₅, respectively. AES depth profile measurements showed that the O concentrations at the surfaces of the alloys became decreased by raising temperature, and that O atoms diffuse into the inner part of the metals. This is in good agreement with the results that the apparent activation energy for the H₂ absorption becomes decreased with increasing reaction temperature [9, 21, 27].

LaNi₄.₅Al₀.₅ with a 4.₄ μm median particle size: the initial H₂ absorption rate was decreased with prolonged air exposure time (Fig. 3(a)). The pressure dependence of the initial H₂ absorption was constant, n = 1.₀, independent of air exposure duration. This means that the H₂ dissociation on the surface is rate controlling in the initial activation of the oxidized LaNi₄.₅Al₀.₅ surface. The addition of Al generally increases the durability against oxidation. A slight oxidation of LaNi₄.₅Al₀.₅ increases rₜₜ by a factor 1₀ compared with the alloy with a clean surface at r.t. [28]. This oxidation induced enhancement of rₜₜ seems to be caused by the H trapping at the pure Al/oxide interface.

LaNi₄.₅Co₂.₅ with a 2₅.₆ μm median particle size: the initial H₂ absorption rate was decreased with increasing air exposure time (Fig. 3(b)). With increasing surface oxidation, the pressure dependence, n of the rate increased from n = 0.3 to 1.₀. In spite of the largest particle size, i.e., the smallest surface fraction among the alloy samples used, the measured rates were comparable with those of LaNi₄.₅Al₀.₅ and LaNi₄.₅Mn₀.₅ (Fig. 3(c)). Thus, the Co substitution effect is much more marked than the particle size effect on the rate. The Co with a clean surface exhibits a higher rₜₜ and a higher H chemisorption coverage than does the clean Ni [29]. The Co containing alloy surface is likely to be covered with high concentrations of H atoms compared with the alloy surfaces without Co. As the surface becomes saturated with a high H concentration, the rate of reaction tends to become independent of pressure change, yielding n → 0 (n = 0.₃ in Fig. 4(b)). As the surface oxidation proceeds further, the subsequent H₂ dissociation on the surface seems to become strongly inhibited and rate controlling, resulting in n = 1. In the presence of surface oxide, the Co–Ni alloys exhibit higher rₜₜ than Co or Ni does [29]. And the oxidized LaNi₄.₅Co₂.₅ has a higher rₜₜ and a higher H chemisorption coverage than the oxidized LaNi₅ at r.t. [29].

LaNi₄.₅Mn₀.₅ with a 1₄.₄ μm median particle size: the relatively low reaction rate for LaNi₄.₅Mn₀.₅ may be ascribed to the low reactivities of H₂ with Mn and Mn oxides in the surface layers which inhibit the H₂ dissociation. With extended oxidation, n becomes reduced from n = 1 to 0.₇, and the apparent activation energy, Aₑ becomes decreased [27]. The changes in n and Aₑ are similar to those of the oxidized Ta and LaNi₅ as shown in Fig. 2, indicating a shift of the rate controlling step between the H₂ dissociation and H permeation.

More details for the effects of substituent elements of Al, Co, Mn, Al–Co and Al–Co–Mn on the cyclic hydriding–dehydriding behavior are reported elsewhere [25].

5. Enhancement of the initial activation by alkaline atoms (Li, Na, K)

The RE–HSA heated in alkaline solutions such as LiOH, NaOH and KOH exhibit markedly enhanced rates in the H uptake both in H₂ gas and electrochemical reactions [25,3₀,3₁]. Fig. 4 shows the effect of the KOH alkaline pretreatments on the initial activation of the oxidized LaNi₅ at 2₉₈ K in the 8 MPa H₂ gas phase. Even after a 3₀ days air exposure of this sample, the initial activation was markedly facilitated by the alkaline pretreatments in comparison with that for the untreated sample. In spite of a subsequent rinse
by distilled water after the alkaline pretreatment, the marked effect can still be seen for the results for 3 M/H₂O and 1 M/H₂O in Fig. 4. Similar enhancement in the rate can be seen for an electrochemical H uptake in a 6 M KOH solution at 298 K by the LaNi₂.₅Co₂.₅ pretreated with LiOH, KOH and NaOH in Fig. 5(a) for the measured current density vs the H concentration absorbed and (b) the H concentration vs time, respectively. The marked effect of the alkaline treatments can be seen at the initial stage. Fig. 6 shows the AES depth profiling of LaNi₂.₅Co₂.₅ samples with and without alkaline treatments: (a) an untreated sample; (b) for the 3 M LiOH; (c) for the 6 M NaOH and (d) for the 6 M KOH treated samples at 353 K for 3 h, respectively. (The depth profilings were measured with 3 kV Ar⁺ with a sputtering rate of about 1–2 nm/min). The penetration of the alkaline atoms was found at depths ranging from several tens to 100 nm in the order Li > Na > K. The alkaline atoms were distributed mainly in the surface oxide layers and part of them in the alloy. The results for the H₂ gas and electrochemical reactions are indicative that the rate of the dissociation of the covalent H₂ or H₂O molecules are facilitated at the alkaline atom/surface oxide interface. Further kinetic investigation is now underway.
6. Surface protection from contaminations by fluorination

