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13. SUPPLEMENTARY NOTES

14. ABSTRACT

We worked on ab-initio calculation on Max-Phases materials in two directions:

1) Electronic structures of high pressures phases

Our efforts have been directed to ab-initio calculation of Max phases at ambient and high pressure conditions. In particular, continuing our work in $Ti_3Si_{0.5}Ge_{0.5}$ (Orellana, W., et al, J. Ph.. Ch. Solids **67**, 2149-2153 (2006), we have performed electronic structure calculation in series M_2AX, in particular Ti_2GaN.

2) Surface properties of Max phases: One of our goals in the present project was the determination of the electronic and bonding properties of surfaces in Ti-based MAX phases. In particular, we are interested in the surfaces properties like oxidation and corrosion as well as their relative strengths. In order to do that, we i)Find the most stable terminations of Ti_3SiC_2 along the (001) direction. ii) Study the stability of the most stable terminations at high temperatures. iii) Study the oxidative evolution of the most stable terminations after the exposure to O_2 and H_2O at high temperatures.

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Thermophysical modeling of novel machinable ceramic materials

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Period 1 Dec. 2006-30 Nov. 2009

1) Introduction

Here we present a Final Report of our project, corresponding to the period Dec, 1st, 2006 to Nov. 30, 2009.

2. Objectives: *(List the objectives of the research effort or the statement of work: This may be omitted if there has been no change. State new or revised objectives if they have changed and the reason why.)*
No changes.

3. Status of effort: *(A brief statement of progress towards achieving the research objectives. (Limit to 200 words))*
We worked in ab-initio calculation on Max-Phases in two directions:
1) Electronic structures of high pressures phases
Our efforts have been directed to ab-initio calculation of Max phases at ambient and high pressure conditions. In particular, continuing our work in $Ti_3Si_{0.5}Ge_{0.5}$ (Orellana, W., et al, J. Ph.. Ch. Solids **67**, 2149-2153 (2006), we have perdormed electronic structure calculation in series M_2AX, in particular Ti_2GaN.
2) Surface properties of Max phases: One of our goals in the present project was the determination of the electronic and bonding properties of surfaces in Ti-based MAX phases. In particular, we are interested in the surfaces properties like oxidation and corrosion as well as their relative strengths. In order to do that, we i)Find the most stable terminations of Ti_3SiC_2 along the (001) direction. ii) Study the stability of the most stable terminations at high temperatures. iii) Study the oxidative evolution of the most stable terminations after the exposure to O_2 and H_2O at high temperatures.
(See Appendix for more details).

4. Accomplishments/New Findings: *(Describe research highlights, their significance to the field, their relationship to the original goals, their relevance to the AF's mission, and their potential applications to AF and civilian technology challenges.)*
Perhaps the most interesting result so far is in relation to the surface properties of the oxidation of the C-terminated Ti_3SiC_2 (0001) surface. Our preliminary results indicate that singlet O_2 is highly reactive, dissociating after react with a C surface atom. An atomic oxygen binds with a Ti subsurface atom destroying the surface. On the other hand, triplet O_2, which in the gas phase is most stable than the singlet one by about 1.1 eV, do not react spontaneously with the same surface, requiring overcome a barrier. These calculations are in progress. This study could give some clue about the oxidation and corrosion process of Ti_3SiC_2.

5. Personnel Supported: *(List professional personnel (Faculty, Post-Docs, Graduate Students, etc.) supported by and/or associated with the research effort.)*
Faculty: Dr. Gonzalo Gutiérrez (U. de Chile), Dr. Walter Orellana (now at Department of Physics, Universidad Andrés Bello, Santiago, Chile)
PhD. Student: Eduardo Valdebenito, (retired) Universidad de Chile.
PhD Student Joaquin Loyola, finishing his thesis (see attached file), Jan. 2010.
PhD student Claudia Loyola, finishing her thesis (March 2010.

