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Ab initio study of beryllium surfaces with different hydrogen coverages

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ABSTRACT

The effect of hydrogen concentration on principal hexagonal close-packed beryllium surfaces (basal, prismatic type I and II, pyramidal type I and II) at 0 K was studied with the help of *ab initio* methods. The configurations with critical hydrogen coverage were revealed. Relaxation of outermost atomic layers at critical coverage drastically differs from that found for clean beryllium surfaces. The presence of hydrogen atoms significantly changes the energy of all studied beryllium surfaces except for prismatic type II plane. Influence of hydrogen concentration on equilibrium shape of hydrogen covered voids was investigated by means of construction of Wulff polyhedra. In addition we generalized Gibbs-Wulff approach for accounting of different hydrogen coverages at crystallographic non-equivalent surfaces and temperature effect. The results of the construction were compared with classical Gibbs-Wulff approach as well as the available experimental data on ion or neutron irradiation at elevated temperatures.

1. Introduction

Beryllium has a number of remarkable physical properties. Being very light and possessing high hardness, beryllium is commonly used as an alloy component for aerospace and aircraft industry to increase alloys' strength, fatigue and corrosion resistance, anti-galling characteristics etc [1–3]. In nuclear industry beryllium is widely used as neutron reflector and moderator [4].

Light chemical elements (Be, Li, Mg and Al) are preferable for maximization of hydrogen storage per unit mass [5–8]. Therefore various beryllium compounds are studied as prospective hydrogen storage materials [9–13]. Consequently, theoretical study of various mechanisms of hydrogen trapping in metals is important for practical realization of hydrogen driven vehicles [14].

Besides impurities, hydrogen can be trapped by intrinsic defects in metals such as vacancies, dislocations, grain boundaries and pores [15]. Fukai and co-workers have shown experimentally that for some metals loaded with hydrogen at high temperature and pressure anomalously high vacancy concentration of about 10 at.% was observed. They found that for metals with low vacancy formation energy this process usually results in formation of metal hydrides with high hydrogen gravimetric density, which is important characteristic of candidate materials for hydrogen storage.

The second light metallic chemical element, beryllium, with its vacancy formation energy as low as 0.8 eV [16] could be by far one of the most encouraging metals for these applications. However, relatively high binding energy of hydrogen with vacancy (~ 1.3 eV) [16] suggests somewhat higher temperature (~ 300 °C) of its release than would be economically desirable for hydrogen storage (~ 200 °C, see Ref. [5]). Multiple hydrogen occupation of vacancy is possible and results in a gradual decrease of the binding energy with increase of the number of trapped hydrogen atoms [16]. Nevertheless, complete hydrogen release (de-trapping of the last most bound hydrogen atoms within a vacancy) is possible only at higher temperature.

It is well established that at elevated temperatures gaseous atoms in metal promote formation of gas bubbles [17–20]. Such temperatures are relevant for beryllium applications in fusion technology as plasma facing [21] and neutron multiplier material in tritium breeding blanket [22,23]. Above 500 °C vacancies are mobile in beryllium and gather into gas-vacancy clusters giving rise to growth of gas bubbles [24]. Experiments on deuterium and tritium desorption have shown that deeper traps than vacancies should exist in beryllium, which are most probably gas bubbles, according to commonly accepted view [25–27]. It is, however, not clear presently whether hydrogen is trapped in the elastic field near gas

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bubble, at its surface or within bubble as molecule. Understanding of deep hydrogen trapping in irradiated beryllium is necessary for evaluation of residual tritium inventory accumulated in beryllium pebbles after the end of life of fusion reactor blanket. Such assessment is important for preventing burst release of trapped tritium due to plasma excursions to the first wall as well as for proper handling of radioactive wastes during decommissioning of the fusion blanket.

Therefore this work is devoted to one of the important mechanisms of hydrogen trapping on the surface of voids, in particular, to clarification of the effect of hydrogen interaction with pure beryllium surface including relaxation of the near-surface interlayer distances and the change of surface energies causing modification of the shape of hydrogen covered voids.

Hydrogen interaction with metal surface is an important issue for development of catalysts, which are often composed of nanoparticles spread over a support material [28–30]. It is commonly assumed that a shape of nanoparticles is described in asymptotic limit of thermodynamical equilibrium by the Wulff construction and presence of gas results in a change of surface energy only. It should be, however, noted that the equilibrium surface concentration of gas atoms is different for various closed packed surfaces even within one bubble. Moreover, in case of not completely covered surfaces, their configurational entropy should be also taken into account.

Both experimental studies [31,32] and previous *ab initio* calculations [33–36] show that the presence of hydrogen atoms considerably affects beryllium surface properties. Significant interplanar relaxation of the outermost atomic layers accompanied with the change of the structural and energetic characteristics occurs with increase of hydrogen coverage [36–45]. However, majority of the available *ab initio* studies are considering basal and prismatic type I surfaces only. In order to investigate the effect of hydrogen isotopes on the equilibrium shape of bubbles, information related to the energetics of other principal hcp beryllium surfaces with and without hydrogen is necessary.

