Journal of Alloys and Compounds 408–412 (2006) 319–322

Journal of
ALLOYS
AND COMPOUNDS

www.elsevier.com/locate/jallcom

Hydrogen absorption kinetics and mechanisms of rare earths (La, Ce, Pr, Nd, Tb, Dy) in the H_2O surface reaction at room temperature

Hirohisa Uchida*, Shunsuke Kato

Course of Applied Science, Graduate School of Engineering, Tokai University, 1117 Kita-Kaname, Hiratsuka-City, Kanagawa 259-1292, Japan

Abstract

The quantitative reactivities of H_2O and H_2 gases with clean surfaces of rare earth (RE) metals La, Ce, Pr, Nd, Tb and Dy were measured volumetrically at 298 K as a function of the amount of reacted gas. The H_2O reactivity was found higher by factors of $10–10^3$ than the H_2 reactivity, resulting in much higher rates of hydrogen (H) absorption of the metals than in H_2 exposure. Quantitative data of reactivities of H_2O and H_2 with the metals are reported, and mechanisms of the H absorption of the RE metals in H_2 and H_2O exposures are discussed.

Keywords: Hydrogen absorbing materials; Rare earth alloys and compounds; Surfaces and interfaces; Gas–solid reactions; H_2O

1. Introduction

Rare earth (RE) metals absorb large amounts of hydrogen and form di- and trihydrides [1]. The H_2 dissociation pressure of the hydrides of RE metals and RE-based alloys is markedly influenced by the number of 4f electrons [2,3]. Compared with thermodynamic investigations [2–6], little work was done on the surface reactions of RE metals. This may be attributed to the highly reactive surface property of RE metals. Careful approach using a clean surface technique should be made in the investigation of the surface property. We have applied the Wagener method [7,8] using ultra high vacuum condition to evaluate the quantitative reactivity of a gas (H_2, O_2, N_2, H_2O) on the surface of a metal as a function of the amount of reacted gas for many metals such as transition metals (Ti, Ta, W, Fe [9,10], Co, Ni [11]), RE metals (La, Ce, Tb, Dy [12–17]), and RE-based alloys ($LaNi_5$ [11,18–20], Sm_2Fe_{17} [21]).

In this study, we systematically measured the quantitative reactivity of H_2O with the surface of RE metals: La, Ce, Pr, Nd, Tb, and Dy at room temperature. Discussions are made on the surface processes of H_2O adsorption on the surface of these metals, and emphasis is made to elucidate the mechanisms of H absorption in H_2O exposure of these metals in comparison with the H absorption in H_2 exposure.

2. Experimental procedure

Each block sample of a RE metal (La, Ce, Pr, Nd, Tb, Dy) was degassed thoroughly by heating up to 1300 K in a vacuum below 5×10^{-8} Pa. The degassing of the sample and the out-gassing of a whole glass system were made alternately until the total vacuum attained below 5×10^{-8} Pa by monitoring residual gases in the system using a quadrupole mass spectrometer (QMS). Each film sample with a thickness of 100 nm was deposited onto the wall of a glass reaction tube by evaporating each block sample under an ultra high vacuum below 5×10^{-8} Pa. After the preparation of a film sample with a clean surface, H_2O gas was supplied using an ultrahigh purity droplet with a specific resistivity higher than 15 MΩ cm. The volumetric Wagener method was used to measure the amount N, the number of adsorbed or absorbed gas molecules per cm^2, and the reaction probability (reaction coefficient) r, the ratio of the rate of adsorption or absorption of gas molecules to the impinging rate of gas molecules on the metal surface. In this study, for convenience, the reacted gas amount N is expressed in molecules per cm^2 or mono layers

---

[*] Corresponding author. Tel.: +81 463 58 1211x4136; fax: +81 463 58 1812.
E-mail address: huchida@keyaki.cc.u-tokai.ac.jp (H. Uchida).