The fluorination of the surface of HSA is effective to protect the surface against contaminations [7,8]. In fact, the fluorinated LaNi5 could be readily activated even after 6 months air exposure. However, the kinetic data reported so far for this effect are not yet consistent with each other. This inconsistency seems to come from different methods of fluorination and resulting different structures of the fluorinated layers [8]. Therefore, different reaction mechanisms may be anticipated for the surfaces modified by different fluorination methods. Discussions are made based on our fluorination method which is precisely described elsewhere [7,8]. The fluorination was made by soaking the alloy samples into a 100% HF solution with 12 N purity for 3 h at 293 K, and then the samples were dried in a 100 Pa N2 gas flow at 393 K for 3 h. AES analyses of the formed fluorinated layers showed a thickness of about 50–80 nm. AES depth profilings are shown for the LaNi4.7Al0.3 samples in Fig. 7(a) without and (b) with the HF pretreatment. The topmost layer of the treated surface was found composed of the elements in the order of Ni > F > Al > O > La where the

La concentration was strongly decreased, and the Al concentration was slightly increased. At the topmost layer, the presence of AlF3 was confirmed. With depth, the Ni concentration increases where layers with the mixtures of Al, O, F and La atoms are formed. Our recent study for the fluorinated surfaces under UHV condition revealed that the formation of such fluorinated layers are effective against surface oxidation or hydroxidation [8]. However, the fluorination effect on \( \text{H}_2 \) becomes quite different according to the chemical composition of the alloy surface.

For high reactivities of \( \text{H}_2 \) on the fluorinated surfaces, the induction of catalytic actions for the \( \text{H}_2 \) dissociation by the following mechanisms is assumed: the mixing alumina and AlF3 or the fluorination of alumina where the O atoms in the alumina surface are replaced by F and OH, resulting in a HO–AlF4 bonding on the fluorinated alumina surface. This localized OH with large electronic strains is assumed to act as catalysis for the dissociation of the covalently bonded gas molecules.

Fig. 8 shows the effect of 1000 ppm CO mixture in the \( \text{H}_2 \) gas on the cyclic hydriding–dehydriding properties of the untreated and fluorinated LaNi4.7Al0.3 samples at 353 K. The cyclic property is demonstrated with the H transfer, defined as the ratio of the H amount desorbed to that absorbed. The HF pretreated sample exhibits a high cyclic durability, and compared with the cycling in a pure \( \text{H}_2 \) gas, the decrease in the H transfer is about 20% at the cycle of 100. The untreated sample exhibits a significant damage after the several cycles. This result clearly shows that the fluorinated layer is effective also against the CO attack on the surface. The investigation for this protective mechanism is underway.
7. Conclusions

Typical changes in the H2 process on the surfaces of RE–HSA have been reviewed. Spontaneous or intentional surface modifications drastically change the kinetics of H2 absorption, where the H2 dissociation is crucial for the whole reaction rate. The shift in the rate controlling of the H2 absorption according to the surface conditions should be considered in kinetic measurements and analyses. Partial substitutions of Ni with Al, Co and Mn for RE–HSA are widely applied to improve cyclic hydriding and dehydriding properties both in the H2 gas and electrochemical reactions. The substitution of each element results in different surface processes of H2. A significant enhancement of the initial activation by the alkaline pretreatment provides a new issue for the interactions of H2 at the alkaline atom/surface oxide interface. The fluorination of the surface of RE–HSA yields quite a high durability, especially against impurities in H2O or CO in H2 gas or vacuum, and this effect is very desirable for actual applications of HSA.

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