6. Publications: *(List peer-reviewed publications submitted and/or accepted during the 12-month period starting the previous 1 October (or since start for new awards).)*
None. Two manuscripts under preparation

7. Interactions/Transitions:

a. *Participation/presentations at meetings, conferences, seminars, etc.*

Preliminary results has been presented at Simposium of the Chilean Physical Society, Nov 2006, Plenary talk of Dr. G. Gutiérrez, and several Colloquia in different Department of Physics and research group in Santiago, Chile.

b. *Consultative and advisory functions to other laboratories and agencies, especially Air Force and other DoD laboratories. Provide factual information about the subject matter, institutions, locations, dates, and names(s) of principal individuals involved.*
None.

c. *Technology Assists, Transitions, and Transfers. (Describe cases where knowledge resulting from your effort is used, or will be used, in a technology application. Transitions can be entities in the DoD, other federal agencies, or industry. Briefly list the enabling research, the laboratory or company, and an individual in that organization who made use of your research.)*
None

8. New discoveries, inventions, or patent disclosures. *(If none, report None.)*
None.

9. Honors/Awards: *(List honors and awards received during the grant/contract period. List lifetime achievement honors such as Nobel Prize, honorary doctorates, and society fellowships prior to this effort.)*
None.

Appendix 1.

a) Structural and electronic properties of Ti_2GaN at ambient and high pressure

I.   Goals
- To find, by means of density functional theory, the minimun energy structure, the bulk modulus and the electronic structure of the material
- To determine the changes of these properties under pressure

II.   Method
The calculations were carried out in the framework of density functional theory, within the generalized gradient approximation to the exchange-correlation potential, using the VASP code.

III.   Results

Structural properties.

Unit cell: the spatial group is P63/mmc, with 8 atomic layers, The basis vectors are $a_1=2c2(1,-c3,0)$; $a_2 =2c2(1,c3,0)$ and
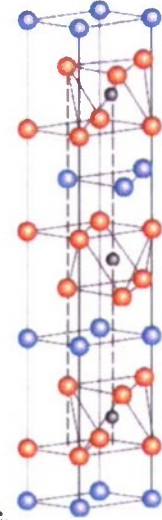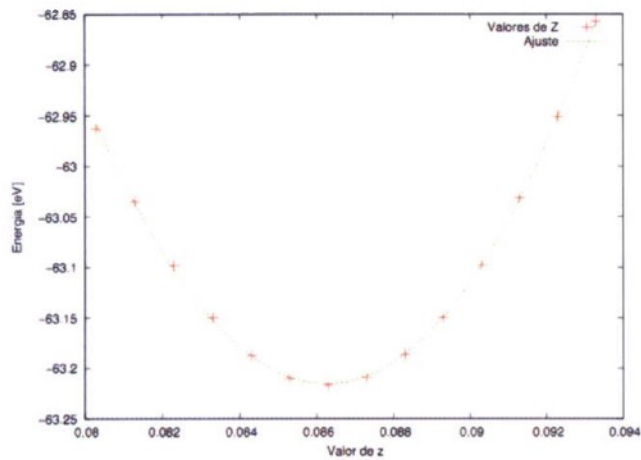

$a_3=c(0,0,1)$, where $c1=1/3$, $c2= 1/4$ and $c3= \sqrt{3}$ and the atom positions are described in the Table.

Tipo	Número	Posición
X	1	0
M	2	$c_1(\vec{a}_1 + 2\vec{a}_2) + z_m\vec{a}_3$
A	3	$c_1(2\vec{a}_1 + \vec{a}_2) + c_2\vec{a}_3$
M	4	$c_1(\vec{a}_1 + 2\vec{a}_2) + (2c_2 - z_m)\vec{a}_3$
X	5	$2c_2\vec{a}_3$
M	6	$c_1(2\vec{a}_1 + \vec{a}_2) + (2c_2 + z_m)\vec{a}_3$
A	7	$c_1(\vec{a}_1 + 2\vec{a}_2) + 3c_2\vec{a}_3$
M	8	$c_1(2\vec{a}_1 + \vec{a}_2) + (1 - z_m)\vec{a}_3$

