

**ДИФФУЗИОННЫЕ БАРЬЕРЫ АТОМА ВОДОРОДА В γ -ГИДРИДЕ ЦИРКОНИЯ:
РАСЧЕТЫ ИЗ ПЕРВЫХ ПРИНЦИПОВ**

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DIFFUSION BARIERS OF HYDROGEN ATOM IN ZIRCONIUM γ -HYDRIDE:

FIRST PRINCIPLE CALCULATIONS

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В работе представлены результаты первопринципных расчетов диффузионных барьеров атома водорода в γ -гидриде циркония. Вычисления проводились в рамках теории функционала электронной плотности линеаризованным методом присоединенных плоских волн. Показано, что водород в γ гидриде циркония диффундирует преимущественно по пути тетрапоро-октапоро-тетрапоро.

Introduction

There is a problem related to the negative influence of hydrogen (hydrogen embrittlement, corrosion, etc.) on the properties of zirconium-based alloys used at the modern nuclear power plants for fabricating fuel cladding, fuel channels and etc. [1]. To solve this problem, it is important to understand the processes occurring in a metal-hydrogen system at macroscopic and microscopic levels. Actually, first principle calculations of the electronic and atomic structure of metal-hydrogen systems allow to promote the understanding the features of hydrogen interaction with metals at an atomic level. It should be noted that one of the main directions of the zirconium-hydrogen system studies is diffusion processes of hydrogen in zirconium and its alloys. Knowing the features of hydrogen migration in the lattice of metal and its compounds, it is possible to create cladding impeding penetration of hydrogen in pure zirconium. The purpose of this research is to do the first principle calculations of diffusion barriers of hydrogen atoms in zirconium γ -hydride (ZrH)₁₆H using the software package FLEUR [2].

Method and details of calculations

The self-consistent calculations of the diffusion barriers of hydrogen atom in γ -hydride (ZrH)₁₆H were carried out within the density functional formalism [3] by a linearized method of augmented plane waves (LAPW method) [4] realised in the software package FLEUR [2]. The exchange-correlation potential was calculated using the general-gradient approximation [5]. The radii of muffin-tin (MT-) spheres of Zr and H atoms were chosen equal to 1,217 and 0,529 Å, respectively, allowing hydrogen atoms to diffuse freely from one interstitial site of zirconium lattice to another. Terms with $l < 9$ for Zr and with $l < 5$ for H were considered in

decomposition of a wave function into spherical harmonics in MT-spheres. Diffusion barriers were defined in the following way. The net of points through which a hydrogen atom is «moved» was chosen in a linear section joining two nearby interstitial sites. For each of these points, the procedure of self-consistent calculation of the electronic density was conducted and total energy of the system was calculated. In each iteration of the self-consistent calculations, Hamiltonian eigenvalues were calculated in 16 k -points of the irreducible part of Brillouin zone. The self-consistency of the electron density was achieved when the convergence of total energy became less than 0,02 meV. It corresponds to the difference between the input and output charge density of valence electrons less than 10^{-3} eL/(Å)³.

