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Phase stability and mechanical properties of niobium dihydride





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ARTICLE INFO

Article history: Received 13 July 2014 Received in revised form 30 August 2014 Accepted 3 September 2014 Available online 5 October 2014

Keywords: Niobium dihydride Phase stability Mechanical properties First-principles calculation

ABSTRACT

First-principles calculation shows that the NbH_x phases ($1 \le x \le 2$) with face-centered cubic (FCC), orthorhombic (FCO), and tetragonal (FCT) modifications are all energetically favorable with negative heats of formation, while FCC NbH₁ and NbH_{1.25} could not be formed due to their mechanical unstableness. It is also revealed that FCT and FCO could coexist in NbH₁ and NbH_{1.25}, FCC and FCT coexist in NbH_{1.5} and NbH_{1.75}, while only FCC in NbH₂. Calculations also indicate that the magnitude of the elastic moduli of NbH_x phases at each H concentration is as follows: E > B > G, and the *G*, *E*, and *G*/*B* values of NbH_x phases reach a minimum when x = 1.5. Moreover, electronic structures are discussed to provide a deep understanding of various properties, and the derived results are in good agreement with similar experimental evidence in the literature.

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Introduction

The metal niobium and its hydrides have attracted great research interests during the past decades [1–13]. On the one hand, Nb is well regarded as one of the most promising materials for hydrogen separation and purification as it possesses much higher hydrogen permeability and lower price than various Pd alloys [1–3]. Furthermore, Nb and its alloys have been extensively used in hydrogen-related high-temperature structural applications such as ITER divertor and nuclear fuel cladding, due to good corrosion resistance, very high melting point, excellent mechanical properties, and small cross section of neutron absorption, etc. [4–7]. In addition, niobium and its hydrides are commonly believed as one of the important superconductors with superior and unique superconducting properties [8–10].

It is well-known that the niobium dihydride NbH_x ($1 \le x \le 2$) has several possible modifications, e.g., the facecentered orthorhombic phase (FCO, β phase) [13–15], facecentered cubic structure (FCC, δ phase) [8,13,14,16,17], and face-centered tetragonal structure (FCT, γ phase) [10,13,18]. Nevertheless, the concentrations and stability of these phases are still ambiguous to the materials society, as their phase boundaries in the current Nb–H phase diagram are shown as dashed lines [10,13]. In addition, the β and δ NbH_x phases have been extensively discovered by various experimentalists in the literature [8,13–17], while the γ phase has not yet been confirmed experimentally [10,13,18]. Further essential investigations are therefore needed to verify the phase stability of NbH_x (1 \leq x \leq 2).

Regarding mechanical properties of various niobium dihydrides, there are only several experimental investigations in the literature [10,19–22]. It is well recognized that both β and δ structures of niobium dihydride are very brittle, while the magnitude of brittleness as well as the detailed elastic properties of NbH_x (1 \leq x \leq 2) phases have not been reported in

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http://dx.doi.org/10.1016/j.ijhydene.2014.09.033

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Fig. 1 – Schematic picture of the FCC unit cell of the NbH_x $(1 \le x \le 2)$ phase. The small spheres lettered $a \sim h$ stand for H atoms located at the tetrahedral interstitials of the FCC lattice.

the literature. Moreover, the effects of crystal structure and H concentration on mechanical properties of niobium dihydride are still unclear, and the intrinsic mechanism of H brittleness is in need of fundamental clarification.

Before various applications of niobium dihydrides, it is of vital importance to investigate the NbH_x phase systematically at an electronic scale. By means of highly accurate first principles calculation, the present study is therefore dedicated to investigate the phase stability, mechanical properties, and electronic structures of the FCC NbH_x (δ phase) within a wide concentration range ($1 \le x \le 2$). Meanwhile, two other possible structures, i.e., FCT (γ phase) and FCO (β phase), are also calculated to have a direct comparison with the FCC structure. The derived results will be compared with available experimental evidence in the literature, and the fundamental mechanism will be discussed in terms of electronic structures, which could provide a deep understanding of the relationship between structures and properties of niobium dihydrides.