0925-8388/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2005.04.092

(ML) where 1 ML = 10^{15} molecules per cm^2. Surface roughness factors more than 10–20 should be taken into account for deposited film samples [12]. Details of this measurement method are described elsewhere [8].

3. Results and discussions

3.1. RE metals–H_2O system

Fig. 1 shows the change in the reaction probability r_{H_2O} with a clean Ce surface at 298 K as a function of the reacted amount N_{H_2O} of H_2O molecules. At the initial stage, $N_{H_2O} <$ 30 ML, the H_2O reactivity was measured as the highest value, $r_{H_2O} = 1$. This means that all H_2O molecules impinging the surface adsorb on the clean Ce surface. As the H_2O exposure was extended, r_{H_2O} became lower, and marked H_2 gas desorption from the surface was observed as this can be seen in the increasing H_2 partial pressure in Fig. 1. This suggests that adsorbed H_2O molecules dissociate into H atoms and hydroxyl (OH), and that part of the dissociated H atoms combine with each other to form H_2 molecules. From the measured H_2 partial pressure, the dissociation rate β (β-factor) of H_2O, and the reaction probability r_{2H/H_2O} of the H atoms dissociated from the adsorbed H_2O molecules were calculated by assuming the following reaction [12],

$$H_2O \rightarrow \text{O (adsorbed)} + 2\beta\text{H (adsorbed, absorbed or used for OH formation)} + (1-\beta)H_2\text{ (desorbed)}$$

where the dissociated H atoms are assumed to form H solid solutions, hydrides, and/or surface hydroxide with the dissociated O atoms. We assumed this simple reaction in order to calculate the quantitative amount of H atoms which were dissociated from H_2O molecules and reacted with the surface. In this assumption, we ignored complicated surface processes of oxidation or hydroxidation, which did not affect the calculation.

When $\beta = 1$, no H_2 desorption from the surface takes place, and the dissociated H atoms dissolve into the Ce to form H solid solutions and then to form Ce dihydride phase with increasing H concentration in Ce. The absorbed H amount $N_{2H/H_2O} = 150$ ML corresponds to the H concentration of about [H]/[RE] = 1 in atom ratio. As the H_2O adsorption proceeds, the surface becomes covered with increasing coverage of hydroxides, and the rate of H_2O dissociation becomes lower. And the dissociated H atoms cannot easily penetrate into the metal. Then, part of the H atoms tend to recombine forming H_2 molecules, and resulting in the H_2 desorption at $\beta < 1$. This is in good agreement with the result obtained so far that the hydroxide layers on the metal surface strongly hinder the H_2 dissociation and subsequent H absorption [12,15].

Similar results of the H_2O adsorption kinetics at 298 K were obtained for the surface of the other RE metal samples investigated in this study. Fig. 2 shows summarized r–N curves for the La–H_2O, Ce–H_2O, Pr–H_2O, Nd–H_2O, Tb–H_2O and Dy–H_2O systems. For these metals with a clean surface, the $r_{H_2O} = 1$ at the initial stage, suggesting that all H_2O molecules impinging the surface adsorb. With increasing coverage of hydroxides, r_{H_2O} decreases when the H_2 desorption takes place at $\beta < 1$.

Among these metals, the r_{H_2O} for the Tb and Dy surfaces is much higher than for the surfaces of the other metals, La, Nd, Pr and Ce. This systematic tendency in the measured reactivities of H_2O adsorption is quite different from those of the O_2 adsorption where the Ce surface exhibits much higher r_{O_2} than the surface of Tb or Nd [16]. The systematic change in the O_2 reactivity seems to be interpreted with respect to the readiness of the ionization potential of the metals [23]. However, this interpretation cannot be applied to the systematic change in the H_2O reactivity. The surface property of these elements seems to change drastically as the hydroxidation proceeds by the H_2O adsorption where formations of hydride and hydroxidation competitively proceed. For example, Ce becomes more metallic with increasing H concentration [22], and this seems to facilitate the dissociation of covalent molecules. In a previous study [15], we reported that the hydrided Ce surface exhibits higher reactivities with O_2 by a factor of 10^3 than a clean Ce surface. For the hydroxidation kinetics of the RE metals, further study is needed.

