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The effect of surface state on the kinetics of cerium-hydride formation

H.T. Bach*, T.J. Venhaus, S.N. Paglieri, H. Oona, T.H. Allen, R.B. Schwarz, J.R. Wermer

Los Alamos National Laboratory, P.O. Box 1663, MS-927 Los Alamos, NM 87545, United States

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Abstract

We studied the effects of surface oxidation on the kinetics of hydrogen (H) absorption into two commercial samples of Ce: bulk samples and thin rolled foils. A Sieverts' apparatus was used to measure the H absorption kinetics and X-ray photoelectron spectroscopy (XPS) was used to determine the surface oxidation state and the presence of impurities, notably carbon (C). In the as-received condition, the bulk Ce specimen was covered by a Ce_2O_3 film (sesquioxide) whereas the as-received foil was covered with a CeO_2 film (dioxide). In this condition, the H absorption rate at room temperature was approximately an order of magnitude faster in the bulk sample than in the foil. Vacuum annealing at $P \leq 1 \times 10^{-4}$ Torr and $T = 773$ K significantly increased the rate of H uptake, making it similar in both samples. This annealing reduced the Ce_2O_3 in the bulk samples so that the samples became more metallic, but produced little change in the XPS signal from the CeO_2 film on the foil sample. The study suggests that the differences in H uptake kinetics are affected not only by the nature of the oxide (sesquioxide versus dioxide) but also by the integrity of the surface oxide film, which may be affected by the thermal treatment.
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Keywords: Cerium-hydride; Dioxide; Sesquioxide; Hydriding kinetics; Vacuum annealing; X-ray photoelectron spectroscopy

1. Introduction

The low equilibrium pressure between a solid-solution of Ce–H and the hydride CeH_2 ($<10^{-2}$ Torr at 773 K) [1] suggests that Ce could be used to getter H isotopes from the molten liquids used to cool nuclear reactors and also for the removal of tritium from gaseous streams [2,3]. However, like the other elements in the lanthanide series, Ce reacts readily with O to form a passive surface layer [4]. This layer slows the rate of H uptake. Because this layer is often poorly characterized, studies on the absorption kinetics of H into Ce, especially untreated or aged Ce, are difficult to reproduce. Studies of H absorption are usually performed on samples that have been annealed under vacuum to promote a certain "conditioning" of the surface [5]. It is assumed that contaminants such as O and C desorb from the metal surface or are absorbed into the metal during this conditioning. Either process increases the reactivity of the surface towards H uptake, reduces the induction period often encountered before the onset of steady state absorption into the metal, and makes the overall measured kinetics more reproducible.

The purpose of the present study is to understand the dependence of the rate of H uptake by Ce on the nature of the surface oxide layer and the effect of vacuum annealing on this surface oxide layer. This short report addresses the kinetics of H uptake by two commercial Ce samples, bulk pieces and 2.54-mm thick foils, with surfaces that were characterized using X-ray photoelectron spectroscopy (XPS).

2. Experimental

Bulk Ce samples (~2 cm^3) were provided by Santoku America (Tolleson, Arizona) and 2.54-mm thick foils were provided by Alfa-Aesar (Ward Hill, Massachusetts). Both had a stated rare-earth metal purity of 99.9%. The samples were packed in Ar gas. All sample preparation (e.g., cutting into ~0.5-g pieces) was performed inside an Ar glovebox with O_2 and H_2O concentrations below 3 ppm. Research-grade (99.99995% pure) H_2 gas (Air Liquide, LaPorte, Texas) was supplied from the cylinder without further purification.

A Sieverts'-type apparatus was used for the H uptake experiments. Ancillary equipment included a compact gas delivery manifold (Celerity), a 1.27-cm diameter quartz-tube reactor, capacitance manometer pressure transducers (MKS Instruments), and an oil-free turbomolecular pumping system (Varian). For a typical H uptake experiment, a Ce sample (0.2–0.5 g) was placed inside a thin W crucible, which was then located inside the quartz-tube reactor. The sample temperature was measured with an Au-plated 1.6-mm diameter type-K thermocouple located inside the quartz tube and in contact with the W crucible. A background pressure of $<10^{-6}$ Torr was readily attainable by pumping the system. After evacuating the tube, a quantifiable amount of H_2 gas was

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* Corresponding author. Tel.: +1 505 667 0626; fax: +1 505 665 4849.
E-mail address: hbach@lanl.gov (H.T. Bach).

