ELSEVIER

Journal of Alloys and Compounds 330–332 (2002) 498–501

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Reaction kinetics of cerium thin films with H_2, O_2 and H_2O systems at 298 K

M. Hadano*, N. Urushihara, S. Terada, D. Katsuya, H. Uchida

Department of Applied Physics, School of Engineering, Tokai University, 1117 Kita-Kaname, Hiratsuka, Kanagawa 259-1292, Japan

Abstract

Cerium (Ce) thin films were prepared under an ultra high vacuum condition, and each reactivity of H_2, O_2 or H_2O with the Ce surface was quantitatively measured for the reaction probability r and the gas amount reacted at 298 K. A clean Ce surface exhibited the highest reactivity, $r=1$ for H_2, O_2 and H_2O. Oxidized Ce surfaces exhibited higher reactivities with H_2 than oxidized surfaces of other rare earths, La, Tb, Dy [1], however, the H_2O preadsorption layers on the Ce surface strongly reduced H_2 reactivities. CeH_{2+x} hydride layers exhibit higher reactivities with O_2 than the Ce oxide surface, suggesting a high metallic property of Ce hydride layers.

Keywords: Cerium; Cerium hydride; Cerium oxide; Cerium hydroxide; Surface process of hydrogen

1. Introduction

Rare earths are well known through their high reactivities with H_2, O_2 and H_2O gases. Among these, Ce is one of the interesting elements because of its high oxidation states and catalytic properties [2,3]. The easy transfer of O atoms between Ce_2O_3 and CeO_2 occurs by the ready change between the valence states Ce^{+4} and Ce^{+3}, and this feature is utilized as a catalyst, for example, to purify the exhaust gas of automobiles. A well known Mm (misch metal) is used widely as $MmNi_5$ based hydrogen storage alloys for nickel–metal hydride rechargeable batteries and heat pumps because of its ready activation and high durability against impurity gases compared with $LaNi_5$ [4,5]. Mm contains Ce (40–60 wt.%) and La (25–30 wt.%) as main elements. Therefore, some role of Ce is supposed in the high reactivity of initial activation of the oxidized $MmNi_5$ based alloys. In addition, with increasing content of Ce in $La_{1-x}Ce_xNi_5$ by the substitution of La with Ce, the plateau pressure of the alloys–H system can be raised from 2×10^5 to 4×10^6 Pa at 298 K [6].

In spite of these interesting features and effects of Ce, quantitative and precise data for the reactivities of H_2, O_2 and H_2O with Ce with clean and modified surfaces are lacking. This study aimed to measure quantitatively and systematically the reactivity of these gases with the Ce surfaces with various conditions, and to clarify the kinetic property of the Ce surface.

2. Experimental procedure

Each Ce film sample with a thickness of 50 or 100 nm was evaporated from a block sample onto the walls of a glass sphere under an ultra high vacuum condition below 5×10^{-8} Pa. Before the evaporation, the block sample was degassed thoroughly by heating up to 1300 K in an ultra high vacuum below 5×10^{-8} Pa. Subsequently, a reaction gas (H_2, O_2, H_2O) was supplied from a gas reservoir to a reaction cell. H_2 and O_2 gases were purified through Pd and Ag cells, respectively. H_2O gas was supplied using a ultrahigh purity droplet with a specific resistivity of 15 MΩ cm. The volumetric Wagener method was used to measure the amount N, the number of absorbed or adsorbed gas molecules per square centimeter, and the reaction probability r, the ratio of the rate of absorption or adsorption of gas molecules to the impinging rate of gas molecules on the metal surface. In this study, the reacted gas amount of N is expressed in molecules cm^{-2} or monolayers (ML) where 1 $ML=10^{15}$ molecules cm^{-2}. Details of this measurement method are described elsewhere [7,8]. During the measurements, we measured total pressure by a B-A type ionization gauge and partial pressure by Quadrupole Mass Spectrometer.

---

*Corresponding author.