The first step is to adjust the value c/a. The result are displayed in the figure:
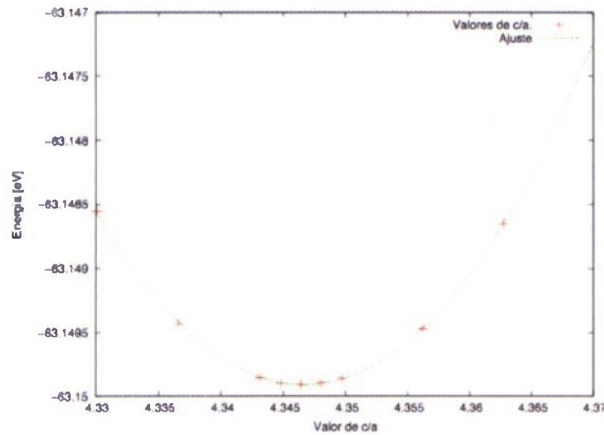
The next step is to adjust z, a free parameter of certain atoms:
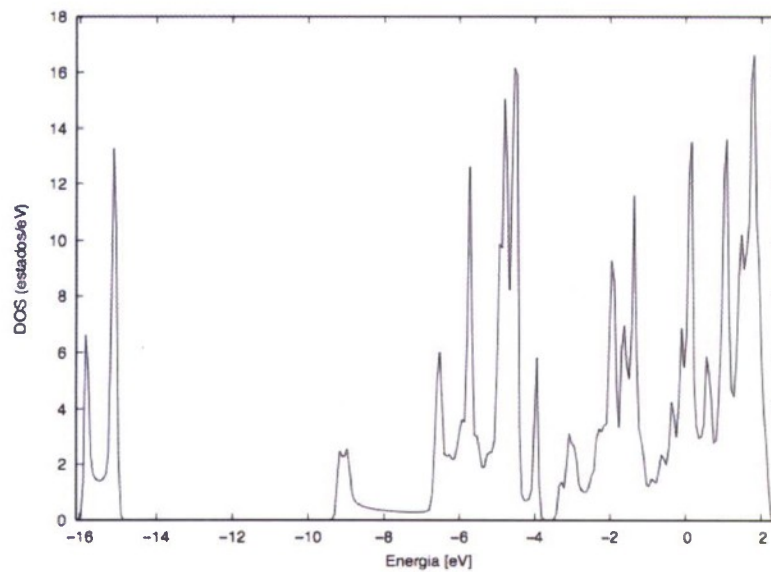
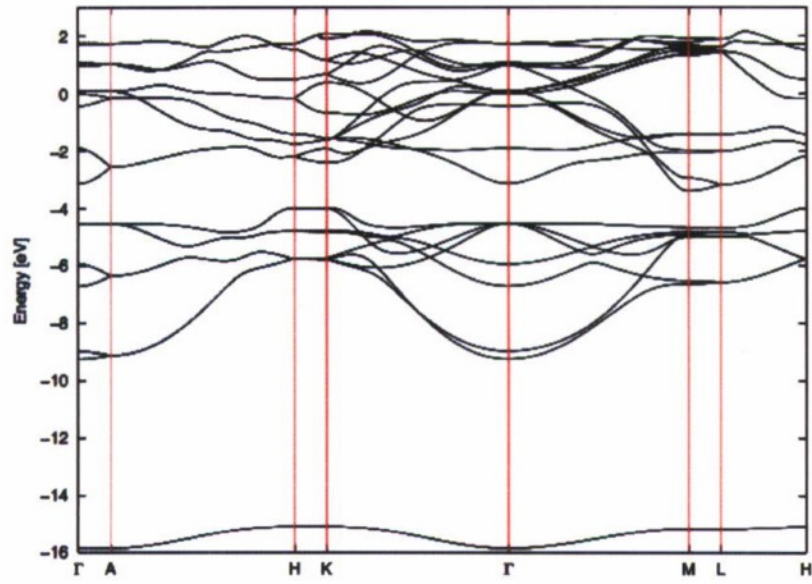Now, with relaxed strucuture, we calculate the bulk modulus:
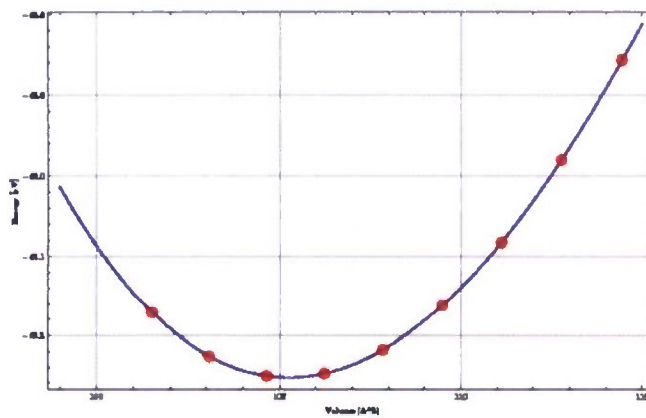
The fitting of the curve against the Birch-Murnaghan equation gives the value of 180 GPa. The experiental value is 160 GPa.
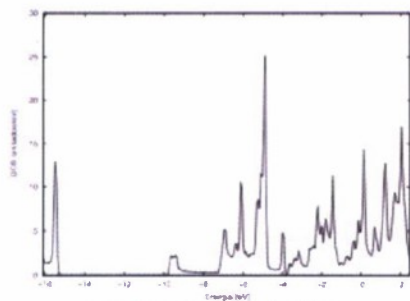
Electronic properties:

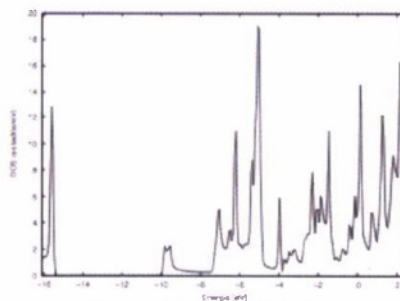Electronic Density of States (DOS) at room pressure.
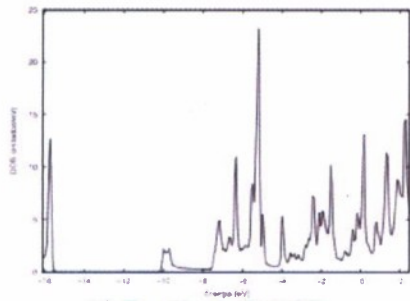
Band Structure at room pressure:
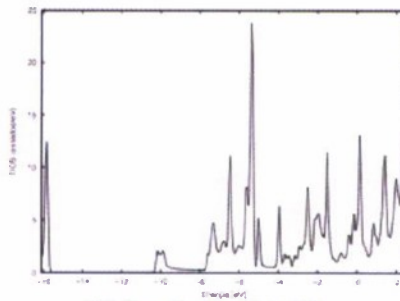

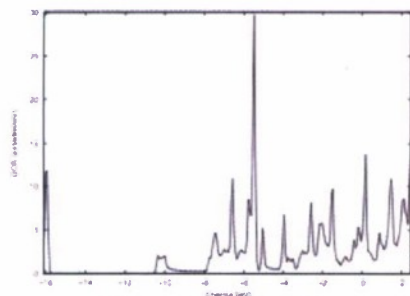e-DOS at high pressure:

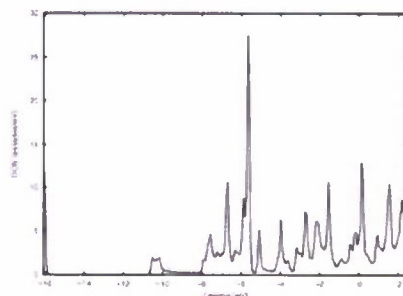(a) Presión de 11.1 GPa

(b) Presión de 20.0 GPa

(c) Presión de 29.0 GPa

(d) Presión de 40.0 GPa

(e) Presión de 52.0 GPa

(f) Presión de 66.0 GPa

b) Atomic-scale oxidation of ceramic compound surfaces Ti$_3$SiC$_2$(001) at high temperature by ab initio calculations

I. Goals

- Find the most stable terminations of Ti$_3$SiC$_2$ along the (001) direction.

- Study the stability of the most stable terminations at high temperatures.

- Study the oxidative evolution of the most stable terminations after the exposure to O$_2$ and H$_2$O at high temperatures.

II. Theoretical Method

The calculations were carried out in the framework of density functional theory, within the generalized gradient approximation to the exchange-correlation potential. We use a basis set of localized atomic orbital and norm-conserving pseudopotentials for the electron-ion interaction, as implemented in the *ab-initio* simulation package SIESTA [1]. Bulk Ti$_3$SiC$_2$ shows two kinds of chemical bonds for titanium: C-Ti1-C and C-Ti2-Si. Thus, six different terminations along the (001) direction can be identify, which are termed as: C(Ti1), C(Ti2), Si(Ti2), Ti1(C), Ti2(C), and Ti2(Si), in parenthesis are indicated the subsurface atomic layer. To study the stability of the different terminations, we use a symmetrical slab with up to 23 monolayers (MLs) in a (1_1) surface unit cell. Here, the vacuum region is chosen in 10 Å. For the Brillouin zone sampling we use a mesh of 7_7_1 according to the Monkhorst-Pack scheme. The geometry optimization is performed for the first 8 MLs at both sides of slab, fixing the central MLs at the equilibrium geometry of bulk Ti$_3$SiC$_2$. The residual force of the relaxed structure is fixed at 0.05 eV/Å. To study the surface stability and the oxidative reactions after the adsorption of O$_2$ and H$_2$O molecules onto the most stable terminations of Ti$_3$SiC$_2$(001), we consider an asymmetrical slab with 7 MLs in a (3_3) surface unit cell, containing 15 Å of vacuum region. In this case, the relaxation is performed for topmost 6 MLs.