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admitted into the reactor and allowed to equilibrate before opening the valve to the sample. The subsequent decrease in pressure due to the H uptake by the Ce was recorded versus time until the pressure reached a constant value, typically in the sub-millitorr range. From the rate of pressure decrease, the amount of H gas absorbed by the metal was calculated as a function of time. The results were normalized to the constant value measured at a sufficiently long time when equilibrium was reached to yield a reacted fraction, α. These tests were performed on as-received foil and bulk Ce that had been cut into smaller samples with or without vacuum annealing in the reactor. Initial H_2 aliquot pressures were in the range of 50–500 Torr, and temperatures from 298–323 K.

All XPS spectra were taken with a Kratos Axis-Ultra system. A monochromatic Al Kα X-ray (1486.7 eV) source was used for all scans. A pass energy of 40 eV was used to discern the various chemical states of the species of interest. The Ce samples were vacuum annealed on an analysis stage, which is capable of reaching a temperature of 873 K. The background pressure in the system was approximately 10^{-10} Torr. During vacuum annealing, pressures would rise to as high as 10^{-7} Torr for brief periods. Residual gas analysis (RGA) revealed the majority of the gas to be H.

A Ce bulk or foil was loaded into an airtight sample transfer container inside an Ar glovebox and transferred to the XPS station load lock. The as-received or freshly cut surfaces of the Ce samples were examined before, during, and after *in situ* vacuum annealing in the XPS system. During vacuum annealing, the sample stage was heated to a specified temperature in UHV ($<10^{-9}$ Torr). XPS spectra were recorded initially and in 10-min intervals at each temperature.

3. Results and discussion

3.1. Hydriding kinetics

The hydriding kinetics of the as-received (not vacuum annealed) bulk and foil Ce samples are shown in Fig. 1, measured at 298 K and a starting H_2 aliquot pressure of approximately 50 Torr. Details of the H absorption experimental parameters are summarized in Table 1. The bulk Ce sample clearly has faster H absorption kinetics than the foil. The Ce hydriding reaction consists of four distinct stages: (a) initial rapid uptake of a small amount of H, (b) an induction stage, (c) a nucleation and bulk reaction stage characterized by steadily increasing and then linear uptake, and (d) a period during the end of absorption where the reaction slows down considerably [3,6]. The small initial uptake of H by the Ce bulk seen in the inset in Fig. 1 may be due to H interaction with the O and C sorption layer on the surface. H may quickly come into equilibrium with the surface with the formation of hydroxyl or carboxyl groups.

The inset in Fig. 1 shows that the overall induction period for both Ce bulk and foil lasted approximately 1.5 h before the beginning of the linear stage of H absorption. This induction period may be attributed to the transfer of H atoms from the gas phase through the surface oxide layer leading to nucleation and growth of hydride spots at the surface or near the surface region [7].

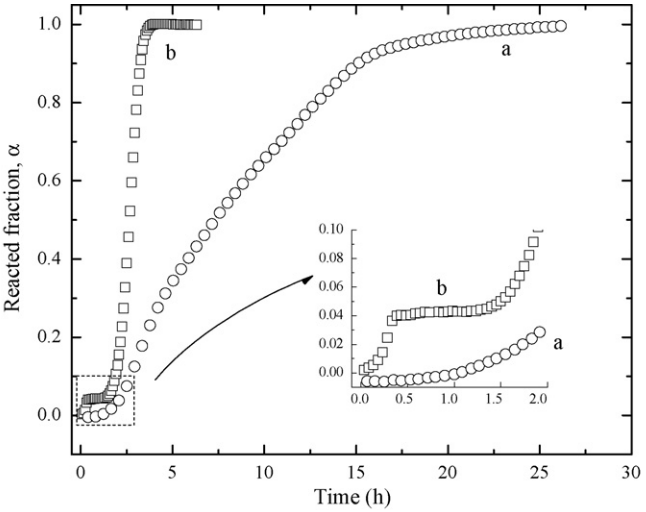

Fig. 1. Hydriding kinetics of as-received Ce foil (a) and as-received cerium bulk (b) at 298 K with a 50 Torr aliquot of H_2. The inset is a magnification of the induction period.

