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The effect of O_2 preadsorption on the rate of H_2 absorption on the surface of rare earths (La, Ce, Tb, Dy) at 298 K

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Abstract

The reactivities of H_2 and O_2 with La, Ce, Tb and Dy were measured at 298 K under UHV condition. The reactivity of H_2 with these rare earths was very high and decreased with increasing coverage of the dihydride phase on the surface. As hydriding proceeds, a drastic change in the color of the rare earths was observed, indicating the change in the feature from metal to nonmetal of the hydrides. The O_2 reactivity was quite different for various rare earths. The oxidized Ce surface exhibits the highest H_2 reactivity in comparison with the other rare earth oxides.

Keywords: Rare earth hydrides; Lanthanum; Cerium; Terbium; Dysprosium

1. Introduction

In the process of hydriding, rare earths (R) absorb a large amount of H and form stable dihydrides, RH_2 first and subsequently transform to trihydrides, RH_3. In the formation of RH_3 with increasing H concentration, LaH_2 [1] and CeH_2 [2] form trihydrides without any phase transformation, while NdH_2 [2], SmH_2 [1], DyH_2 [3] form trihydrides accompanied by a phase transformation from fcc of RH_2 to hcp of RH_3. In previous reports [4,5], we demonstrated that the La surface exhibits very high reaction probability with H_2, $r_{H_2}=1$ at the initial stage even at low temperatures such as 77 K and 298 K. Quite an interesting fact found was that the La surface covered with the O_2 preadsorption layer, containing relatively a large amount of O_2 still exhibits high reactivity with H_2 even at 298 K [6]. In general, the O_2 preadsorption layer of low O_2 concentration or oxides on the surface of metals like Ta [7] markedly inhibits the dissociation of H_2 molecules, resulting in a difficult initiation of the activation at room temperature. However, as is well known, rare earth based hydrogen storage alloys can be activated at room temperature even after a long exposure to air. This may be caused by the presence of rare earth oxides with high reactivities with H_2 [6]. The crucial point to initiate the reaction of a metal surface with H_2 is the occurrence of the H_2 dissociation sites, at which the exchange of electrons between the surface and the H_2 molecule could take place [8,9]. Recently, we found that the presence of alkaline atoms on the metal surface reduces the work function of electrons of the surface [10,11], which effectively enhances the rate of H_2 dissociation.

This study aims at obtaining fundamental data for the reactivity of the surfaces of La, Ce, Tb and Dy with H_2, and examining the effect of the O_2 preadsorption layer on the H_2 reactivities of these rare earths.

2. Experimental procedure

The H_2 reactivity was assessed by the measurement of the number N of adsorbed or absorbed gas molecules per square centimeter, the reaction probability r, which is defined as the ratio of the rate of adsorption or absorption of gas molecules to the impinging rate of gas molecules on the metal surface. The details of this method, the Wagener method, is described elsewhere [12]. In this paper, the gas amount N is denoted by monolayers (ML) where 1 ML$=10^{15}$ molecules cm^{-2}. The block samples of La, Ce, Tb and Dy (purities: 99.9%) were degassed under UHV condition until no appreciable residual gas was able to be detected by using a mass spectrometer with a detection limit over 10^{-9} Pa. Subsequently, the polycrystalline films of these metals with a thickness of 100 nm were deposited

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on the walls of glass reaction cells separately by evaporating the degassed block samples under UHV ($<5\times10^{-8}$ Pa). H_2 or O_2 was supplied through a Pd or Ag diffusion cell, respectively. For the measurement of the effect of the O_2 preadsorption on r and N, the films were first exposed to O_2 gas, and then to H_2 in a second run.

3. Results and discussion

3.1. H_2 reactivity

Fig. 1 shows the change in the H_2 reaction probability r_{H_2} for La, Ce, Tb and Dy as a function of the amount of absorbed H_2 molecules N_{H_2} at 298 K. As shown in Fig. 1(a), $r_{H_2}=1$ at the initial stage of the H_2 absorption by these metals. This means that all H_2 molecules impinging the surface dissociate and the dissociated H atoms dissolve into the metals. At this initial stage, the H solid solution phase may be formed for each system. Since the H_2 dissociation pressures of the dihydride of La, Ce, Tb and Dy are lying at very low levels such as 6×10^{-25} Pa for LaH_2, 2×10^{-22} Pa for CeH_2, 9×10^{-24} Pa for TbH_2 and 9×10^{-30} Pa for DyH_2 at 298 K [13], the dihydride phase of these metals can easily be formed at H_2 gas pressures higher than 10^{-8}–10^{-6} Pa in this experimental condition. The formation of the dihydride on the surface decreases r_{H_2} from $r_{H_2}=1$ to $r_{H_2}=3$–5×10^{-1} for La, Tb and Dy and to 5×10^{-2} for Ce, respectively. This reduction in r_{H_2} can be ascribed to the slower diffusion rate of H atoms inside the surface dihydride, and to the retarded dissociation of H_2 molecules on the dihydride because the H atoms inside the metals or hydrides consume conduction electrons to form rather ionic rare earth hydrides with H^-–R^+ bonds as the H concentration in the hydrides is increased [14,15].