0925-8388/02/$ – see front matter
PII: S0925-8388(01)01627-9

3. Results and discussions

3.1. Ce–H_2

The initial reactivity of H_2 with Ce films with clean surfaces at 298 K is shown in Fig. 1(a) for samples with different thicknesses of 50 and 100 nm for small gas amounts, i.e. $N_{H_2} < 0.5$ MLH_2. The change in the reaction probability r_{H_2} is shown as a function of N_{H_2}. Both film samples exhibit the highest reactivity, $r_{H_2} = 1$ at the initial stage, $N_{H_2} < 0.05$ MLH_2, and then sudden decrease at $N_{H_2} = 0.05$ MLH_2 for the thin film and at $N_{H_2} = 0.1$ MLH_2 for the thick film, respectively. These sudden decreases in r_{H_2} may be ascribed to the segregation and formation of CeH_2 hydride on the surfaces of these film samples because the Ce–H system has a extremely low H solubility limit at 298 K [1]. With increasing N_{H_2}, r_{H_2} gradually decreases from $r_{H_2} = 10^{-2}$ to 10^{-3} with increasing reacted gas amount until $N_{H_2} = 110$ MLH_2 for the thin film and $N_{H_2} = 250$ MLH_2 for the thick film, respectively. From the results indicated in Fig. 1(a) and (b), the dependence of r_{H_2} on the film thickness suggests that the reaction proceeds not only on the outer surface but inside the film, namely, the formation and growth of Ce hydride layers proceed in the clean Ce film at 298 K.

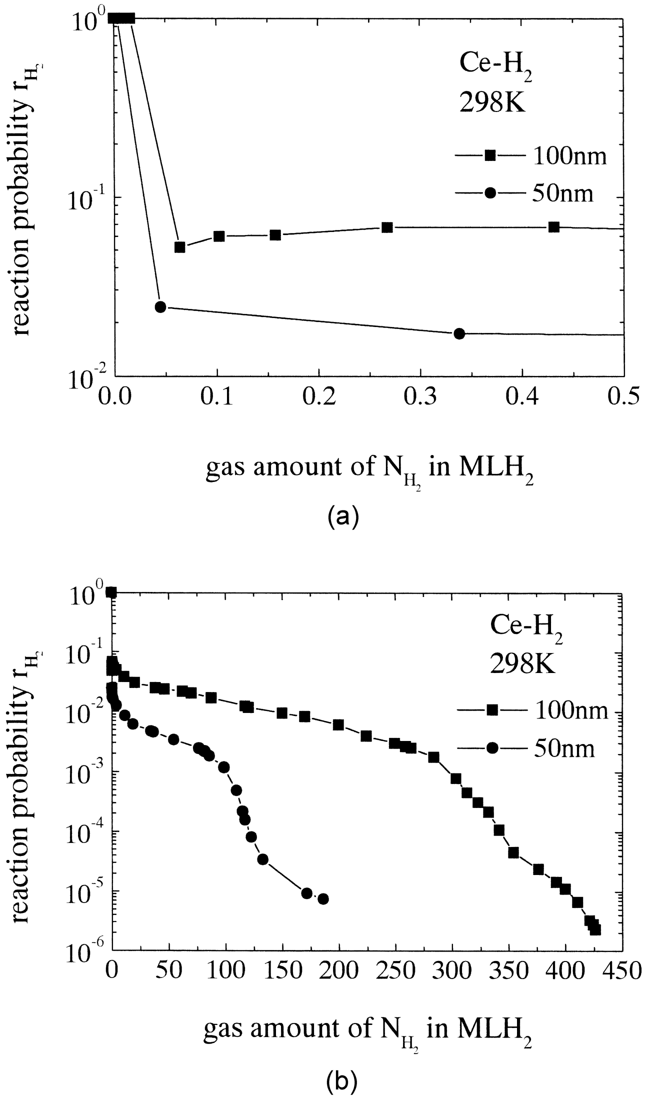

Fig. 1. (a) Reaction probability of H_2 with Ce at 298 K $N_{H_2} < 0.5$ MLH_2. (b) Reaction probability of H_2 with Ce at 298 K $N_{H_2} < 450$ MLH_2.

Assuming that a diffusion process of H in the film samples, the flux J of H atoms diffusing through a surface hydride layer with a thickness d can be expressed as follows,

$$J = D\,C_s/d \tag{1}$$

where D is the diffusion coefficient of H atom in Ce, C_s is the surface H concentration, respectively, and the initial H concentration inside the film is assumed to be zero. From the definition of r_{H_2}, the flux J can be expressed using r_{H_2} and the impinging rate Z as

$$J = r_{H_2}\,Z \tag{2}$$

where Z is assumed to be high enough to maintain the surface concentration constant to yield diffusion controlling kinetics in the formation of a surface hydride layer. This assumption is realistic because the applied H_2 pressure during the measurement in these concentrations was maintained in the range of 10^{-2} Pa. Therefore, the relation between r_{H_2} and d of a hydride layer formed on the surface can be expressed as

$$r_{H_2} = D\,C_s/Z\,d \tag{3}$$

where D, Z and C_s are assumed constant. Since the surface area of the film sample is constant, d may be substituted with the a hydride volume or the absorbed H amount N_{H_2}. Then,

