Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he

# First-principles study of hydrogen incorporation into the MAX phase $Ti_3AlC_2$

*Haimin Ding* [a,*], *Nicolas Glandut* [b], *Xiaoliang Fan* [a], *Qing Liu* [a], *Yu Shi* [a], *Jinchuan Jie* [c]

[a] School of Energy Power and Mechanical Engineering, North China Electric Power University, Baoding, 071003, PR China

[b] SPCTS, UMR 7315, CNRS, University of Limoges, European Ceramics Center, 12 Rue Atlantis, Limoges, 87068, France

[c] School of Material Science and Engineering, Dalian University of Technology, Dalian, 116024, PR China

ARTICLE INFO

*Article history:*
Received 2 December 2015
Received in revised form
13 February 2016
Accepted 2 March 2016
Available online 22 March 2016

*Keywords:*
First-principles calculations
Hydrogen storage
Diffusion
Vacancies

ABSTRACT

First-principles calculations have been performed to study hydrogen incorporation into the MAX phase $Ti_3AlC_2$. It is found that H atoms are thermally favorable to be incorporated into the interstitial sites of Ti-Al layers in stoichiometric $Ti_3AlC_2$. Only when C vacancies exist, H atoms can be incorporated into Ti-C layers. In Ti-Al layers, the hexagonal interstitial site ($I_{hexa}$) consisting of three Al atoms and two Ti atoms, the tetrahedral interstitial site ($I_{tetr}$-2) consisting of one Al atom and three Ti atoms, and the octahedral interstitial site ($I_{oct}$-3) consisting of three Ti atoms and three Al atoms are all possible sites for H incorporation. Among them, $I_{tetr}$-2 is the most stable one, followed by $I_{oct}$-3, and the last one is $I_{hexa}$ sites. The linear synchronous transit optimization study shows that the diffusion of H in the Ti-Al layers is feasible which could be helpful for the continuous insertion and the following extraction of H in $Ti_3AlC_2$.



## Introduction

The MAX phases ($M_{n+1}AX_n$, where n = 1, 2 or 3, M is an early transition metal, A is an A-group element, and X is either carbon or nitrogen) are a group of layered hexagonal compounds which contain two alternately stacked fundamental structural units: the non-stoichiometric transition metal carbide or nitride slabs in NaCl-type crystal structure and the close-packed A-group atomic plane [1–3]. Due to the structural characteristics, MAX phases exhibit some outstanding properties combining the advantages of both metals and ceramics, such as low density, high bulk modulus, good high-temperature stability, high thermal and electrical conductivity, excellent thermal shock resistance, and microscale ductility at room temperature, etc. [4–6].

Among these compounds, $Ti_3AlC_2$ is one of the most lightweight and oxidation resistant layered ternary carbide and it has been extensively studied by many researchers [7–11]. According to these works, $Ti_3AlC_2$ holds promise in diverse applications such as high temperature structural component [8,9], machinable ceramics, kiln furniture, heat exchanger [10], structural and fuel coating applications in future fission and

* *Corresponding author*. Tel.: +86 312 7525031; fax: +86 312 7525045.
E-mail address: dinghaimin@ncepu.edu.cn (H. Ding).

http://dx.doi.org/10.1016/j.ijhydene.2016.03.015

fusion reactors [11–13], raw materials to synthesize the graphene-like transition metal carbides [14–16] and so on.

Besides the above applications, it is considered that $Ti_3AlC_2$ may also be used in hydrogen storage field according to recent works [17]. During studying the hydrogen storage in $TiC_x$, it is found that carbon vacancies and stacking faults (SFs) are very helpful for the storage and diffusion of H [18–22]. H diffusion in SFs layers of $TiC_x$ is much easier than that in normal stacking layers [19–21]. Therefore, it is deduced that introducing SFs should be an efficient method to improve the hydrogen storage ability of $TiC_x$. However, it is difficult to form large amount of SFs in $TiC_x$ due to high SFs formation energy. As we know, the structure of $Ti_3AlC_2$ could be considered as two-dimensional close packed layers of Al periodically intercalated into the (111) twin boundary of $TiC_{0.67}$ ($Ti_3C_2$), while the SFs in TiC can be considered as a very thin twin with the thickness of one (intrinsic SF) or two (extrinsic SF) (111) planes [23,24]. Therefore, due to the structure similarity between $Ti_3AlC_2$ and SFs in $TiC_x$, it is considered that the $Ti_3AlC_2$ can be used as an effective additive to improve the hydrogen storage and diffusion in $TiC_x$. In order to verify this assumption, it should be to clarify how H could be incorporated into $Ti_3AlC_2$ firstly.

Therefore, in this work, the first principles calculations are used to study the hydrogen incorporation into stoichiometric $Ti_3AlC_2$, as well as with Ti, Al and C vacancies. In addition, the diffusion of H in different layers is also examined.