With increasing H concentration, r_{H_2} gradually decreased until $N_{H_2}=300\times10^{15}$ molecules cm^{-2} where two phases of H solid solutions and dihydride may coexist. The H_2 reaction probability r_{H_2} with Ce is lying lower by an order of magnitude than those of the other metals. This may be caused because the H_2 equilibrium pressure for the Ce–H system is the highest among the systems (Table 1). The H_2 reactivity in this two phase region is decreased in the order r_{H_2} for Dy, La, Tb and Ce as the equilibrium pressures become lower (Table 1).

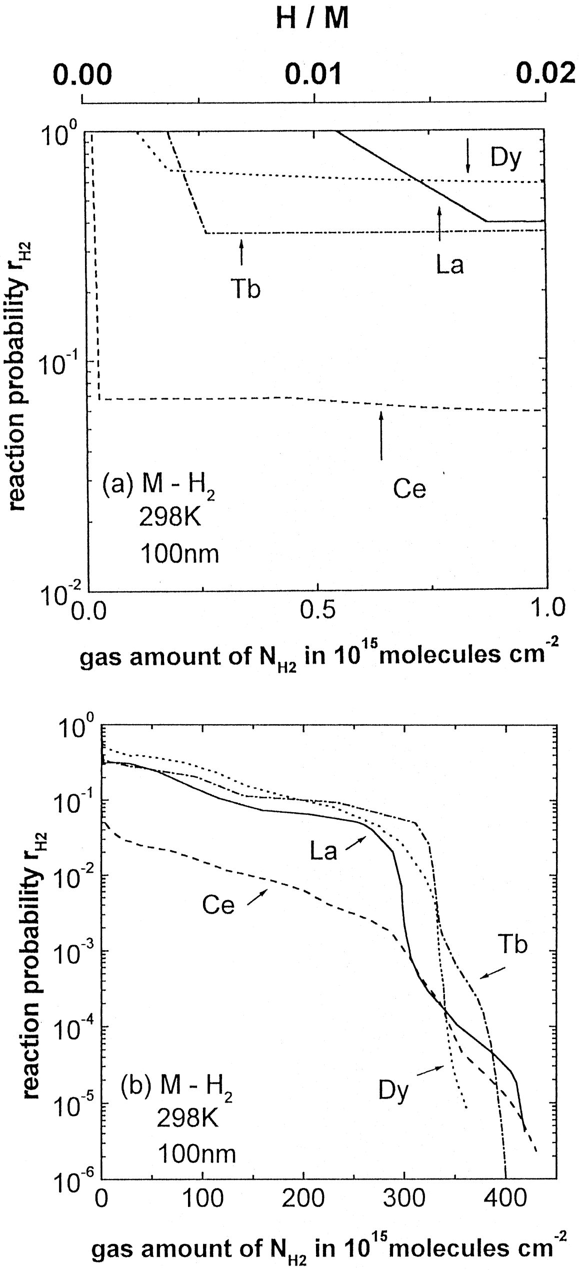

Fig. 1. Change in H_2 reaction probability r_{H_2} as a function of H_2 amount N_{H_2} absorbed by La, Ce, Tb and Dy (a) $N_{H_2}<1\times10^{15}$molecules cm^{-2} (b) $N_{H_2}<450\times10^{15}$molecules cm^{-2}.

At $N_{H_2}>300\times10^{15}$ molecules cm^{-2}, r_{H_2} sharply drops for all samples. Two possible factors may be considered for this sharp drop in r_{H_2}. One is the marked reduction in the number of conduction electrons, which strongly hinders the H_2 dissociation. Another is due to the increase in the H_2 dissociation pressures of the RH_{2+x} hydrides with increasing H concentration. For the formation of the RH_3 phase, much higher H_2 pressures were applied in the reaction cell. With increasing H concentrations the H_2 dissociation pressures become much higher than those of the dihydrides as shown in Fig. 2(a) for LaH_{2+x}, (b) for CeH_{2+x}, (c) for TbH_{2+x} and (d) for DyH_{2+x}, respectively, where the dotted lines are applied H_2 gas pressures and the solid lines are the H_2 dissociation pressures of each RH_{2+x} hydride at the H concentration between [H]/[R]=2 and 3

Table 1
The H_2 dissociation pressures (Pa) of the dihydride of lanthanum, cerium, terbium and dysprosium at 298 K