The surface energy (γ) of a symmetrical-terminated slab at zero temperature and negligible pressure is given

$$\gamma = \frac{1}{2A}\left(E_t - \sum_i n_i \mu_i\right)$$

where E_t is the total energy of the slab, A is the slab area, n_i the number of atoms of the atomic species i=Ti,Si,C and μ_i the respective chemical potential. The chemical potentials are restricted to vary according to the stoichiometric relation of the structure:

$$\mu_{Ti_3SiC_2} = 3\mu_{Ti} + \mu_{Si} + 2\mu_C$$

Thus, combining the above equations and considering that μ_{Ti} and μ_{Si} take the total energy value of their respective bulk phases, the surface energy can be calculated by

$$\gamma = \frac{1}{2A}\left[E_t - \frac{n_C}{2}\mu_{Ti_3SiC_2} - \left(n_{Ti} - \frac{3}{2}n_C\right)\mu_{Ti} - \left(n_{Si} - \frac{n_C}{2}\right)\mu_{Si}\right]$$

To study the oxidative evolution of the most stable terminations we performed constant-temperature *ab-initio* molecular dynamic simulations within the Nosé thermostat approach [3], using the asymmetrical slab above described. We consider temperatures of 800, 1000, 1200, and 1400 °C, over 1 ps (10^{-12} s) of simulation time with a time step of 1 fs (10^{-15} s). We investigate the stability of the pristine surfaces and their oxidation resistance at high temperatures. Our goal is to determine the critical temperatures where these surfaces can maintain their structure and establish the oxidation mechanisms with temperature.

III. Results

(a) Surface stability

Our results for the surfaces stability calculated with the (1_1) symmetrical slab are listed in Table I. We find that Ti2(Si) is the most stable termination follows by Si(Ti2) and Ti1(C), suggesting that they are favorable to form and would correspond to those found experimentally. Whereas those terminated in carbon have higher surface and relaxation energies, as compared with the others terminations, indicating that they would not form. These results are in good agreement with previous calculations [2] and gave us room to

study the stability and oxidative properties of the terminations of $Ti_3SiC_2(001)$ that probably form in the growing process: Si(Ti2), Ti1(C) and Ti2(Si).

Table I. Surface energy (γ) and relaxation energy (E_R) for different terminations of the Ti_3SiC_2 (001) calculated by the symmetrical slab method within a (1_1) surface unit cell.

Surface termination	Monolayers	E_R (eV)	γ (eV/Å²)
C(Ti1)	21	0.409	0.738
C(Ti2)	23	0.835	0.534
Si(Ti2)	19	0.074	0.157
Ti1(C)	19	0.286	0.164
Ti2(C)	23	0.101	0.259
Ti2(Si)	21	0.083	0.119

To obtain the surface equilibrium geometries, we performed calculations considering the (3_3) asymmetrical slab. Our results are shown in Fig. 1. Here the surfaces are represented in an extended (6_6) unit cell. We find that Si(Ti2) undergoes a strong reconstruction forming an amorphous top layer where the Si atoms are fourfold coordinated, binding with three Si neighbors plus a subsurface Ti neighbor. This reconstruction opens up clearances that expose the Ti subsurface, as shown in Fig. 1(a). On the other hand, both Ti-terminated surfaces preserve their hexagonal symmetries.
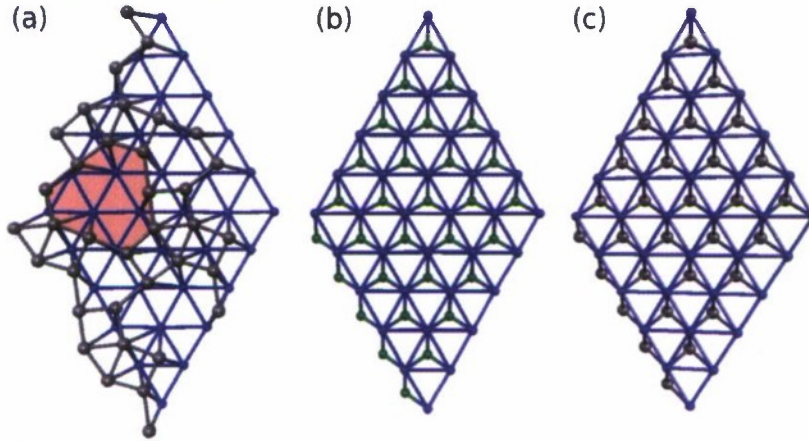

