



# First-principles calculations of $\text{Ti}_3\text{SiC}_2$ and $\text{Ti}_3\text{AlC}_2$ with hydrogen interstitial



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## ABSTRACT

In this paper, the effects of hydrogen interstitial defect on the structural stability of two kinds of MAX materials ( $\text{Ti}_3\text{SiC}_2$  and  $\text{Ti}_3\text{AlC}_2$ ) were investigated by first-principles calculations. The results indicated that the hydrogen interstitial energetically prefers to reside at the 2Ti3Si site for  $\text{Ti}_3\text{SiC}_2$  and 3TiAl site for  $\text{Ti}_3\text{AlC}_2$ , respectively, and the latter has much lower formation energy. Both of these MAX phases are slightly hardened and the elastic anisotropy is reduced appreciably after the introduction of hydrogen interstitial. The hydrogen interstitial in  $\text{Ti}_3\text{SiC}_2$  and  $\text{Ti}_3\text{AlC}_2$  leads to an electronic localization effect on the Si/Al atom and the effect is more remarkable in  $\text{Ti}_3\text{AlC}_2$ . The interlayer bonding strength of  $\text{Ti}_3\text{AlC}_2$  is more weakened by hydrogen interstitials than that of  $\text{Ti}_3\text{SiC}_2$ . As a result, the interatomic bonding between Si/Al and Ti atom layers is deteriorated and their structural stabilities degrade subsequently.

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## 1. Introduction

Because of the excellent performance, the nanolaminated MAX (M is a nearly transition metal, A is an A-group element, and X is C or N) phases has shown great potential as candidate structural materials for use in core components of future fission and fusion reactors (such as GENIV and ITER) [1]. The  $\text{Ti}_3\text{SiC}_2$  and  $\text{Ti}_3\text{AlC}_2$  are two of the most important MAX phase ceramics, and have drawn much research attention due to the unique combination of ceramic and metal-like properties [2–5]. Specifically, many studies have demonstrated that the MAX phases of  $\text{Ti}_3\text{SiC}_2$  and  $\text{Ti}_3\text{AlC}_2$  exhibit strong tolerance to irradiation damage, which is advantageous for applications in nuclear industry [6–9]. Meanwhile, as applied to the future nuclear power systems, either the ceramic cladding or zirconium coating material in light water reactor or the plasma-facing material (PFM) in viable fusion power reactor, the hydrogen rich environment is an inevitable challenge that the MAX

phases of  $\text{Ti}_3\text{SiC}_2$  and  $\text{Ti}_3\text{AlC}_2$  have to face. It is thus very important to study the hydrogen tolerance properties of these materials. However, to our knowledge, very few researches have been done on the behavior of hydrogen in MAX phases of  $\text{Ti}_3\text{SiC}_2$  and  $\text{Ti}_3\text{AlC}_2$ .

It is well known that the dissolved hydrogen atoms in metals cause a significant degradation of mechanical properties and several possible mechanisms have been proposed [10,11]. Although the interaction between hydrogen and ceramics is not terribly prominent, the hydrogen-induced degradation, especially in the moisture-related hydrogen environments, is a subsistent challenge in various ceramics. For example, Chen et al. [12] found that atomic hydrogen diffuses easily into the  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  ceramic lattice and leads to a quick degradation on its dielectric properties. Similar results have been reported by Xiong et al. [13] for ferroelectric oxide ceramics. As for hydrogen in MAX phase materials, Wang et al. suggested that the Si(001) plane is the energetically favorable position for hydrogen atom to reside in defect-free  $\text{Ti}_3\text{SiC}_2$ , and the imposed hydrogen atoms may decrease the cohesive strength of the lattice [14]. Rong et al. investigated the vacancy trapping behavior of hydrogen in  $\text{Ti}_3\text{SiC}_2$ , and suggested that one Si mono-vacancy can trap as many as five hydrogen atoms without  $\text{H}_2$