$$r_{H_2} \propto 1/d \text{ or } 1/N_{H_2} \tag{4}$$

From the measured declining slopes of the r_{H_2} along the N_{H_2} in Fig. 1(b), the decreasing ratio of r_{H_2} with respect to the increasing H content N_{H_2} of the thick film sample is about 0.2 between $N_{H_2} = 50$ MLH_2 and 250 MLH_2 and the decreasing inverse ratio in $1/N_{H_2}$ is $50/250 = 0.2$ at these gas amounts. This coincidence between the decreasing ratios in r_{H_2} and $1/N_{H_2}$ is similar also for the thin film sample. The decreasing ratio of r_{H_2} is about 0.4 between $N_{H_2} = 30$ and 75 MLH_2 and the decreasing ratio in $1/N_{H_2}$ is $30/75 = 0.4$ at these gas amounts. Thus, independent of the sample thickness, these results indicate that the growth rate of the surface hydride layer seems to be controlled by H diffusion. The difference in r_{H_2} for the thick and thin samples at a similar N_{H_2} is caused by different Ce volumes and H atom flux densities in the samples because H atoms rapidly diffuse into the samples.

3.2. Ce–O_2 and H_2/Ce–O_2

Fig. 2 shows the changes in r_{O_2} for a clean Ce surface and a CeH_{2+x} surface. For the Ce–O_2 system, the r_{O_2} exhibits the highest reactivity $r_{O_2}=1$ at the initial stage, and then sharply drops with increasing N_{O_2}. This reduction in r_{O_2} may be ascribed to the increasing difficulties in the supply of electrons from the surface, which is crucial for the O_2 dissociation [9], and in the ion movement inside the formed oxides with increasing O_2 coverage [10].

The O_2 exposure of a CeH_{3-x} hydride surface was made immediately after the H_2 exposure of a Ce film until $N_{H_2}=425$ MLH_2 as shown in Fig. 1(b). At the initial stage, r_{O_2} exhibits $r_{O_2}=1$, and the oxidation proceeds at high reactivities $r_{O_2}>10^{-1}$ until 100 MLO_2. At N_{O_2} between 60 MLO_2 and 120 MLO_2, r_{O_2} for this Ce hydride surface is higher than that for the Ce oxide surface. This may be attributed to the fact that the rare earth dihydrides contrary to rare earth oxides are metallic [11], and therefore the dissociation of O_2 molecules may take place relatively easily. On the other hand, the metallic property becomes reduced when H concentration exceeds $[H]/[Ce]\geqq 2.75$ in atom ratio where a metal-to-semiconductor transition takes place [12]. Therefore, the H concentration of the Ce hydride layer formed in this measurement seems to be lower than $[H]/[Ce]=2.75$.

For the high O_2 reactivities with the Ce hydride surface in Fig. 2, two mechanisms may be assumed, the oxidation of the hydride by the adsorption of O atoms on the surface, and/or the formation of H_2O gas by the combination of the dissociated O atoms with the H atoms of the hydride. Fig. 3 shows the changes in the partial pressures of O_2, H_2O and H_2 gases during the O_2 exposure of the hydride surface. As the O_2 adsorption on the Ce hydride surface proceeds, the partial pressure of H_2O increases (Fig. 3). This effect may be attributed to the combination of the H atoms of the hydride with the O atoms dissociated from O_2 gas. From these data, the amount of O atoms contributing to the H_2O gas formation was found to be about 1.6 MLO_2 which is negligibly small compared with the amount reacted $N_{O_2}=160$ MLO_2. Therefore, the effect of H_2O gas formation can be omitted in the measured high O_2 reactivity on the Ce hydride surface. Most O_2 molecules reacted with the hydride surface seem mainly to form hydroxides.

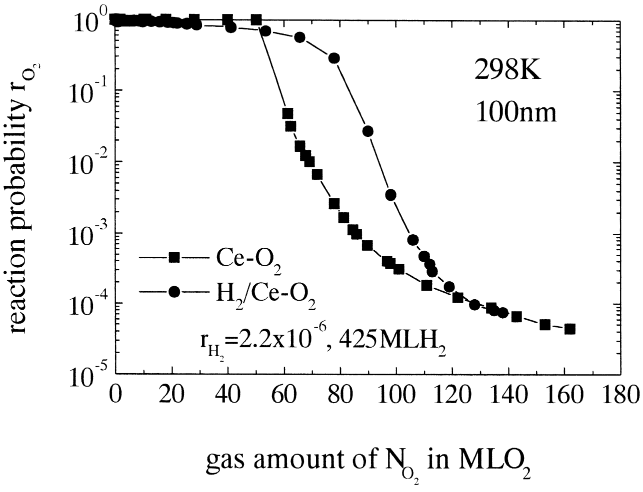

Fig. 2. Reaction probability of O_2 with Ce and H_2/Ce at 298 K.

