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Corrosion characteristics of $LiBH_4$ film exposed to a $CO_2/H_2O/O_2/N_2$ mixture

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ABSTRACT

$LiBH_4$ films were prepared by pulsed laser deposition using a LiB target in a background pressure of hydrogen. The corrosion characteristics of $LiBH_4$ films were measured by exposing them to a gas mixture of $CO_2/H_2O/O_2/N_2$ at ambient temperature for 1–24 h. Scanning electron microscopy images show some cracks on the surface of corrosion films, which could act as easy paths for H_2O and CO_2 to further react with Li^+ and B^{3+}. The X-ray photoelectron spectroscopy results and theoretical analysis show that $LiBH_4$ tends to react with H_2O and CO_2 to form $Li_2B_4O_7$, Li_2CO_3 and LiOH during the corrosion process.

1. Introduction

$LiBH_4$ consists of low atomic number elements, with high hydrogen content and low density [1–3]. It has drawn considerable interests as a candidate material in the laser inertial fusion. Up to now, most investigations have focused on the synthesis of $LiBH_4$ powders or bulk material, which could be used in the catalysis field [1–4]. Comparatively, the reports on $LiBH_4$ films are relatively few. $LiBH_4$ films are of considerable interest due to their intrinsic chemical and physical properties. In certain cases, it may be desirable to preserve the film structure, giving rise to a variety of important technological applications.

On the other hand, during the synthesis, storage, packaging, device fabrication, and in service, $LiBH_4$ films are inevitably exposed to various environmental conditions such as atmosphere, elevated temperatures, moisture, and oxidizing media. Thus there occurs a new questionnaire, including measures of important influence of exposure of $LiBH_4$ to a certain ambient on structural, chemical and physical properties due to its a gas-sensitive chemically active media, which would adversely affect the performance of the devices [5,6]. The oxidation and corrosion resistances are required in some applications of $LiBH_4$, such as batteries, a neutron/energy capturing blanket in fusion reactors, and for hydrogen storage [4]. To our knowledge, studies on the corrosion characteristics of other materials, such as LiH [7–11], CaH_2 [12], have extensively reported in terms of versatile applications. However, there are few reports on the corrosion characteristics of $LiBH_4$, which might be very essential for developing application fields of $LiBH_4$.

The aim of this paper is to introduce a simple method to generate $LiBH_4$ films and study the corrosion characteristics of them. The films were prepared by pulsed laser deposition (PLD) from a LiB target under a low hydrogen pressure of 70 Pa at ambient temperature. The effects of exposure to a gas mixture of $CO_2/H_2O/O_2/N_2$ on the structural and chemical properties of $LiBH_4$ films were investigated at ambient temperature for 1–24 h. Besides, a corrosion mechanism of $LiBH_4$ films for exposing to the ambient environment is discussed in detail.

2. Experimental details

The PLD system has been described in detail in our previous paper [13]. The LiB target with the B/Li mol ratio of 0.25 was provided by the General Research Institute for Nonferrous Metals in Beijing. The LiB target with the optimum distance of about 50 mm away from the substrates was rotated during the ablation process to reduce the possible nonuniform erosion. NaCl(1 0 0) and Si(1 0 0) substrates were used to facilitate the Fourier transform infrared (FT-IR) spectrometry and other measurements of the films, respectively. Hydrogen (99.99% purity) gas was supplied into the chamber at a flow rate of 5 sccm. The films were deposited in the background pressure of $\sim 6 \times 10^{-5}$ Pa and experimental pressure of $\sim$70 Pa. Plasma was produced between the substrates and the LiB target by a focused KrF (248 nm) laser with a energy density

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of ~0.5 J cm^{-2} and a repetition rate of 2 Hz. The as-deposited $LiBH_4$ films were exposed to a gas mixture of $CO_2/H_2O/O_2/N_2$ (their percentages were approximately fixed at 15%, 15%, 20%, and 50%, respectively) for 1–24 h. All the employed gases have the purity of about 99.99%.

Structural characterizations and bonding configurations of the films were performed by X-ray diffraction (XRD, Cu K_α radiation, the angle of incidence was 0.5°), Fourier transform infrared and Raman spectra, respectively. The surface morphologies of the films were analyzed by scanning electron microscopy (SEM). The composition of samples was characterized by X-ray photoelectron spectroscopy (XPS) using Al K_α (1486.6 eV) radiation as an X-ray source with a voltage of 12 kV and a power of 240 W at a pressure of $\sim 1 \times 10^{-9}$ Torr. The takeoff angles of the electron emission ranged between 40° and 50° counted from normal to the surface. The samples were analyzed after sputter cleaning by a 3 keV Ar^+ beam for 45 s. All energy positions were adjusted by fixing the binding energy of the C 1s peak to 284.8 eV [14] to compensate the charge effect in the XPS measurement. X-ray fluorescence (XRF) was one of the most popular spectroscopic techniques in elemental identification and quantification [15–19]. To obtain further information of the elements map, the synchrotron X-ray fluorescence (SXRF) microprobe was also employed at the Shanghai Synchrotron Radiation Facility (SSRF). It was carried out at the BL15U1 beam line of SSRF. In view of a higher absorption cross section and in order to excite a maximum element signal, the excitation energy was kept at 11 keV and the beam current was fixed at 157 mA. Optical path was operated in the background pressure of ~100 Pa to reduce the fluorescence signal attenuation of low Z elements. Elemental information on Li and O was not obtained by SXRF. The data of B and C element was collected at high excitation energy. The sampling time for each data point was a constant value of 20 s. The spatial resolution of the element distribution maps was kept at 500 μm.