The mechanism for initial hydride nucleation seemed to be different for the bulk and the foil (see Fig. 1 inset). Different oxide layers present on both the as-received bulk and foil samples probably served as a barrier to penetration of H atoms from the gas phase into the metal, leading to a slow initial build-up of H in the metal and delaying the onset of hydride nucleation.

At the stage where a continuous hydride layer advances into the metal, a faster bulk reaction rate is observed (Fig. 1) for the Ce bulk in comparison to the foil under the same experimental conditions. The rate-determining step of this reaction has been studied [8]. However, since the geometrical shape (and surface area) of the bulk and foil are not the same, the comparison in this study is only qualitative. In the case of the Ce foil, which had freshly cut surfaces along its edges, the changing velocity front with time can be referred to as the edge-preferred attack where the surface area of the hydride–metal interface is much smaller than the contracting envelope case observed for the Ce bulk [8]. This may explain the slower reaction rate of the foil compared to the bulk during the linear region of H uptake. The foil, which was examined after the reaction, had very ragged edges indicating that the nucleation probably started from these freshly cut edges and the reaction front advanced toward the center of the foil.

In addition to the properties of the oxide layer, the reaction pressure and temperature also affected the H absorption rate. The hydriding kinetics of several as-received and vacuum annealed

Table 1
Experimental parameters for H absorption data presented in Figs. 1 and 2

H absorption curve	Sample type	Annealing temperature (K)	Reaction temperature (K)	H_2 aliquot pressure (Torr)	Final [H]/[Ce]
a	Foil	No anneal	298	50	0.173
b	Bulk	No anneal	298	50	0.185
c	Bulk	No anneal	298	380	1.778
d	Bulk	No anneal	323	50	0.326
e	Bulk	773 (4 h)	298	50	0.366
f	Foil	773 (20 h)	323	50	0.304

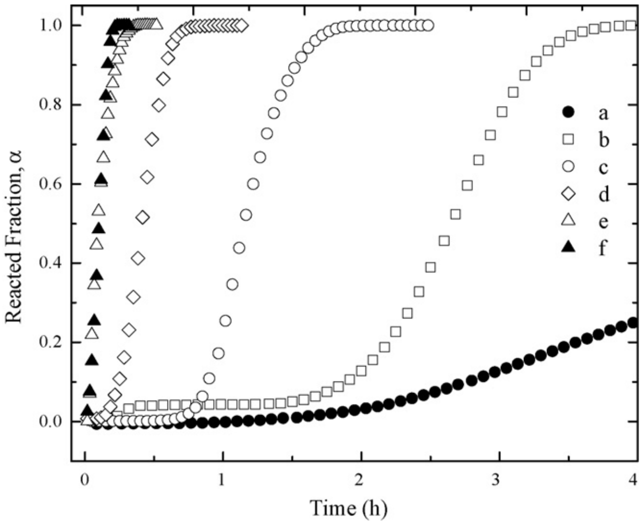

Fig. 2. H uptake curves for as-received and vacuum annealed Ce foils and bulks at various temperatures and starting H-aliquot pressures. Experimental conditions for curves a–f are listed in Table 1.

Ce bulks and foils at 298 and 323 K under 50 Torr or 380 Torr H_2 are displayed in Fig. 2. The experimental parameters are summarized in Table 1. Reduced induction times and increased bulk reaction rates were observed with increasing aliquot pressures or reaction temperatures, and after vacuum annealing.

3.2. XPS analysis

The oxidation of Ce metal has been shown to proceed through the formation of Ce_2O_3 at low O exposure [4], followed by the formation of CeO_2 at higher O exposures [9]. Before annealing, the Ce 3d spectra of as-received Ce foil had six peaks (*A, B, C, D, E, F*) corresponding to three pairs of spin–orbit doublets (Fig. 3b) while that for the freshly cut surface of a Ce bulk had two pairs of doublets (*A, B, C, D*) (Fig. 3a). These pronounced characteristics of the Ce 3d spectra are associated with the presence of CeO_2 on the surface of the as-received Ce foil and Ce_2O_3 on the freshly cut Ce bulk [10–12]. These spectra are consistent with those reported previously for a fully oxidized CeO_2 [1 1 0] single crystal film and an oxidized and annealed Ce_2O_3 foil [13].