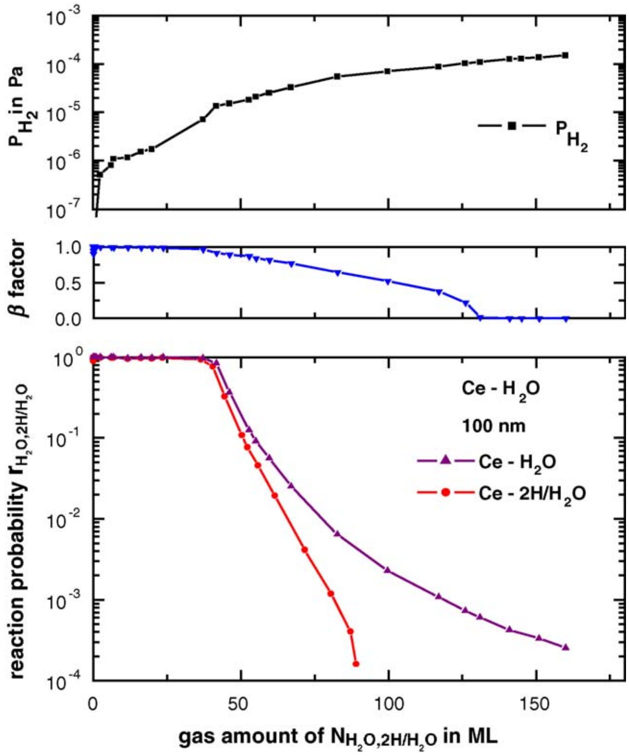

Fig. 1. Changes in the reaction probabilities of H_2O, r_{H_2O}, and of H atoms, r_{2H/H_2O}, dissociated from H_2O on the Ce surface, the rate of dissociation of H_2O, β-factor, and the partial pressure of H_2, P_{H_2}, as functions of reacted gas amounts of H_2O, N_{H_2O}, and of H atoms, N_{2H/H_2O}, dissociated from H_2O in mono layers (ML) at 298 K.

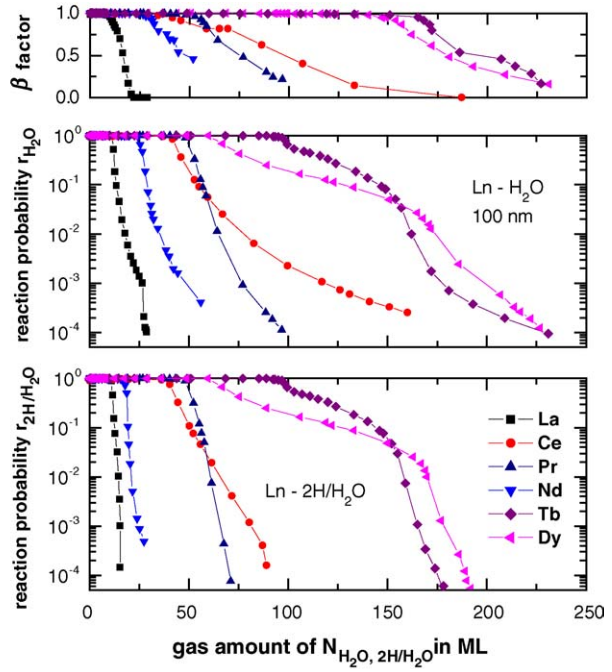

Fig. 2. Changes in the reaction probabilities of H_2O, r_{H_2O}, and of H atoms, r_{2H/H_2O}, dissociated from H_2O r_{H_2O} on the surfaces of La, Ce, Pr, Nd, Tb and Dy, the rate of dissociation of H_2O, β-factor, and the partial pressure of H_2, P_{H_2}, as functions of reacted gas amounts N_{H_2O} of H_2O, and N_{2H/H_2O} of H atoms dissociated from H_2O in mono layers (ML) at 298 K.