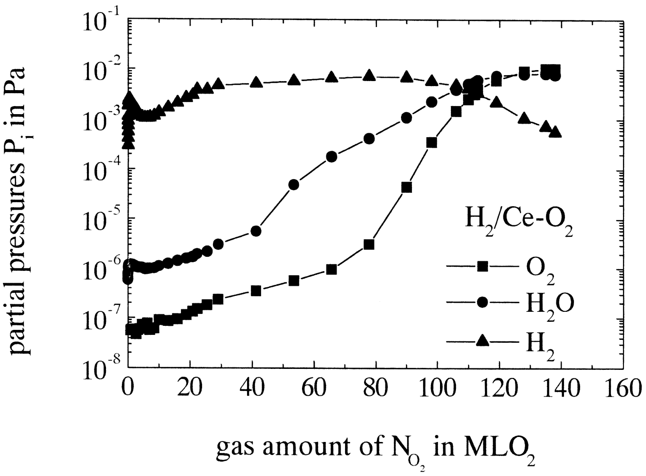

Fig. 3. Changes in the partial pressures p_{O_2}, p_{H_2O}, p_{H_2} as a function of N_{O_2}.

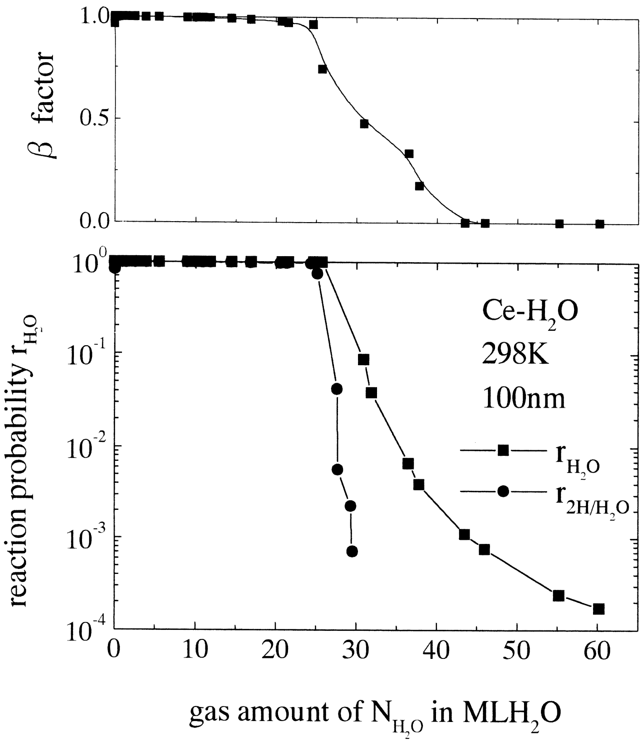

Fig. 4. Reaction probability of H_2O with Ce at 298 K.

3.3. *Ce–H_2O*

Fig. 4 shows the change in r_{H_2O} for the Ce–H_2O system where r_{2H/H_2O} is the reaction probability of the H atoms dissociated from the H_2O molecules, and the dissociation rate of the H atoms from H_2O, β, was estimated from the measurement of the increasing H_2 partial pressure, and is expressed by the following reaction [10],

$$H_2O \rightarrow 2\,\beta\,\mathrm{H\ (adsorbed)} + (1-\beta)\,H_2\ \mathrm{(desorbed)} + \mathrm{O\ (adsorbed)}$$

where the dissociated H atoms are assumed to form hydrogen solid solutions, hydride and/or hydroxide with the dissociated O atoms.

At the initial stage, r_{H_2} and r_{2H/H_2O} exhibit the highest reactivity. At $N_{H_2O}=25$ MLH$_2$O, r_{H_2O} and r_{2H/H_2O} sharply drop. At this H_2O coverage, the β factor also decreases. This may be caused by the formation of increasing amounts of $Ce(OH)_x$ on the surface. With the increasing $Ce(OH)_x$ layers, the dissociation of H_2O and the penetration of the dissociated H atoms become hindered.