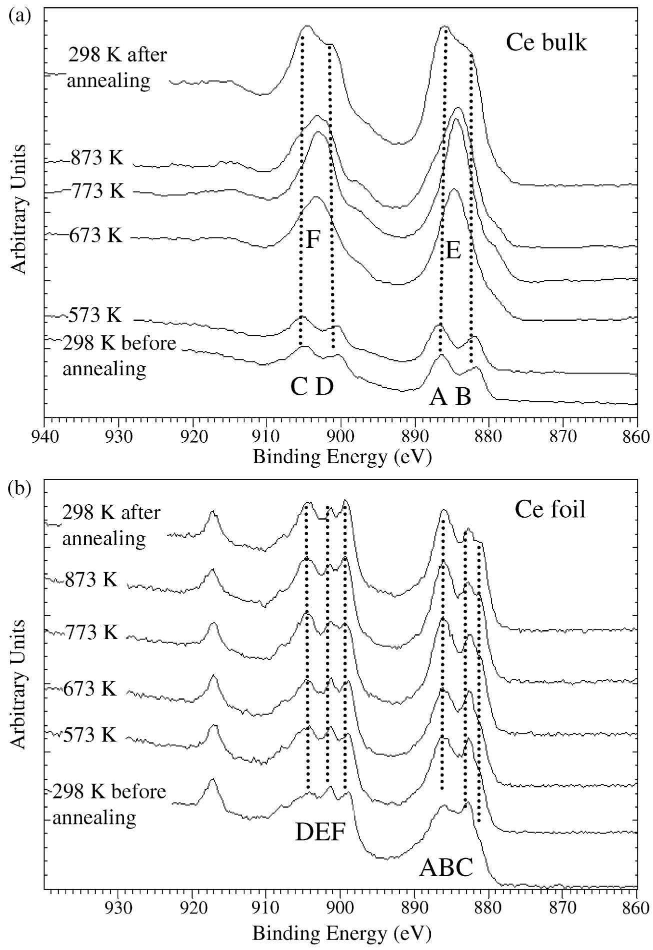

Fig. 3. XPS spectra of the Ce 3d level of Ce bulk (a) and Ce foil (b) at 298 K before vacuum annealing, after 10 min at different annealing temperatures, and at 298 K after vacuum annealing. Dashed lines are for visual guidance.