3. Results and discussion

3.1. The structure of the $LiBH_4$ films

Fig. 1a shows the FT-IR absorption spectra of the as-deposited $LiBH_4$ films. The peaks at around 1240, 1640, 2268, 2325 and 2355 cm^{-1} are attributed to vibration modes of $LiBH_4$. Moreover, the peaks at around 900 and 2500 cm^{-1} confirm the existence of the intermediate compound $Li_2B_{12}H_{12}$ [13,20]. Fig. 1b presents the Raman spectra of the films. The peak at around 2300 cm^{-1}, deriving from B–H bending modes of $LiBH_4$, is observed. Additionally, the strong peaks in the range of 500–1000 cm^{-1} and around 2500 cm^{-1}, attributed to the B–H bending and stretching modes of the intermediate compound $Li_2B_{12}H_{12}$, respectively, indicate much $Li_2B_{12}H_{12}$ in the films. Our Raman results are in good agreement with the previously reported results [1]. A typical polycrystalline phase is observed from XRD pattern of as-deposited $LiBH_4$, as shown in Fig. 1c. The peaks of (1 0 2), (1 1 0), (1 1 1), (1 1 3), (2 1 1) and (3 0 0) etc., corresponding to crystalline $LiBH_4$ phase [13], are clearly observed. And no diffraction peaks of $Li_2B_{12}H_{12}$ are found in Fig. 1c, indicating $Li_2B_{12}H_{12}$ is not well-crystallized in our films. The XRD results are consistent with that reported by Orimo [1]. It indicates that polycrystalline $LiBH_4$ films with amorphous $Li_2B_{12}H_{12}$ can be prepared by PLD with the background gas of H_2.

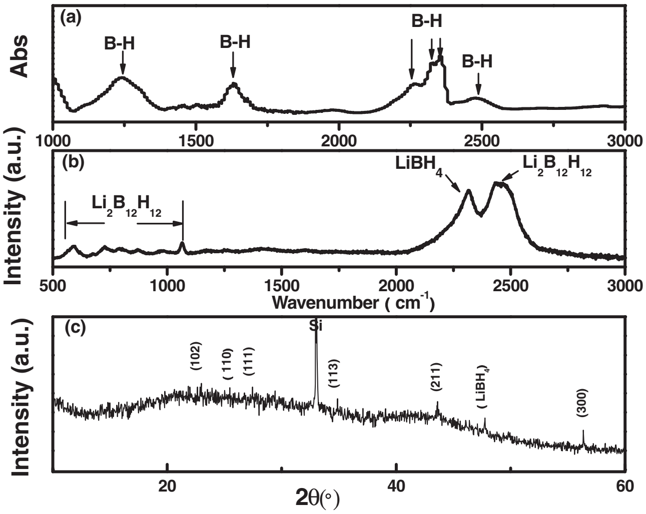

Fig. 1. (a) FT-IR absorption spectra, (b) Raman spectra and (c) XRD pattern of the as-deposited $LiBH_4$ films.

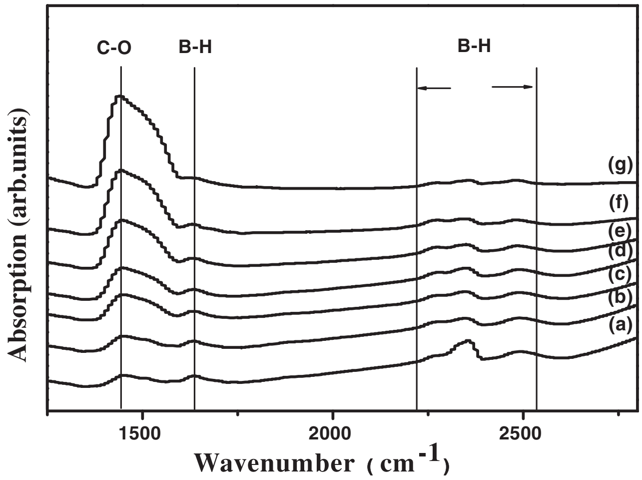

Fig. 2. FT-IR absorption spectra of the $LiBH_4$ films after exposure to the mixture gas of $CO_2/H_2O/O_2/N_2$ at various time of (a) 0 h, (b) 1 h, (c) 2 h, (d) 3 h, (e) 4 h, (f) 5 h, and (g) 24 h.

3.2. The corrosion results of the $LiBH_4$ films

Fig. 2 presents the FT-IR absorption spectra of the $LiBH_4$ films after exposure to the mixture gas of $CO_2/H_2O/O_2/N_2$ with various lengths of time. As shown in Fig. 2a, the absorption peaks around

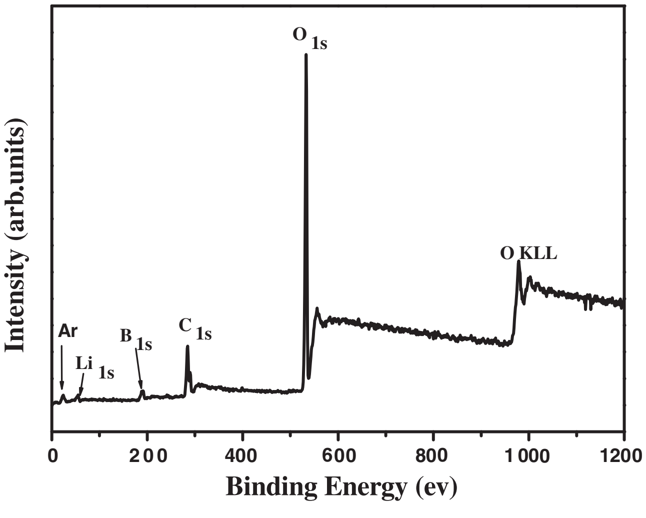

Fig. 3. XPS survey spectra of the $LiBH_4$ films with the exposure time of 5 h.