

# Effects of O<sub>2</sub> and H<sub>2</sub>O preadsorptions on the H<sub>2</sub> reactivity with the Cr surface

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## Abstract

The H<sub>2</sub> reactivity with the Cr surface intentionally modified by O<sub>2</sub> or H<sub>2</sub>O preadsorption was quantitatively investigated compared to the clean surface prepared under UHV condition and at 298 K by using volumetric method. The O<sub>2</sub> preadsorption layers on the Cr surface remarkably decreased the reaction probability of H<sub>2</sub> compared with the H<sub>2</sub>O preadsorption layers. The effect of O<sub>2</sub> poisoning on the H<sub>2</sub> reactivity was reduced by the presence of H chemisorption layers on the clean surface of Cr.

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## 1. Introduction

Ti–Cr based alloys are utilized as a low temperature type of hydrogen storage alloy, and applied to metal-hydride (MH) freezer systems. In our group, the surface features of Ti–Cr based alloys and its compositional element Cr have been focused on [1,2]. Cr is an interesting element because of its high oxidation states and catalytic properties. There have been reports that Cr oxide is one of the most effective catalysts for nano-crystalline Mg based systems on the hydrogen sorption kinetics [3,4]. However, information about the surface properties of Cr with respect to the H<sub>2</sub> reactivity is lacking, especially at low temperature and low pressure.

Our previous study was made to clarify the kinetic properties of a clean Cr surface on the reactivities of H<sub>2</sub>, O<sub>2</sub>, and H<sub>2</sub>O gases under UHV condition at 298 K and also for H<sub>2</sub> at 77 K. As well, the reactivity of H atoms dissociated from H<sub>2</sub>O molecules was measured in comparison with that of H<sub>2</sub> molecules at 298 K. We reported that the Cr surface exhibits a much higher reactivity with H<sub>2</sub> compared to Ni and Co surfaces, and that the uptake

of H atoms in H<sub>2</sub>O adsorption on the Cr surface is higher than in the adsorption of H<sub>2</sub> molecules as a result of the formation of the hydroxide layers [2]. In the present study, we aimed to investigate quantitatively the effects of O<sub>2</sub> and H<sub>2</sub>O preadsorption layers on the H<sub>2</sub> reactivity with the Cr surface by using the same UHV technique. The reaction probability of H<sub>2</sub> on the intentionally modified Cr surfaces was measured volumetrically at 298 K and pressures ranging from 10<sup>−8</sup> to 10<sup>−2</sup> Pa.

## 2. Experimental

The UHV condition below 5 × 10<sup>−8</sup> Pa was attained by degassing thoroughly a Cr block sample and out-gassing a whole glass system repeatedly. The partial pressures of residual gases were carefully checked by monitoring with a quadrupole mass spectrometer (QMS) during an entire process. The Cr film samples with a thickness of 100 nm were deposited onto the wall of a glass reaction cell by evaporating the degassed block sample below 5 × 10<sup>−8</sup> Pa. The structure of the prepared film sample was found to be polycrystalline, and the surface roughness factors more than 10–20 should be taken into account for the prepared film samples [5]. After the preparation of the film sample with a clean surface, a reaction gas (H<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O) was supplied from a gas reservoir to a reaction cell through a calibrated capillary. H<sub>2</sub> and O<sub>2</sub> gases were purified through a hot Pd or Ag cell, respectively. H<sub>2</sub>O gas was supplied from an ultrahigh purity droplet with a specific resistivity higher than 15 MΩ cm. The volumetric Wagener method was used to measure the amount of adsorbed or absorbed gas molecules *N*, and 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. In this study, the reacted amount *N* is expressed in monolayers (ML) where 1 ML = 10<sup>15</sup> molecules cm<sup>−2</sup>. Details of

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this measurement method are described elsewhere [6,7]. In order to examine the surface effect on H<sub>2</sub> reactivity, the sample surface was modified by exposing to O<sub>2</sub> or H<sub>2</sub>O before the subsequent H<sub>2</sub> exposure.