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

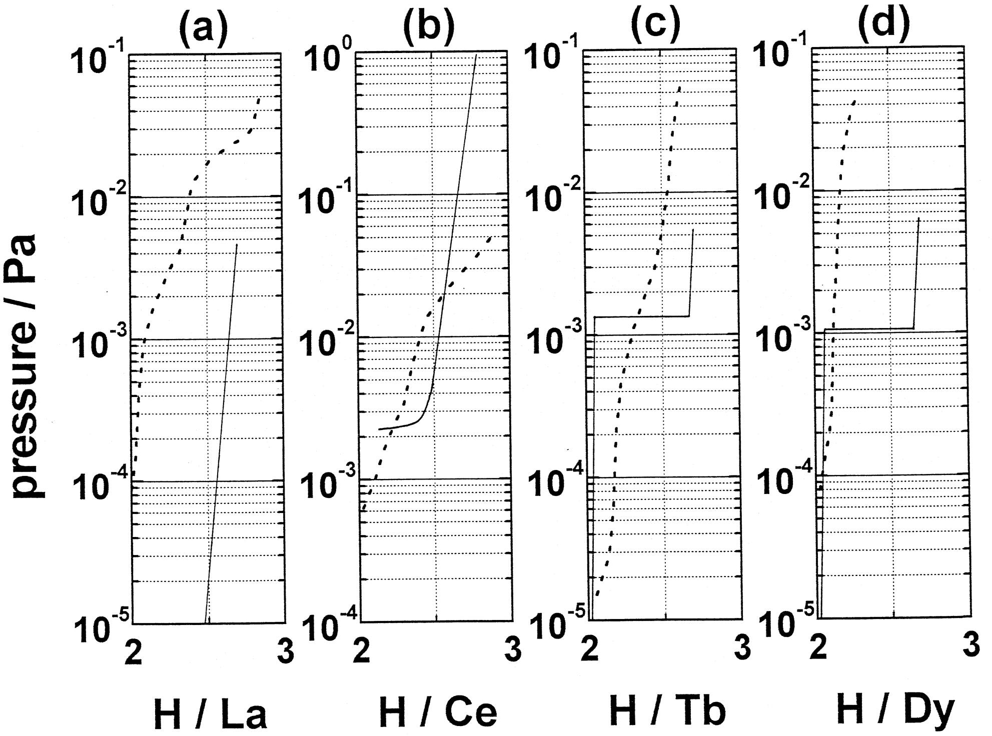

Fig. 2. H_2 dissociation pressures at 298K shown by solid lines and H_2 partial pressures in the reaction cell shown by dotted lines (a) for La, (b) for Ce, (c) for Tb, (d) for Dy.

[3,16]. In these regions, the competitive relation between the applied pressures and the dissociation pressures strongly affects the reactivity r_{H_2}.

3.2. Change in color of the hydrides of La, Ce, Tb and Dy

During the initial exposure of the film samples to H_2, the color of the samples was metallic silver. However, as the H concentration became close to [H]/[R]=2, the surface of different rare earth films exhibited different colors. The H induced color change was characteristic for each rare earth: from metallic silver for all samples with low H contents to deep green for LaH_2, to brown for CeH_2, to blue for TbH_2 and to gold for DyH_2, respectively. As the H concentration became close to [H]/[R]=3, the films of all samples became transparent, indicating the change in the feature of the films from metal to nonmetal by the consumption of conduction electrons by H atoms to form ionic hydrides [17].

3.3. O_2 reactivity

Fig. 3 shows the change in the O_2 reactivity r_{O_2} with La, Ce, Tb and Dy at 298 K as a function of the amount of adsorbed O_2 molecules N_{O_2}. At the initial stage, all samples exhibited $r_{O_2}=1$. Particularly, Ce exhibited a long plateau at $r_{O_2}=1$, meaning the highest O_2 reactivity compared with other rare earths. For the rare earths used in this experiment, the potential for the fourth ionization increases in the order Ce<Tb<Dy<La [18]. This may be the main reason for the highest reactivity of O_2 with Ce. The length of the plateau for $r_{O_2}=1$ of a rare earth metal becomes shorter as its fourth ionization potential becomes higher as shown in Fig. 3, with potentials varying in the order Ce<Tb<Dy<La.

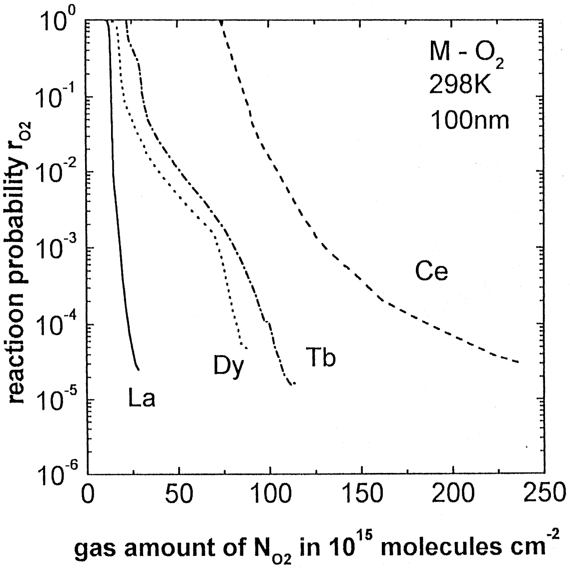

Fig. 3. Change in O_2 reaction probability r_{O_2} as a function of O_2 amount N_{O_2} reacted with La, Ce, Tb and Dy.