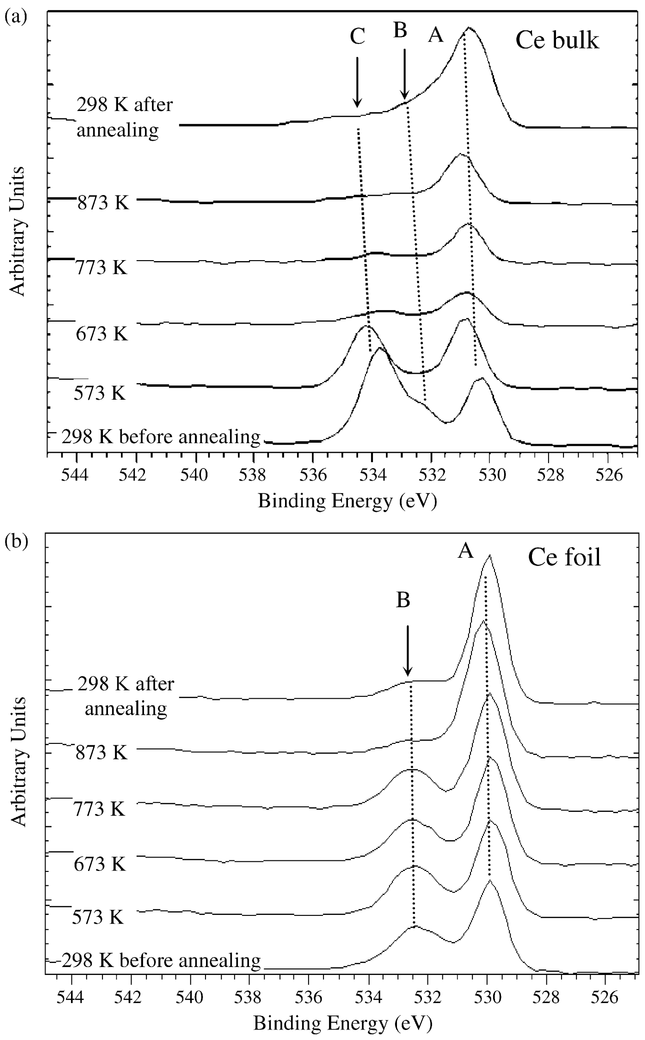

Fig. 4. XPS spectra of the O 1s level of Ce bulk (a) and Ce foil (b) at 298 K before vacuum annealing, after 10 min at different annealing temperatures, and at 298 K after vacuum annealing. Dashed lines are for visual guidance.

The O 1s spectra of the surfaces of the freshly cut Ce bulk (Fig. 4a) and the as-received Ce foil (Fig. 4b) reveal the presence of three types of surface O. The peak *A* at 530 eV is associated with the metallic oxides: CeO_2 (foil) and Ce_2O_3 (bulk). The peak *B* at 532 eV could be assigned to surface-adsorbed O. The peak *C* at 534 eV is tentatively attributed to a combination of a number of species, including surface hydroxyl groups [14], adsorbed water, and molecular O species (peroxides, superoxides) [12,15–17]. The relative proportion of these three types of O depends on the sample treatment history or surface preparation. The data suggests that there is more O in the form of hydroxyl groups and less surface-adsorbed O on the surface of the freshly cut bulk sample than on the as-received foil sample.

During vacuum annealing of the Ce bulk, O appears to have dissolved into the bulk metal at 673 K (Fig. 4a) so that the surface region possessed increased metallic character at 673 K, peaks *E* and *F* in Fig. 3a, and C were simultaneously converted into carbides (spectra not shown). This made the surface of the vacuum annealed bulk sample more reactive towards H than the vacuum annealed foil. The CeO_2 on the foil was reduced slightly, peaks *B* and *E* in Fig. 3b, during vacuum annealing as evidenced by the growth of the Ce_2O_3, peaks *A* and *D* in Fig. 3b. Moreover, annealing eliminated most of the hydroxyls from the surface of the bulk sample at 673 K (Fig. 4a) and surface-adsorbed O from the surface of the foil at 873 K (Fig. 4b). However, it is difficult to determine if the change in the state of the surface oxide was a result of vacuum annealing or X-ray exposure [16]. Because the C on the foil appeared to be chemically unchanged during annealing, the formation of Ce_2O_3 and potential microcracks in the surface CeO_2 layer could explain the increased surface activity towards H absorption.

4. Conclusions

In the beginning stage of hydride nucleation, a Ce bulk exhibited a faster rate of H uptake than a Ce foil. XPS analysis showed that the Ce bulk was covered with Ce_2O_3 and hydroxyls, whereas the foil was covered primarily with CeO_2 and surface-adsorbed O. Ce_2O_3 apparently presents a smaller barrier to H absorption than CeO_2. Additional H uptake experiments demonstrated that higher reaction temperature, pressure, and higher vacuum annealing temperature reduce the induction time for H absorption in Ce and increase the bulk reaction rate.

From XPS spectra, reduction of the surface oxide on a freshly cut Ce bulk from Ce_2O_3 to Ce_2O_{3-x} began at 673 K whereas the state of the surface CeO_2 on an as-received Ce foil was only slightly changed after annealing in UHV at 873 K for 2 h. Nevertheless, both Ce bulks and foils exhibited shorter induction periods and faster reaction rates when they were vacuum annealed compared with samples without vacuum annealing.

The influence of surface O and C compounds on H uptake kinetics requires further examination to gain a complete understanding. Continuing studies on samples with well-defined surface areas and O coverage will allow better understanding of the surface changes that occur during vacuum annealing and the subsequent effect on hydriding kinetics.

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