3.2. RE metals–H_2 systems

The changes in the H_2 reactivity with the metals are summarized in Fig. 3. In comparison to the reactivity of H atoms in H_2O and H_2 exposures (Figs. 2 and 3, respectively), an interesting fact is that the reactivity of H, r_{2H/H_2O}, is higher by factors 10–10^2 than r_{H_2}. This means that the RE metals with a clean surface absorb H atoms in much higher rates in contact with the H_2O gas than with the H_2 gas even at room temperature.

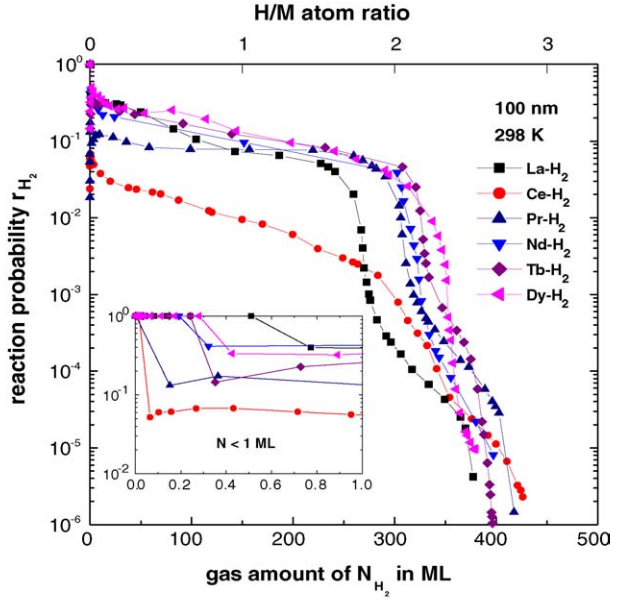

Fig. 3. Changes in the reaction probability of H_2, r_{H_2}, on the surfaces of La, Ce, Pr, Nd, Tb and Dy as a function of reacted H_2 gas amount, N_{H_2} in mono layers (ML) at 298 K.

Table 1
The H_2 dissociation pressures (Pa) of the dihydrides of La, Ce, Pr, Nd, Tb and Dy at 298 K

LaH_2	CeH_2	PrH_2	NdH_2	TbH_2	DyH_2
6×10^{-25}	2×10^{-22}	7×10^{-25}	1×10^{-24}	9×10^{-24}	9×10^{-30}

In H_2 exposure, H_2 molecules adsorb at the highest rate, $r_{H_2} = 1$, at the initial stage. The adsorbed H_2 molecules dissociate into H atoms to form H solid solutions at $N_{H_2} < 0.8$ ML or $[H]/[RE] < 0.005$ in atom ratio, and then dihydride phase is formed at $0.8 < N_{H_2} < 300$ ML or $0.005 < [H]/[RE] < 2$. As H concentration is increased, r_{H_2} drops steeply by factors 3–20 at around $0.1 < N_{H_2} < 0.8$ ML, firstly because the dihydride phase begins to precipitate on the surface at $0.1 < N_{H_2} < 0.8$ ML, and the rate of H permeation through the formed hydride layers becomes lower [16], and secondly because the H_2 equilibrium pressures become high as the dihydride phases are formed on the surface. Table 1 shows the H_2 dissociation pressures of the dihydrides of La, Ce, Pr, Nd, Tb and Dy. The data were calculated from plateau pressure data of the RE metals–H systems [2]. The Ce dihydride has the highest H_2 dissociation pressure among these RE dihydrides, and the H_2 desorption from the hydride reduces r_{H_2} more effectively for the Ce dihydride surface, resulting in the lower r_{H_2}. The gradual decreases in r_{H_2} with increasing amount of absorbed H_2 gas can be interpreted by the decreasing rate of H permeation through the growing surface dihydride layer [16].