### 3. Results and discussion

#### 3.1. Effects of O<sub>2</sub> and H<sub>2</sub>O preadsorption layers

Fig. 1 shows the reactivity of a gas (H<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O) with the clean surface of Cr as a function of the amount of gas molecules reacted  $N_{\text{gas}}$  at 298 K, and also, the reactivity of H atoms dissociated from H<sub>2</sub>O molecules is shown, which was calculated from the partial pressure of H<sub>2</sub> molecules desorbed in H<sub>2</sub>O adsorption [2]. At the initial stage, the reactivities of H<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>O with the clean surface of Cr were measured as the highest reaction probability  $r_{\text{gas}} = 1$ . This means all gas molecules impinging the surface dissociate, and dissociated atoms react with the Cr surface. For Cr-H<sub>2</sub>, as H<sub>2</sub> exposure was extended, at  $N_{\text{H}_2} > 18$  ML H<sub>2</sub>, the reaction probability  $r_{\text{H}_2}$  was gradually decreased and then sharply dropped. This abrupt reduction in  $r_{\text{H}_2}$  seems to be caused by backward reaction of H<sub>2</sub> molecules from the surface since the H<sub>2</sub> equilibrium pressure for Cr hydride formation is quite high even at low H concentration: over 1 GPa at H/Cr < 10<sup>-6</sup> and 300 K [8]. Owing to the endothermic reaction for the Cr-H system, the reaction process is expected to take place only in the surface region. Further details of the reaction kinetics of a gas (H<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O) with the clean surface of Cr were reported in the previous paper [2]. In the present study, in order to examine the poisoning effects of O<sub>2</sub> and H<sub>2</sub>O preadsorptions on the H<sub>2</sub> reactivity, the clean surface of Cr was intentionally contaminated by exposing to O<sub>2</sub> or H<sub>2</sub>O gases with the amounts of 5 and 14 ML for each gas before H<sub>2</sub> exposure (shown in Fig. 1). During O<sub>2</sub> and H<sub>2</sub>O exposures until 5 and 14 ML, the Cr surface exhibited the highest reactivities with O<sub>2</sub> and H<sub>2</sub>O,  $r_{\text{O}_2, \text{H}_2\text{O}} = 1$ , and the stable oxide or hydroxide layers were formed on the Cr surface. During H<sub>2</sub>O exposure, no H<sub>2</sub> desorption from the Cr

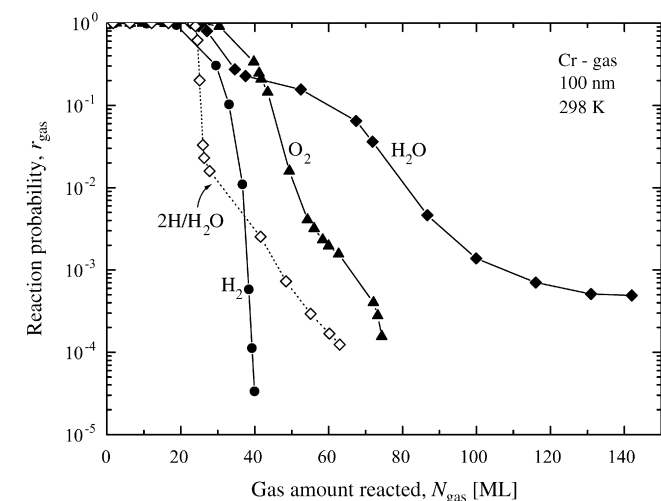


Fig. 1. Changes in the reaction probability of a gas (H<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O),  $r_{\text{gas}}$ , on the surface of Cr as a function of gas amount reacted,  $N_{\text{gas}}$ , in monolayers (ML) at 298 K.

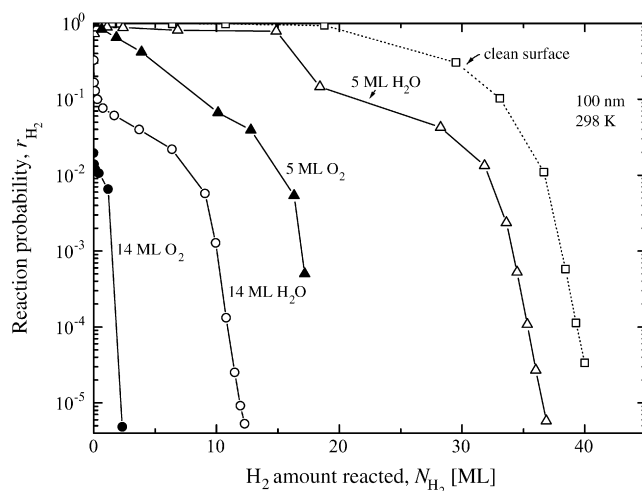


Fig. 2. Effects of O<sub>2</sub> and H<sub>2</sub>O preadsorption layers on the reaction probability of H<sub>2</sub>,  $r_{\text{H}_2}$ , on the surface of Cr as a function of H<sub>2</sub> amount reacted,  $N_{\text{H}_2}$ , in monolayers (ML) at 298 K.