## Method of calculations

The calculations are based on the density-functional theory and performed using the program package CASTEP. The local density approximation (LDA) was utilized for structure optimization and energy calculation due to its better agreement with experimental data in study of the hydrogen incorporation into solids [25]. It is known that, $Ti_3AlC_2$ crystallizes in hexagonal structure with space group of P63/mmc, as shown in Fig. 1. The unit cell of $Ti_3AlC_2$ consists of alternating layers of Al and two layers of an edge-shared TiC octahedron. The lattice constants are a = 3.072 Å and c = 18.73 Å [26]. The atomic positions of Ti correspond to 2a and 4f, Al to 2b, and C to 4f. For the convenience of discussion, Ti atoms at 2a sites are denote as Ti (1) and those in 4f as Ti (2) in the following sections. Ultrasoft pseudopotentials (USP) was chosen and the plane-wave cut off energy of 450 eV was employed in the calculations, and the grids of K-points were sampled by $9 \times 9 \times 4$. The self-consistent field (SCF) tolerance was set to be $5.0 \times 10^{-7}$ eV/atom. During the calculations, all atoms in the supercell were fully relaxed. The convergence was achieved by allowing atoms to relax until the force on each atom was less than 0.01 eV/A.

The formation energies of H atoms occupying different sites in stoichiometric $Ti_3AlC_2$ are first calculated by

$$E_f = E_{tot}^{nH} - E_{tot} - n\frac{E^{H_2}}{2} \quad (1)$$

Where $n$ is the number of H atoms, $E_{tot}^{nH}$ is the total energy of the system with $n$ H atoms, $E_{tot}$ is the total energy of $Ti_3AlC_2$, and $E^{H_2}$ is the total energy of the hydrogen molecules [27].

Then, Ti, C and Al vacancies are introduced in $Ti_3AlC_2$, and the formation energies of H atoms occupying these vacancies are calculated by

$$E_f = E_{tot}^{nH-V_c} - E_{tot}^{V_c} - n\frac{E^{H_2}}{2} \quad (2)$$

Where $E_{tot}^{nH-V_c}$ is the total energy of the $Ti_3AlC_2$ with a vacancy and $n$ H atoms, $E_{tot}^{V_c}$ is the total energy of $Ti_3AlC_2$ with a vacancy.

During studying the diffusion of H in $Ti_3AlC_2$, the linear synchronous transit (LST) optimization method was used. In LST optimization, a series of single point energy calculations are performed on a set of linearly interpolated structures between an initial and final state. The maximum energy structure along this path provides a first estimate of the transition state structure. Then, an energy minimization in directions conjugate to the reaction pathway is performed [28]. This yields a structure closer to the true transition state which can be used to determine the energy barrier of the diffusion process.

## Results and discussion

The H incorporation into stoichiometric $Ti_3AlC_2$ is firstly studied. As mentioned above, $Ti_3AlC_2$ has layered hexagonal structure with space group of P63/mmc. There are a variety of high-symmetry interstitial sites in $Ti_3AlC_2$ and all of them fall into two parts: the interstices in the open space in Ti-Al layers and the ones in compact Ti-C layers. In order to gain a precise understanding of H incorporation into $Ti_3AlC_2$, the possible stable interstitial positions in Ti-Al as well as Ti-C layers are all considered. Fig. 1 shows the possible occupation sites for H in both cases. For Ti-Al layers, there are three kinds of interstitial sites: the tetrahedral interstitial site $I_{tetr}$-1 consists of three Al atoms and one Ti atom, the tetrahedral interstitial site $I_{tetr}$-2 consists of three Ti atoms and one Al atom, the octahedral interstitial site $I_{oct}$-3 which is centered in an octahedron consists of three Ti atoms and three Al atoms. They are designated as number 1, 2 and 3, respectively in Fig. 1. For Ti-C layers, since C atoms occupy the octahedral interstitial sites, only the tetrahedral interstitial sites are considered to be original sites for H during the calculations. One kind of the tetrahedral interstitial sites designated as $I_{tetr}$-4 consists of one Ti (1) and three Ti (2) atoms; the other one is designated as $I_{tetr}$-5, and consists of three Ti (1) and one Ti (2) atoms. They are illustrated as number 4 and 5, respectively in Fig. 1. After the convergence test, it is found that the $2 \times 2 \times 1$ supercell can reach convergence with reasonable accurateness, which is in agreement with previous works [29,30]. Taking H incorporation into $I_{tetr}$-2 as an example, the calculated formation energy is −0.551 eV for $2 \times 2 \times 1$ supercell, −0.557 eV for $2 \times 3 \times 1$ supercell, −0.566 eV for $3 \times 3 \times 1$ supercell, respectively. As lager size supercell will cause much more computational time consuming, the $2 \times 2 \times 1$ $Ti_3AlC_2$ supercell is used in this work.

The formation energies for H incorporation into various interstices are calculated by Equation (1) and the results are shown in Table 1. It can be seen that the formation energies for H incorporation into all the interstitial sites in Ti-Al layers