On the surface of the formed hydride, the H_2 reactivity is lying between $r_{H_2} = 10^{-3}$ and 10^{-1}. Compared with these H_2 reactivities in the region of the hydride formation ($N_{H_2} >$ 1 ML), the H reactivity, $r_{2H/H_2O} = 1$, in the H_2O exposure is much higher (see Fig. 2). The H_2O molecules adsorb on the metal surface at the highest rate, $r_{H_2O} = 1$. Then, H atoms are produced by the dissociation of H_2O molecules on the surface, and these H atoms form the dihydride phase of the metals at the highest rate, $r_{2H/H_2O} = 1$. These results describe clearly the mechanisms the much higher rate of H absorption of the RE metals with a clean surface in H_2O exposure than in H_2 exposure.

3.3. RE metals–O–H_2 systems

In the H_2O adsorption, oxidation may proceed in addition to hydroxidation and hydriding. In order to examine the effect of surface oxidation on the subsequent H absorption, each RE metal film sample was preadsorbed with O_2 in the range from 18 ML O_2 to 230 ML O_2 before H_2 exposure at 298 K. In Fig. 4, the effect of the O_2 preadsorption layers on r_{H_2} is shown for each metal sample. Generally, surface oxide

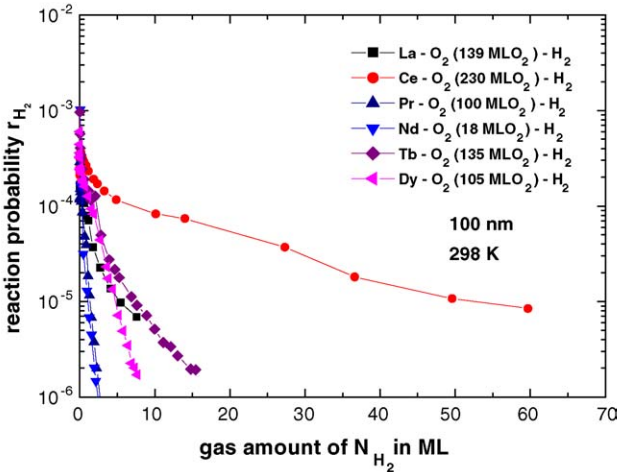

Fig. 4. Effect of O_2 preadsorption on the reaction probability of H_2, r_{H_2}, on the surfaces of La, Ce, Pr, Nd, Tb and Dy as a function of reacted H_2 gas amount, N_{H_2} in mono layers (ML) at 298 K.

layers strongly hinder the dissociation of H_2 molecules, and subsequent H absorption [18,20]. However, a Ce surface with the highest amount of the O_2 preadsorption layers, 230 ML, exhibits the highest r_{H_2} among these metal samples with O_2 preadsorption layers. This suggests that Ce oxides remain metallic, and can dissociate H_2 molecules by exchanging electrons between the surface and the molecules [20,24].

While the oxidized Ce surface exhibits the highest r_{H_2} reactivity, the H absorption rate r_{2H/H_2O} is not highest among the RE metal samples in the H_2O adsorption. This implies that in H_2O exposure the surface of the RE metals may be composed mainly of hydroxides, which markedly hinder the H absorption, rather than oxides.

4. Conclusion

In H_2O exposure of the RE metals: La, Ce, Pr, Nd, Tb and Dy with clean surfaces, the rate of H absorption was found higher by factors of $10–10^3$ than in H_2 exposure even at 298 K. This is explained by the higher H_2O reactivity with the surface of these metals than the H_2 reactivity. The H atoms are dissociated from the adsorbed H_2O molecules with the highest reaction rate, $r_{2H/H_2O} = 1$, and dissolve into the metals and form the RE dihydride phase in much higher reaction rates than in H_2 exposure.