surface was observed at the region with  $r_{\text{H}_2\text{O}} = 1$ , and resulting in  $r_{2\text{H}/\text{H}_2\text{O}} = 1$  (H atoms dissociated from H<sub>2</sub>O molecules) [2].

Fig. 2 shows the effects of O<sub>2</sub> and H<sub>2</sub>O preadsorption layers on the H<sub>2</sub> reactivity with the Cr surface at 298 K compared to the H<sub>2</sub> reactivity with the clean surface in a plot reaction probability  $r_{\text{H}_2}$  versus the amount of H<sub>2</sub> molecules reacted  $N_{\text{H}_2}$ . The Cr surface with H<sub>2</sub>O precoverages of 5 ML H<sub>2</sub>O still exhibited the highest reactivity of H<sub>2</sub>  $r_{\text{H}_2} = 1$  at the initial stage and a high rate of  $r_{\text{H}_2} \sim 1$  until  $N_{\text{H}_2} = 15$  ML H<sub>2</sub>, then  $r_{\text{H}_2}$  became lower. This result indicates that the Cr surface precovered by H<sub>2</sub>O with 5 ML H<sub>2</sub>O is still active in dissociating H<sub>2</sub> molecules. With increasing amount of H<sub>2</sub>O preadsorption to 14 ML H<sub>2</sub>O,  $r_{\text{H}_2}$  on the hydroxidized Cr surface was decreased by one order of magnitude without showing  $r_{\text{H}_2} = 1$  at the initial stage, indicating that the dissociation of H<sub>2</sub> molecules is significantly impeded by thick hydroxide layers.

The Cr surface with O<sub>2</sub> precoverages of 5 ML O<sub>2</sub> exhibited the highest value  $r_{\text{H}_2} = 1$  at the initial stage. However, with extended H<sub>2</sub> exposure,  $r_{\text{H}_2}$  was rapidly decreased. The increased oxide layers to 14 ML O<sub>2</sub> drastically reduced  $r_{\text{H}_2}$  by two orders of magnitude at the initial stage, resulting in a very low reaction amount of  $N_{\text{H}_2} = 2$  ML H<sub>2</sub>. This may be ascribed to the increasing difficulty in electron exchange between H<sub>2</sub> molecules and the Cr surface covered with oxide layers [9,10]. During H<sub>2</sub> exposure to the oxidized Cr surfaces no H<sub>2</sub>O peak (>10<sup>-7</sup> Pa) was observed, indicating that Cr oxides formed on the surface cannot be removed by the H<sub>2</sub>O formation. These results suggest that the Cr surface becomes drastically inactive or passivated as the surface is covered with stable oxide layers. When compared to the effect of H<sub>2</sub>O preadsorption, the H<sub>2</sub> reactivity with the hydroxidized Cr surface is found higher than the oxidized Cr surface. This difference between the influences of O<sub>2</sub> and H<sub>2</sub>O precoverages could possibly be attributed to Cr ions with different oxidation states because an electron supply from the surface is essential to an occurrence of the dissociation of physisorbed H<sub>2</sub> molecules [11]. Or some attractive chemical interactions between the Cr hydroxide and H<sub>2</sub> molecules may take place.