Figure 1: (6_6) representation of the topmost MLs as calculated with a (3_3) surface unit cell at 0 K. (a) Si(Ti2), (b) Ti1(C) and (c) Ti2(Si). Colored balls represent atom positions: Ti (blue), Si (gray), and C (green).

When these surfaces are heated at high temperatures different behaviors are observed, which can be associated with their comparative stabilities. Figure 2 shows a snapshot of surface geometries after 1 ps of MD simulation at 1400 °C. We observe that the Si(Ti2) termination shows a strong mobility where the Si atoms tend to desorb and adsorb continuously, forming Si-Si and Ti-Si bonds, whereas the subsurface Ti layer preserves its hexagonal structure. For the Ti2(Si) termination the situation is different, the topmost Ti layer tries to maintain its structure but the subsurface Si layer introduces a strong amorphization. The interesting case occurs for the Ti1(C) termination, which shows a high stability almost preserving its structure for both the topmost Ti layer and the subsurface C layer, suggesting that this termination would has the better resistance to high temperatures.
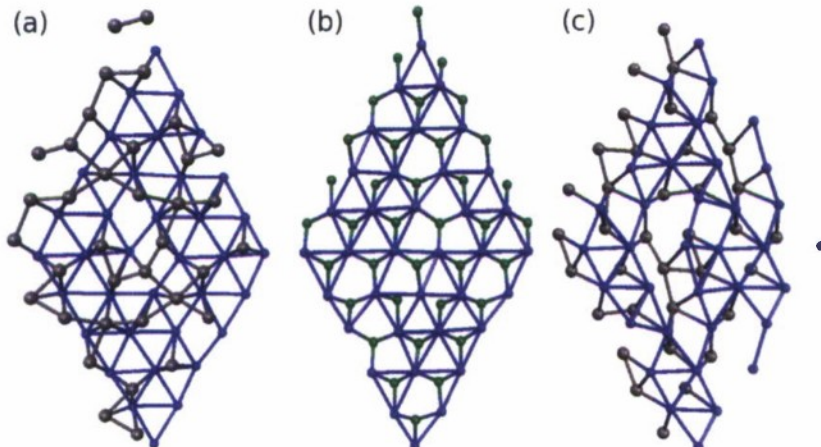
Figure 2. Snapshot geometries of the topmost MLs after 1 ps of MD simulations at 1400 °C. (a) Si(Ti2), (b) Ti1(C) and (c) Ti2(Si).