As the surface becomes covered with increasing amounts of hydroxide layers, the surface hydroxide layers seem to hinder the penetration and diffusion of H atoms, and the H atoms tend to associate to form H_2 gas, and this results in marked H_2 desorption.

Acknowledgements

This study was financially supported by a Grant-in-Aid from the Japan Society for the Promotion of Science (JSPS) for “Study on the surface reactivity of hydrogen storage alloys” with no. 14550690. And this study was made in the frame of Eco Technology Project, Future Science & Technology Joint Research Center, Tokai University.

References

[1] W.M. Mueller, J.P. Blackledge, G.G. Libowitz, Metal Hydrides, Academic Press, New York, 1968, p. 585.
[2] K. Toguchi, M. Tada, Y.C. Huang, J. Less-Common Met. 88 (1982) 469.
[3] H. Uchida, M. Tada, Y.C. Huang, J. Less-Common Met. 144 (1988) 23.
[4] C. Ohki, M. Tada, Y.C. Huang, H. Uchida, H.H. Uchida, J. Less-Common Met. 103 (1984) 103.
[5] C. Ohki, H. Uchida, Y.C. Huang, Z. Phys. Chem. N.F. 163 (1989) 149.
[6] C. Ohki, H. Uchida, E. Ko, J. Jpn. Inst. Met. 54 (1990) 146.
[7] S. Wagener, Br. J. Appl. Phys. 1 (1950) 255.
[8] E. Fromm, H.G. Wulz, J. Less-Common Met. 101 (1984) 469.
[9] H. Uchida, E. Fromm, J. Less-Common Met. 95 (1983) 139.
[10] H. Uchida, E. Fromm, J. Less-Common Met. 95 (1983) 147.
[11] H. Uchida, S. Nakazawa, K. Ishikawa, T. Irisawa, J. Alloys Comp. 231 (1995) 684.
[12] N. Hosoda, H. Uchida, Y. Ohtani, T. Takahashi, E. Fromm, Z. Phys. Chem. N.F. 164 (1989) 1129.
[13] H. Uchida, Y. Ohtani, T. Kawahata, H. Minamitani, N. Ninomiya, E. Fromm, N. Hosoda, J. Less-Common Met. 172/174 (1991) 832.
[14] T. Suzuki, T. Kawahata, H. Uchida, Z. Phys. Chem. 181 (1993) 423.
[15] M. Hadano, N. Urushihara, S. Terada, D. Katsuya, H. Uchida, J. Alloys Compd. 330–332 (2002) 498.
[16] M. Hadano, N. Urushihara, T. Inoue, H. Uchida, J. Alloys Compd. 293/295 (1999) 403.
[17] D. Katsuya, R. Suzuki, F. Suzuki, D. Tabuse, Y. Tajima, H. Uchida, J. Alloys Compd. 356–357 (2003) 368.
[18] H. Uchida, Y. Ohtani, M. Ozawa, T. Kawahata, T. Suzuki, J. Less-Common Met. 172/174 (1991) 983.
[19] H. Uchida, T. Suzuki, S. Nakazawa, S. Kashima, Z. Phys. Chem. 181 (1993) 429.
[20] H. Uchida, Int. J. Hydrogen Energy 24 (1999) 861.
[21] H. Uchida, K. Ishikawa, T. Suzuki, H.H. Uchida, J. Alloys Compd. 222 (195) 153.
[22] G.G. Libowitz, Ber. Bunsenges Phys. Chem. 76 (1972) 837.
[23] T. Hattori, J. Inoko, Y. Murakami, J. Catal. 42 (1976) 60.
[24] H. Uchida, in: V.A. Goltsov (Ed.), Progress in Hydrogen Treatment of Materials, Donetsk State University, 2001, p. 391, ISBN 966-7418-71-5.