Results and discussion

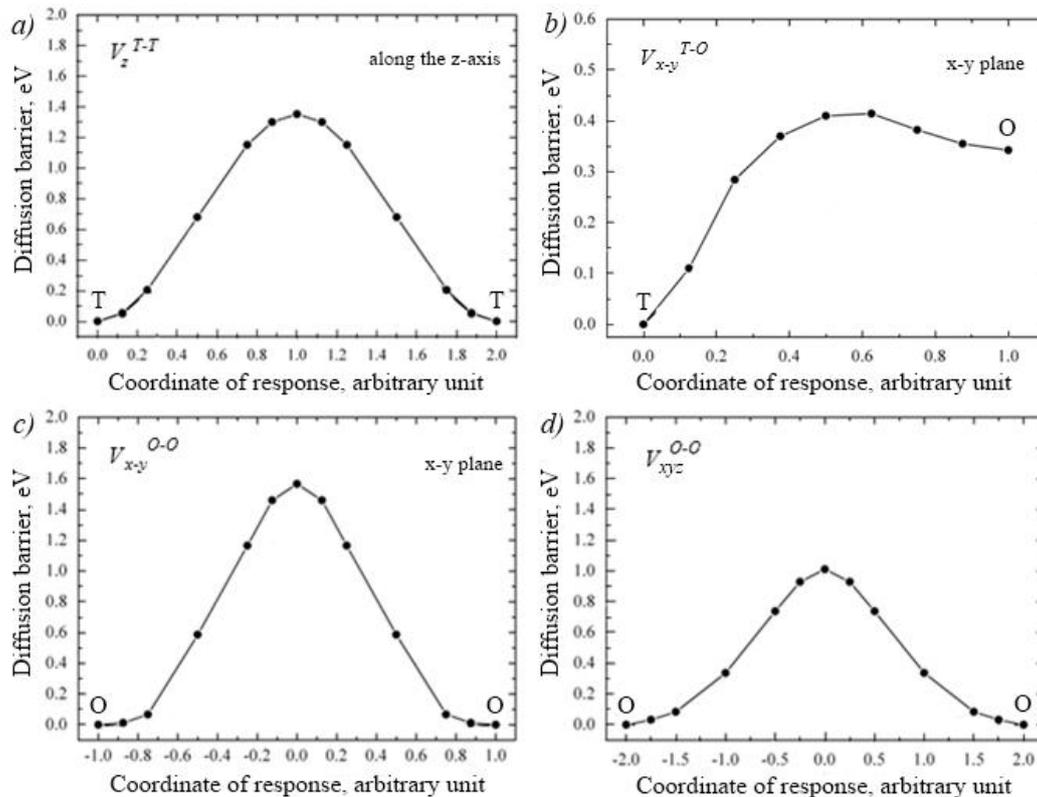


Fig. 1. Diffusion barriers of hydrogen atom in compound $(ZrH)_{16}H$ along the line joining interstitial sites of metal lattice: a) transition V_z^{T-T} ; b) transition V_{x-y}^{T-O} ; c) transition V_{x-y}^{O-O} ; d) transition V_{xyz}^{O-O} .

First of all, before the investigation of diffusion barriers overcome by hydrogen in zirconium it was necessary to define the atomic structure corresponding to a ground state of zirconium γ -hydride. In order to solve this problem, for the composition Zr-H the total energy of unit cells having optimized unit cell parameters with hexagonal close packet (HCP), body-centered cubic (BCC), face-centered cubic (FCC) and face-centered tetragonal (FCT) structures was calculated. It was found that the FCT structure has the lowest total energy and should be the most stable structure for this composition. Moreover, it was defined that the structure of zirconium γ -hydride is characterized by the ordered arrangement of hydrogen atoms in a crystal plane (110) in tetrahedral sites. These results accord with datum of the article survey [6]. Taking everything stated above into account, diffusion barriers of hydrogen atom in γ -hydride of zirconium were calculated in a unit cell with FCT structure containing 16 Zr atoms, 16 H atoms located orderly in a crystal plane (110) in tetrahedral sites and 1 diffusing H atom occupying tetrahedral or octahedral site. So this unit cell has hydrogen concentration of $X = H/Zr = 1,0625$.

The analysis of the studied crystal structure allows us to classify diffusion barriers as barriers in a lateral plane or along the z -axis. For example, there is one barrier between the nearest tetrahedral sites along the z -axis (we will designate it as V_z^{T-T}) in γ -hydride of zirconium. Also detailed consideration of the lattice geometry of γ -hydride demonstrated that the diffusion pathway of a hydrogen atom between the nearest tetrahedral sites in the plane $x-y$ can lie through one of the nearest octahedral site. This transition will be designated as V_{x-y}^{T-O} . Lastly, a transition between octahedral sites can pass in the plane $x-y$ (we will designate it as V_{x-y}^{O-O}) and along the direction not lying in the plane and in the direction of z -axis (we will designate it as V_{xyz}^{O-O}). Thus, there are four possible diffusion barriers for the compound $(ZrH)_{16}H$: V_z^{T-T} , V_{x-y}^{T-O} , V_{x-y}^{O-O} , V_{xyz}^{O-O} .

The results of calculations of hydrogen diffusion barriers in zirconium γ -hydride are presented in fig. 1. As follows from the figure, the hydrogen diffusion passes the way: tetrahedral site – octahedral site – tetrahedral site. It is caused by the fact that the diffusion barrier between tetrahedral and octahedral sites is equal to $V_{x-y}^{T-O} = 0,41$ eV (fig. 1, b) while diffusion barriers between other sites (V_z^{T-T} , V_{x-y}^{O-O} , V_{xyz}^{O-O}) exceed 1 eV. These results indicate that the hydrogen diffusion in γ -hydride passes exceptionally through tetrahedral sites. In the work [7] the diffusion barrier of hydrogen in zirconium hydrides with hydrogen concentration of $X = 1,6-2,0$ was measured by a mechanical spectroscopy method. According to this work, diffusion barriers did not depend on hydrogen concentration and were equal to $0,49 \pm 0,04$ eV. This value comports very well with the datum received in our calculations for the diffusion barrier in γ -hydride of zirconium – 0,41 eV.

Conclusion

The diffusion barriers of a hydrogen atom in zirconium γ -hydride were defined using *ab initio* calculations. It has been shown that diffusion of hydrogen in γ -hydride passes the way: tetrahedral site – octahedral site – tetrahedral site because the diffusion barrier between tetrahedral and octahedral sites in this phase of zirconium hydride is equal to 0,41 eV while diffusion barriers between other sites exceed 1 eV.

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