In this paper, we start with *ab initio* study of critical hydrogen coverages on five principal beryllium surfaces. Then we consider effect of hydrogen concentration on surface energies and interplanar relaxation of the outermost surface layers. These results are used for construction of the equilibrium shape of voids covered with hydrogen. Two cases are considered: the same and different hydrogen concentration at different surfaces. Thereafter we compare our calculated equilibrium shapes with available experimental results on neutron irradiation or hydrogen implantation.

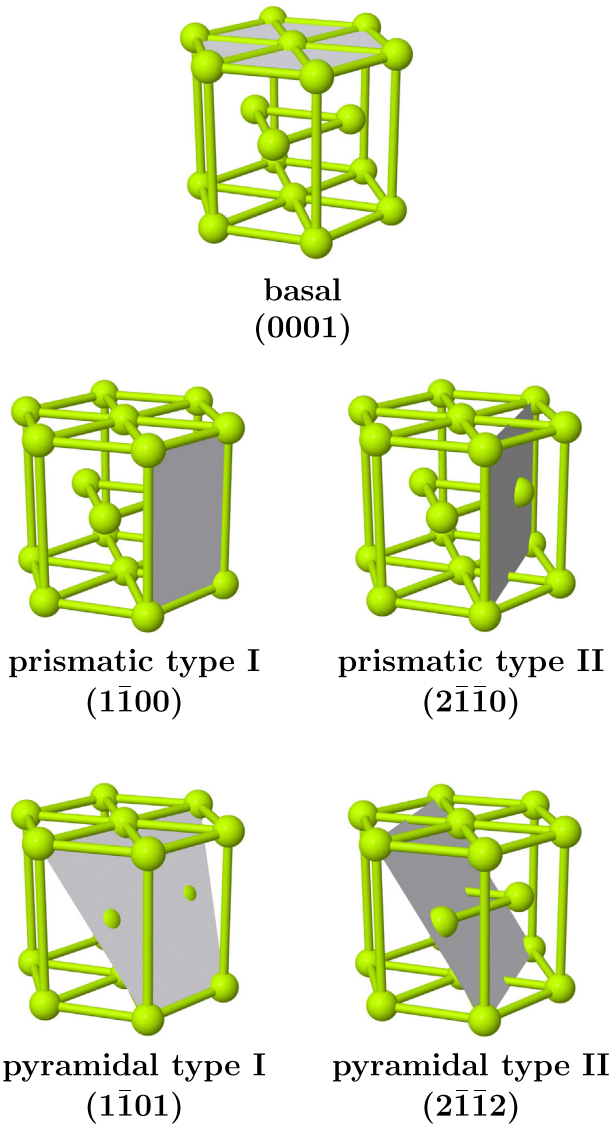

Fig. 1. Principal hcp crystallographic planes shown in unit cell.

2. Computational methods

Static first-principles calculations were performed using the Vienna *ab initio* simulation package (VASP) [46,47]. The pseudopotential based on the projector augmented wave (PAW) method was used to describe the interactions between ions and electrons. The generalized gradient approximation (GGA) of Perdew and Wang [48] was employed for calculation of the exchange-correlation energy. Corresponding standard pseudopotentials for beryllium (with two valence electrons) and hydrogen were taken from the VASP library [49,50].

The effect of hydrogen on surface energies was investigated for five principal close-packed beryllium planes: basal (0001), prismatic type I (1$\bar{1}$00) and prismatic type II (2$\bar{1}\bar{1}$0), pyramidal type I (1$\bar{1}$01) and pyramidal type II (2$\bar{1}\bar{1}$2) (see Fig. 1). Prismatic type I and pyramidal type I surfaces can be terminated in two possible ways. We have considered only the most stable and energetically favorable "short" termination as suggested in Refs. [39,44]. As far as periodical boundary conditions are implied by VASP, an empty space of 17–23 Å (equivalent to four atomic layers) should be introduced into the simulation cell to avoid interaction between the top and the bottom of crystal bounded by closed packed planes being studied. The volume and the shape of the simulation cell were fixed, while no restrictions on the relaxation of atoms were imposed. The optimized lattice constants for bulk material were $a = 2.265$Å and $c = 3.562$Å. A Fermi smearing of 0.2 eV and the cut-off energy of the plane waves of 450 eV were chosen. The tolerance for electronic self-consistency step was set to be 0.01 eV and for ionic relaxation was stopped when forces were smaller than 0.01 eV/Å. The *k*-point mesh was different for crystallographic non-equivalent surfaces and presented in Table 1. The atomic structures were visualized using the program Jmol [51].

The surface area of the simulation cell was chosen large enough to avoid interaction of hydrogen with its periodical images at low hydrogen concentrations. At high hydrogen coverage such interactions are inevitable corresponding to the case of an infinite surface (see Table 1). Initial configurations for various coverages were constructed by addition of hydrogen atoms placed pairwise