(b) Surface oxidation

For Si(Ti2), Ti1(C) and Ti2(Si), we study the surface oxidation by O_2 and H_2O molecules at 0 K. We consider the simultaneous adsorption of two molecules of the same kind onto the (3×3) asymmetrical slab. The molecules are released ~3 Å from the surface without constraints. Our results for the equilibrium geometries are shown in Fig. 3. We find that O_2 and H_2O undergo barrierless dissociative reactions while approach to the Ti1(C) and Ti2(Si) surfaces. After the O_2 dissociation, the O atoms bind strongly with three Ti surface atoms with a binding energy of 9.4 eV, following the same bonding structure of titania (TiO_2). Similar bonding structures are found for H and O atoms after the H_2O dissociation, whereas additional O-H species are also found. The H atoms bind much weaker with on the Ti surface with a binding energy of 4.4 eV. The situation is different on the Si(Ti2) surface, the molecules do not dissociate after reach the Si surface, remaining weakly bonded by physisorption. This interaction can be associated to the covalent character of the Si-Si bond and the absence of partially occupied dangling bonds. However, we find that the O_2 dissociation occurs when the molecule find a Si clearance reacting with the Ti subsurface, in this case the O atoms bind either with three Ti atoms or with two Si atoms forming a Si-O-Si structure, following the same bonding structure of silica (SiO_2), as shown in Fig. 3(a).
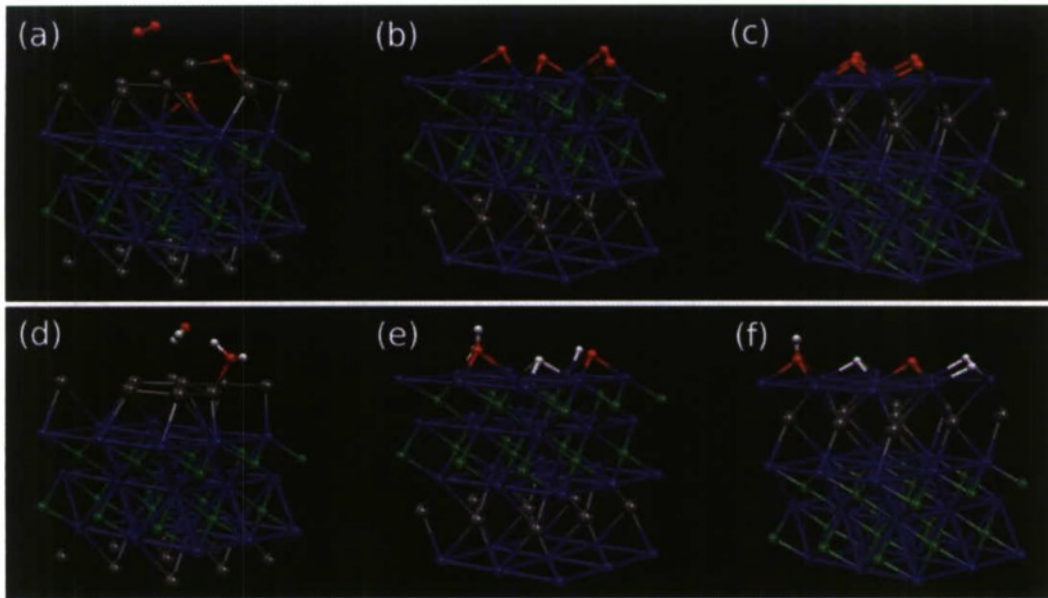

Figure 3. Equilibrium geometries of the most stable surfaces after the adsorption of O_2 and H_2O molecules onto (a) and (d) Si(Ti2); (b) and (e) Ti1(C); (c) and (f) Ti2(Si), respectively.