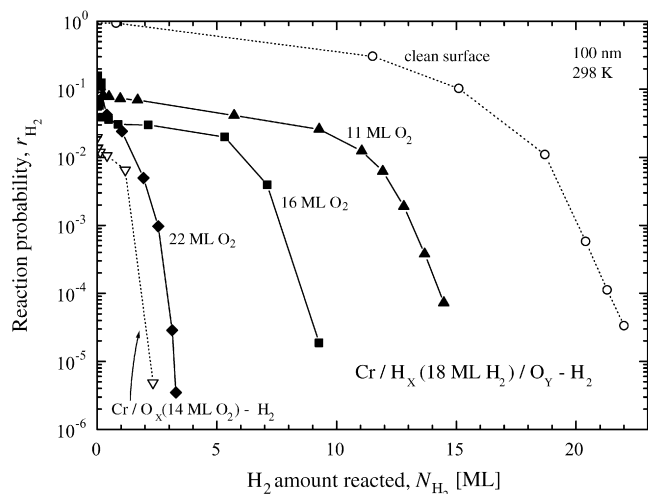


Fig. 3. Effects of  $O_2$  preadsorption layers formed on the H present surface on the reaction probability of  $H_2$ ,  $r_{H_2}$ , on the surface of Cr as a function of  $H_2$  amount reacted,  $N_{H_2}$ , in monolayers (ML) at 298 K.

### 3.2. Effects of $O_2$ preadsorption on the H present surface

In this study, at first, the clean surface was exposed to  $H_2$  until  $N_{H_2} = 18 \text{ ML } H_2$ , where the  $H_2$  reactivity was measured as the maximum value  $r_{H_2} = 1$  (shown in Fig. 1), and H chemisorption layers were formed on the clean surface. Thereafter, the H precovered surface was exposed to  $O_2$  before the subsequent  $H_2$  exposure. During  $O_2$  exposure, the H present surface exhibited the highest reactivity  $r_{O_2} = 1$ , suggesting that all impinging  $O_2$  molecules dissociatively adsorb on the surface, and that the oxidation reaction is not significantly affected by the presence of H atoms on the Cr surface. One possible explanation for the high rate of  $O_2$  adsorption may be due to a much stronger interaction between O atoms and the Cr surface than H atoms, according to the data of the heat of adsorption for  $O_2$  and  $H_2$  on polycrystalline Cr films: 728 kJ/mol for Cr- $O_2$  [12] and 188 kJ/mol for Cr- $H_2$  [13], respectively. Fig. 3 shows the effect of  $O_2$  preadsorptions formed on the H covered surface of Cr on the  $H_2$  reactivity at 298 K. No  $H_2O$  formation ( $>10^{-7} \text{ Pa}$ ) was observed during each  $H_2$  exposure. At the initial stage, the increased  $O_2$  precoverages on the H present surface, equivalent to 11–22 ML  $O_2$ , decreased the initial  $r_{H_2}$  by over one order of magnitude. However, the  $H_2$  reactivity was found to be much higher in comparison to the directly oxidized Cr surface with lower  $O_2$  precoverages of 14 ML  $O_2$ , implying that the Cr surface with  $O_2$  preadsorption layers formed on H chemisorption layers seems more metallic. Judging from a higher reactivity of  $H_2$  on the hydroxidized Cr surface (shown in Fig. 2), the dissociated O atoms may react with the pre-chemisorbed H layers to form hydroxyl groups on the surface. It is worth noting that the presence of H atoms on the clean surface mitigates the poisoning effect of the surface oxidation on the  $H_2$  reactivity with the Cr surface, when the condition of a practical treatment of hydrogen storage alloys containing Cr is taken into account. The alloys

are frequently treated in low vacua where high contents of  $H_2$  and  $O_2$  coexist in a system. Therefore, under such conditions, the surface reactions by  $H_2$ ,  $O_2$ ,  $H_2O$  or other impurity gases competitively take place on the alloy surface after new and highly active surfaces appear from the pulverization of alloys by repeated hydriding and dehydriding processes. When it is considered that the dissociation of  $H_2$  molecules is strongly retarded by the oxide layers formed on the clean surface of Cr (shown in Fig. 2), these results may give a rational explanation for the catalytic behavior of Cr surfaces in hydrogen absorbing materials, especially at low temperature where O atoms of the oxide layers cannot diffuse into the metal.

## 4. Conclusions

The  $H_2$  reactivity on the hydroxidized surface of Cr was found higher than on the oxidized surface at 298 K, and the oxide layers formed on the clean surface remarkably inhibited the  $H_2$  reactivity. This suggests that the hydroxidized surface of Cr may remain more metallic than the oxidized surface, or that some attractive chemical reaction may be present between  $H_2$  molecules and the Cr hydroxide. The poisoning effect of  $O_2$  preadsorption was mitigated by the prior formation of H chemisorption layers on the Cr surface. These results obtained may be helpful to understand the role of the Cr surface on the kinetic reaction of hydrogen absorbing materials containing Cr.

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