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molecules formation [15]. In our previous work [16], the thermal stability of bulk  $\text{Ti}_3\text{SiC}_2$  at high temperature (1200–1400 °C) in hydrogen atmosphere was investigated by scanning electron microscope and X-ray diffraction techniques, and it was found that the dissociation of  $\text{Ti}_3\text{SiC}_2$  was accelerated by the introduction of hydrogen. Similar phenomenon was also observed in bulk  $\text{Ti}_3\text{AlC}_2$  [17]. It clearly showed that the hydrogen atoms could affect the structural stability and the properties of MAX phase ceramics, but there still lacks fundamental understanding of the underlying mechanisms for these interesting phenomena. The first-principles method can be used to study the structural, energetic and electronic properties of these systems, which will be very helpful to understand the interaction mechanisms between hydrogen and the MAX phase materials at electronic levels. Thus, in order to expedite the applications of MAX phases of  $\text{Ti}_3\text{SiC}_2$  and  $\text{Ti}_3\text{AlC}_2$  in future advanced nuclear systems, it is of crucial importance to gain insight into the interaction between hydrogen and  $\text{Ti}_3\text{SiC}_2$  and  $\text{Ti}_3\text{AlC}_2$ , as well as the other irradiation induced defects therein, by using first-principles method.

In this work, the behaviors of hydrogen interstitial in  $\text{Ti}_3\text{SiC}_2$  and  $\text{Ti}_3\text{AlC}_2$  were investigated by first-principles calculations [18,19]. The influence of hydrogen interstitial defects on the structural stability, elastic properties, as well as the electronic structures of  $\text{Ti}_3\text{SiC}_2$  and  $\text{Ti}_3\text{AlC}_2$  were discussed. These calculated results provide a solid foundation for further understanding of the underlying mechanisms of the interaction between hydrogen and other defects in  $\text{Ti}_3\text{SiC}_2$  and  $\text{Ti}_3\text{AlC}_2$ .

## 2. Calculation method

All the calculations were performed using the projector-augmented wave (PAW) method within density functional theory framework (DFT) [20,21], as implemented in the VASP package (Vienna *ab initio* simulation package) [22]. The choice of exchange-correlation functional was motivated by a better description of the relevant bulk properties of  $\text{Ti}_3\text{SiC}_2$  and  $\text{Ti}_3\text{AlC}_2$  compared to the corresponding experimental results. The exchange-correlation functionals of the local-density approximation (LDA) [23], the generalized gradient approximation (GGA) with Perdew-Wang-91 functional (PW91) [24], and Perdew-Burke-Ernzerhof (PBE) functional [25] were tested.

All defect calculations were performed with a  $3 \times 3 \times 1$  supercell, the energy cutoff of 500 eV for plane wave basis set, and a  $9 \times 9 \times 1$  Monkhorst-Pack k-points grid for integration over the Brillouin zone. The total energies were converged to  $10^{-5}$  eV per cell. The size of supercell was also determined by a series of full-relaxation calculations. It was found that the formation energy difference is about 0.02 eV for one hydrogen interstitial defect with the same configuration in  $2 \times 2 \times 1$  and  $3 \times 3 \times 1$  supercell.

## 3. Results and discussion

### 3.1. Bulk properties

The MAX phase of  $\text{Ti}_3\text{SiC}_2$  and  $\text{Ti}_3\text{AlC}_2$  has a hexagonal structure with space group P63/mmc, in which the Ti atom occupies at  $2a$  (0, 0, 0) and  $4f$  ( $1/3$ ,  $2/3$ ,  $z$ ), Si or Al at  $2b$  ( $1/3$ ,  $2/3$ , 0.25), and C at  $4f$  ( $1/3$ ,  $2/3$ ,  $z$ ) Wyckoff positions. The crystal structure of  $\text{Ti}_3\text{AC}_2$  ( $A = \text{Si}, \text{Al}$ ) is shown in Fig. 1a, which can be described as nanoscale sheets of edge-sharing TiC octahedrons coupled with interleaved planar close-packed A atom layers. In general, the Ti atom sitting at  $2a$  site are denoted as Ti1, and those sitting at  $4f$  (Fig. 1a). By fitting the energy-volume data to the Murnaghan's equation of state [26], the lattice parameters of  $\text{Ti}_3\text{SiC}_2$  and  $\text{Ti}_3\text{AlC}_2$  are calculated and summarized in Table 1, in comparison with experimental and

**Table 1**

The calculated lattice parameters of  $\text{Ti}_3\text{SiC}_2$  and  $\text{Ti}_3\text{AlC}_2$  in comparison with experimental and previous calculated results.