3.4. Effect of O_2 preadsorption

Fig. 4(a) and (b) shows the effect of the O_2 preadsorption layer on the H_2 reactivity for La, Ce, Tb and Dy. In this study, each film surface was precovered with O_2 in the ranges of the precoverages from 28 MLO_2 to 224 MLO_2 and the O_2 reaction probability r_{O_2} was in the range 1.6×10^{-5} to 5.0×10^{-5}.

Among the precovered surfaces, the oxidized Ce surface exhibited the highest H_2 reactivity, $r_{H_2}=1$ at the initial stage (Fig. 4(a)) and then $r_{H_2}=10^{-4}$ to 10^{-5} with increasing N_{H_2} (Fig. 4(b)). In previous reports [5,6], we pointed out the high H_2 reactivities of LaO_x at 298 K. However, CeO_x exhibits much higher r_{H_2}. The oxidized Ce surface seems to remain more metallic than the other rare earths used in this study.

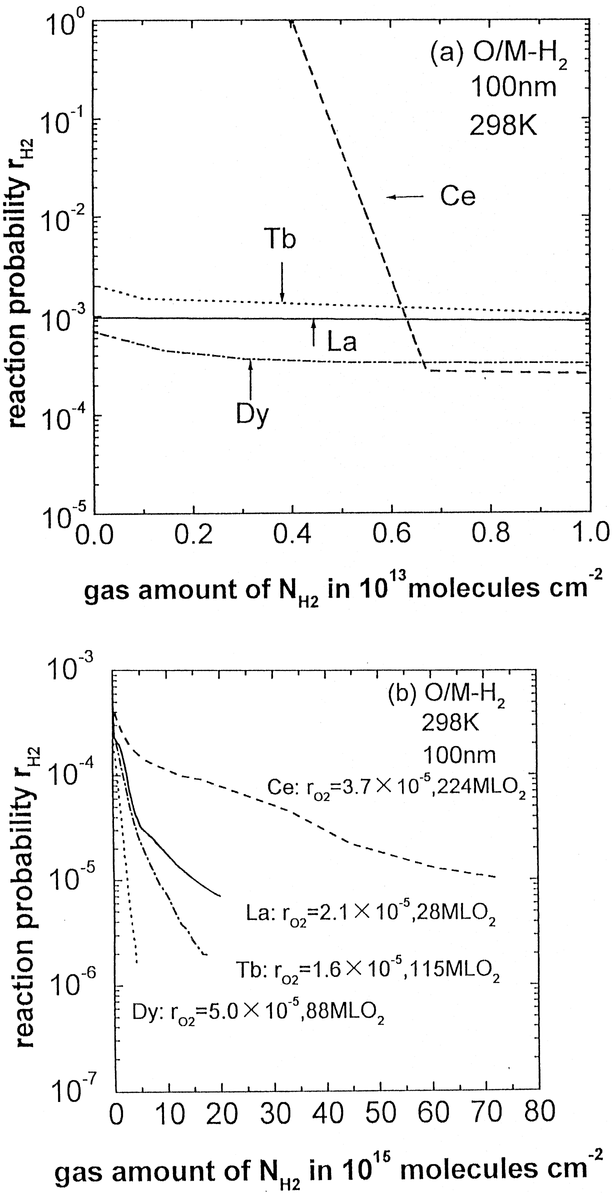

Fig. 4. Effect of O_2 preadsorption on H_2 reaction probability r_{H_2} with La, Ce, Tb and Dy (a) for the initial stage (b) for higher H_2 amounts N_{H_2}.

4. Conclusion

The clean surfaces of La, Ce, Tb and Dy exhibit the highest reaction probability $r_{H_2}=1$ at 298 K. For these metals, r_{H_2} drops by one to two orders of magnitude as the surface is covered with dihydride. The drastic change in the color of the film samples indicates the H induced electronic changes in the hydride of these rare earths. The O_2 reactivity of La, Ce, Tb and Dy becomes higher as the fourth ionization potential becomes lower. The oxidized Ce surface exhibits the highest H_2 reactivity among the other oxidized rare earths used, indicating the strong metallic features of the CeO_x in comparison with the oxides of La, Tb and Dy.

Acknowledgements

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