The oxidation kinetic of Ti_3SiC_2 at high temperatures has been shown to evolve following the parabolic law with the oxidation time in the range of 900-1300 °C [4,5]. In addition, recent experiments have investigated the morphology of the isothermal oxidation at 1200 °C over 100 h [6]. Their results show the formation of a TiO_2 layer covering an inner SiO_2 layer where the oxidation process is believed to evolve by a simultaneous inward diffusion of oxygen and outward diffusion of titanium. We investigate the surface oxidation process at high temperatures by MD simulations, trying to elucidate this mechanism. We start from the atomic geometries of the O_2 and H_2O oxidation obtained at 0 K. Figure 4 shows a snapshot of the oxidation processes for the different surfaces after 1 ps of MD simulation at 1400 °C. Our results show that the Ti1(C) surface notably preserves its structure at high temperatures forming strong TiO_2 cover layer, where the only atomic diffusion observed during the simulation time are due to the hydrogen atoms which continuously desorb and adsorb from the Ti surface. The Ti2(Si) surface also shows a TiO_2 cover but it suffers strong tensions because of the mobility of the subsurface Si atoms, which show an increase amorphization with temperature.
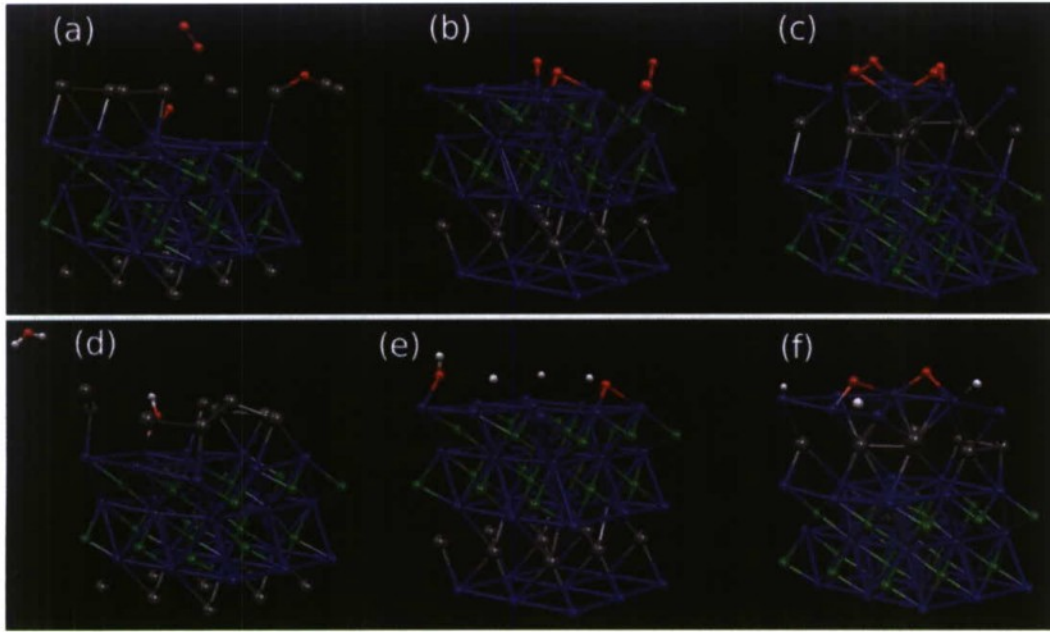
Figure 4. Snapshot of O_2 and H_2O molecules reacting with the most stable surfaces after 1 ps of MD simulations at 1400 °C. (a) and (d) Si(Ti2); (b) and (e) Ti1(C); (c) and (f) Ti2(Si).

For the Si(Ti2) surface the oxidation depend on the molecule. H_2O is physisorbed on Si(Ti2) and because of the high mobility of the Si atoms with temperature, the water molecule cannot reach the Ti subsurface and therefore no oxidation is observed. For O_2 the dissociation take place at the subsurface Ti layer, where the O atoms form both TiO_2 and SiO_2 bonding structures, but at high temperatures the Si-O-Si structures are removed from the Ti subsurface.

According to our results, two scenarios for the $Ti_3SiC_2(001)$ oxidation at high temperatures can occur: (i) On Ti-terminated surfaces, a TiO_2 cover layer is formed after the dissociative reaction with O_2 and H_2O. On the Ti1(C) termination, the TiO_2 cover is strong enough to resist high temperatures, preserving its integrity. Whereas on Ti2(Si), the TiO_2 cover undergoes strong tensions due to the high mobility of the subsurface Si layer which eventually can destroy it. If this occurs, the inner Si layer is left exposed to oxygen producing an underneath SiO_2 layer, which could explain the experimental observations [6]. (ii) On Si-terminated surface, the oxidation only takes place after the dissociative reaction of O_2 with an exposed subsurface Ti layer. The O atoms form a SiO_2 layer weakening the Si-Ti bonds, which at high temperatures can remove SiO_2 structures. Our results also show that neither oxygen nor titanium atoms diffuse inside the material. The O atoms tend to form strong bonds with the Ti and Si substrates, which can survive at high temperature up to 1400 °C.

IV. Conclusions

- The most stable surfaces of $Ti_2SiC_3(001)$ are those terminated in Si(Ti2), Ti1(C) and Ti2(Si), suggesting that are likely to form.

- For Si(Ti2), the surface Si atoms reconstruct forming Si-Si bonds open clearance, exposing the Ti subsurface.

- Ti1(C) notably preserves its structures at high temperatures up to 1400 °C.

- The O_2 and H_2O molecules spontaneously dissociate after reaching the surfaces, forming SiO_2 and TiO_2 cover layer.

- Si-O-Si structures are easily removed from the surfaces with temperature, whereas TiO_2 structures are much stronger, remaining at the surface.

- The Ti and O atoms do not penetrate inside the bulk structure of Ti_2SiC_3.

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[6] H. B. Zhang, Y. W. Bao, and Y. C. Zhou, J. Mater. Sci. Technol. **25**, 1 (2009).