	$\text{Ti}_3\text{SiC}_2$		$\text{Ti}_3\text{AlC}_2$	
	$a$ , Å	$c$ , Å	$a$ , Å	$c$ , Å
GGA-PW91	3.0779	17.7086	3.0854	18.6099
GGA-PBE	3.0770	17.7039	3.0852	18.6091
LDA	3.0270	17.4162	3.0349	18.3054
Ref.(Exp.)	3.068 [2]	17.669	3.075 [27]	18.578
Ref.(Cal.)	3.068 [28]	17.669	3.072 [29]	18.732
	3.0705 [30]	17.670	3.093 [31]	18.687

previous calculated results. It is found that the PAW-GGA (PW91) and PAW-PBE functionals predict quite similar results for lattice parameters, and the values agree better with the experimental data than the LDA functional calculated ones. The LDA functional underestimates the lattice constants as compared with the experimental values. Thus, we employ the PAW-GGA (PW91) for all the subsequent calculations.

### 3.2. Formation energies of hydrogen interstitial defects

Considering the crystal structure of  $\text{Ti}_3\text{AC}_2$  ( $A = \text{Si}, \text{Al}$ ), as schemed in Fig. 1b, there are four possible types of interstitial positions for hydrogen to stay: the hexahedron interstitial configured by four Ti atoms (three Ti2 atoms and one Ti1 atom) and one A atom (4TiA), the hexahedron interstitial configured by two Ti2 atoms and three A atoms (2Ti3A), the octahedron interstitial configured by three Ti2 atoms and three A atoms (3Ti3A) and the cube interstitial configured by three Ti1 atoms, one Ti2 atom and four C atoms (4Ti4C). It is noticed that the hydrogen in 4TiA hexahedron interstitial configuration finally relaxed to the center of the tetrahedron consisted of three Ti2 and one A atom, and the interstitial position is thus marked as 3TiA in the following discussions.

The formation energy of one hydrogen interstitial defect ( $E_H^f$ ) is defined as

$$E_H^f = E_{def} - E_{perf} - E_H \quad (1)$$

where the  $E_{def}$ ,  $E_{perf}$  and  $E_H$  are the total energies of a defected supercell with one hydrogen interstitial, a perfect supercell and a hydrogen atom. In this work, both the total energy of an isolated H atom and half of the total energy of a  $\text{H}_2$  molecule are chosen as the calculation reference, and the zero-point energy (ZPE) correction for hydrogen molecule was also considered. The calculated total energies of isolated H atom and half of  $\text{H}_2$  molecule are  $-1.11$  and  $-3.39$  eV, respectively. The ZPE of  $\text{H}_2$  molecule and related systems can be obtained by summing up the zero point vibrational energies of the normal modes in their respective system, i.e.,  $ZPE = \sum_i \hbar \nu / 2$ , where  $\nu$  is a real normal mode frequency. The calculated formation energies of interstitial hydrogen defects in

**Table 2**

Formation energies (eV) of hydrogen interstitial defects in  $\text{Ti}_3\text{AC}_2$  ( $A = \text{Si}, \text{Al}$ ), which are calculated according to equation (1) with reference to isolated H atom,  $\text{H}_2$  molecule, and  $\text{H}_2$  molecule with zero point energy (ZPE) correction.

	Reference	3Ti1A	2Ti3A	3Ti3A	4Ti4C
$\text{Ti}_3\text{SiC}_2$	Isolated H atom	-1.50	-1.93	-1.85	-1.23
	$\text{H}_2$ molecule	0.78	0.35	0.44	1.05
	$\text{H}_2$ molecule with ZPE	1.13	0.49	0.58	1.49
$\text{Ti}_3\text{AlC}_2$	Isolated H atom	-2.54	-2.35	-2.34	-1.34
	$\text{H}_2$ molecule	-0.25	-0.06	-0.05	0.94
	$\text{H}_2$ molecule with ZPE	0.07	0.09	0.08	1.36

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