3.4. *O_2/Ce–H_2 and H_2O/Ce–H_2*

Fig. 5 shows the effect of the preadsorptions of O_2 and H_2O on the H_2 reactivity of Ce surface. The H_2 exposures were made for a Ce oxide film with $N_{O_2}=162$ MLO$_2$ formed in the O_2 exposure shown in Fig. 2, and for a Ce hydroxide film with $N_{H_2O}=60$ MLH$_2$O in the H_2O exposure shown in Fig. 4. r_{H_2} with the oxide or hydroxide surfaces of Ce becomes strongly reduced by several orders of magnitudes compared with the clean Ce surface (Fig. 1(a) and (b)). However, the Ce oxide surface exhibits higher r_{H_2} than the Ce hydroxide surfaces. The Ce surface with a high amount of O_2 coverage 162 MLO$_2$ exhibits still r_{H_2} reactivities in the order of $r_{H_2}=10^{-4}$–10^{-5}, which is higher by two orders of magnitude than the Ce surface with a lower amount of H_2O coverage 60 MLH$_2$O does.

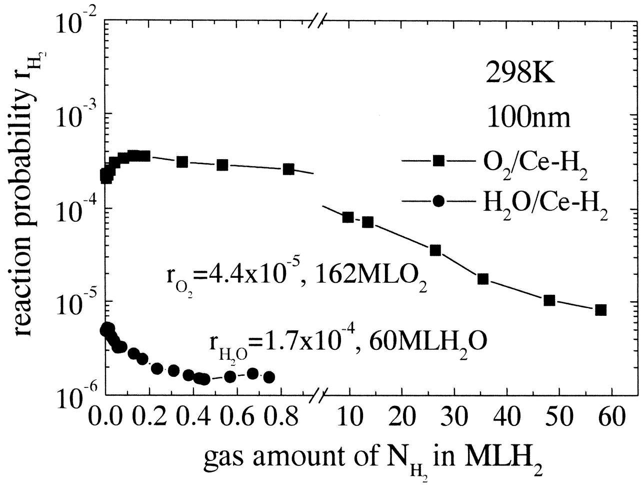

Fig. 5. Effect of O_2 and H_2O preadsorptions on r_{H_2} with Ce.

This indicates that the Ce hydroxide layers hinders the H_2 dissociation much more strongly than the Ce oxide layers, and that the Ce oxides with these O amounts are metallic and still active in dissociating H_2 molecules. These results are similar to that for the O_2/La–H_2 and H_2O/La–H_2 systems [13].

4. Conclusion

The Ce metal with a clean surface was found to exhibit the highest reactivity, $r=1$, with H_2, O_2 and H_2O at room temperature. The CeH_{2+x} hydride was found to be metallic and very active to dissociate the O_2 molecules where the oxidation of the hydride by the O_2 adsorption predominates over the H_2O gas formation. The Ce hydroxides hinder the H_2 dissociation much more strongly than the Ce oxides. The Ce oxides as well as La oxides were found to exhibit relatively high H_2 reactivities $r_{H_2}=10^{-4}$–10^{-5} even with high O_2 coverages at room temperature. This fact may explain the reason why the oxidized $MmNi_5$ based hydrogen storage alloys exhibit easy initial activation because Mm contains Ce and La as major elements.

Acknowledgements

This study was made in the frame of the ECO-TECHNOLOGY Project, Tokai University, and was financially supported by the Tokai University Educational System.

References

[1] M. Hadano, N. Urushihara, T. Inoue, H. Uchida, J. Alloys Comp. 293–295 (1999) 403–406.
[2] T. Hattori, J. Inoko, Y. Murakami, J. Catal. 42 (1976) 60.
[3] G. Meyer, in: G. Meyer, L.R. Morss (Eds.), Synthesis of Lanthanide and Actinide Compounds, Kluwer Academic Publisher, Netherlands, 1991, p. 187
[4] H. Uchida, M. Ozawa, Zeit. Phys. Chem. NF 147 (1986) 77.
[5] Y. Ohsumi, H. Suzuki, A. Kato, M. Nakane, Y. Miyake, J. Chem. Jpn. (1978) 1472
[6] H. Uchida, M. Tada, Yen C. Huang, J. Less-Common Met. 88 (1982) 81.
[7] S. Wagener, Br. J. Appl. Phys. 1 (1950) 225.
[8] E. Fromm, H.G. Wulz, J. Less-Common Met. 101 (1984) 469.
[9] J.K. Norskov, F. Besenbachher, J. Less-Common Met. 130 (1987) 475.
[10] H. Cichy, E. Fromm, Thin Solid Films 195 (1991) 147–158.
[11] C. Ohki, H. Uchida, K. En, Mater. Trans. JIM 54 (2) (1990) 146–152.
[12] G.G. Libowitz, Ber. Bunsenges. Phys. Chem. 76 (1972) 837.
[13] N. Hosoda, H. Uchida, Y. Ohtani, T. Takanashi, E. Fromm, Z. Phys. Chem. NF 164 (1989) 1129.