Calculation methods

The present calculation is executed by means of the wellestablished Vienna *ab* initio simulation package (VASP) within the density functional theory [23], and is conducted by the projector-augmented wave (PAW) method with a planewave basis [24]. The exchange and correlation terms are described by generalized gradient approximation (GGA) of Perdew et al. [25], and the cutoff energies are 350 eV for plane wave basis. For *k* space integration, the first order smearing method [26] and the modified tetrahedron method [27] are used for dynamical and static calculations, respectively.

In the present study, a unit cell of 4 Nb atoms with the FCC structure is used as the starting structure for the NbH_x phase and a series of H atoms are added at the tetrahedral interstitial

sites of the FCC unit, i.e., the additions of 4, 5, 6, 7, and 8H atoms stand for the NbH₁, NbH_{1.25}, NbH_{1.5}, NbH_{1.75}, and NbH₂ stoichiometries, respectively. At each concentration, all possible configurations of H atoms are considered and the total energy of each configuration is calculated as a function of atomic volume, in order to find out the optimized lattice constants. For the crystal structure, Fig. 1 shows the schematic illustration of the FCC unit cell of the NbH_x ($1 \le x \le 2$) phase, and the H atoms at the tetrahedral sites are purposely lettered to provide a clear description of various atomic configurations.

For obtaining the FCT structures, the original c/a value of 1 for each FCC NbH_x (δ phase) is varied from 0.70 to 1.20 with an interval of 0.02, in order to find out the local minima of total energy corresponding to the FCT structure. Similarly, the FCO structure at each H concentration is derived through the variation of the c/a and b/a ratios.

After a series of test calculations, the k-meshes of $11 \times 11 \times 11$ and $13 \times 13 \times 13$ are selected for relaxation and static calculations of all the five NbH_x stoichiometries, respectively. During each calculation, the crystal structure of the unit is kept fixed, and periodic boundary conditions are added in three directions of the unit cell. The energy criteria for electronic and ionic relaxations are set to be 0.01 and 0.1 meV, respectively, while 0.001 meV for static calculations of density of states (DOS) and elastic constants.

Results and discussion

Phase stability

After a series of calculation, the lattice constants of the FCC, FCT, and FCO NbH_x phases with various possible H configurations are calculated, respectively, and the derived values are summarized in Table 1. Moreover, the experimental lattice parameters of niobium dihydrides available in the literature are also included for the sake of comparison [8,19,28,29]. It should be indicated that the combination of the letters ($a \sim h$) in Fig. 1 is used to express the atomic configuration of H, e.g., the symbol of (*abcd*) for the FCC NbH₁ phase means that the 4H atoms are at the tetrahedral interstitial sites of *a*, *b*, *c*, and *d* shown in Fig. 1, respectively.

From Table 1, it could be seen clearly that FCC is derived for all the five NbH_x phases, while FCT and FCO modifications are not obtained for the NbH_2 phase, and no FCO for $NbH_{1.5}$ and $\rm NbH_{1.75}.$ The stability of these phases will be further discussed in Sec. Mechanical properties. One can also observe from Table 1 that the calculated lattice parameters from the present study are in good agreement with corresponding experimental data in the literature [8,19,28,29]. For instance, the present lattice constant of the FCC phase is 4.580 Å, which matches well with the experimental values of 4.53 and 4.56 Å [8,19,28] with an error of less than 1%. In addition, the lattice constants of each modification (FCC, FCT, and FCO) of NbH₁, NbH_{1.25}, and NbH_{1.5} phases with various H atomic configurations are very close to each other, suggesting that the atomic configuration of H has only a very small effect on lattice constants of NbH₁, NbH_{1.25}, and NbH_{1.5}.

The atomic volumes of various niobium dihydrides are calculated, and the derived values are shown in Fig. 2. It could

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