Ab initio Study on the Adsorption Mechanism of Oxygen on Cr₂AlC (0001) Surface

Neng Li,^{1,2,3} Ridwan Sakidja,³ and Wai-Yim Ching³

¹State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology, 122 Luoshi Road, Wuhan, 430070, P.R. China

²Center for Photovoltaics and Solar Energy, Shenzhen Institutes of Advanced Technology, Chinese Academy of Sciences, Shenzhen, 518055, P. R. China.

³Department of Physics and Astronomy, University of Missouri-Kansas City, Kansas City, Missouri, 64110, USA

ABSTRACT

We performed an investigation of the early stage oxidation of the technologically relevant Cr₂AlC (0001) surface by *ab initio* calculations. In this work, the geometrical structure, bonding character, and electronic structure of the Cr₂AlC (0001) bare surface with or without single oxygen atom and molecular adsorption had been systematically investigated by DFT calculation. Four possible terminations Al-, Cr(C)-, C- and Cr(Al)- terminated Cr₂AlC (0001) surface are considered. The corresponding surface energies of the four configurations are compared, indicating that the Al- and Cr(C)-terminated surfaces are more stable than the other two cases C- and Cr(Al)-terminated surfaces. For the most stable case, Al-terminated Cr₂AlC (0001) surface, a detailed model describing the oxygen-surface interactions is developed by assessing the adsorption energetics of various adsorption mechanisms. Based on the evaluation of the energetics and the structural properties of the atomistic models generated, the results point to a consistent picture of the initial stage of the Cr₂AlC (0001) surface oxidation resembling that of (111) layer of pure Al FCC phase .

Keywords: MAX Phases, Cr₂AlC; Surface structure; Oxidation

I. Introduction

The MAX phases have the general formula 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 C or N. In recent years, MAX phases attracted a great deal of research activities, in both in the experimental and simulation fields [1-4]. In the experimental aspect, various properties of MAX phases including oxidation resistance, mechanical and electrical properties have been investigated [3, 4]. In the simulation aspect, the studies are concentrated on the atomic and electronic structures [5-7], phase stability [8-12], elastic and mechanical properties of bulk MAX phases [13-20]. However, theoretical studies that focus on the early stage of the oxidation mechanisms of MAX phases had

rarely been reported despite the growing interests in applying MAX phases as corrosion resistant coatings [21-24]. In addition, there has been a limited understanding of the surface properties and the oxygen adsorption onto the surface during corrosion [25-27]. Cr_2AlC is one type of MAX phases has recently attracted considerable interest due to its excellent high-temperature oxidation and hot corrosion resistance [26, 28-30]. The crystal structure of a Cr_2AlC compound can be described as stacks of nano-laminate comprised of metal carbides that are separated by a continuous layer Al atoms [31]. Since Cr_2AlC forms a continuous protective alumina scale on the surface at high temperature [26], it can potentially be used as protective coatings. However, there are only long-term experimental oxidation database that are available thus far [26, 28-30]. Clearly, the interaction of oxygen molecules at the initial stage with the MAX surface would be very critical in establishing the key alumina formation and thus, should be explored further. Indeed, the oxidation of the Cr_2AlC (0001) surface is a complex reaction involving multi-component and sometime competing atomistic processes, and thus our objective for this work to gain a better insight on the initial oxidation reaction.

Since experimental results showed that thin films of the MAX phase typically grew along the (0001) direction [32, 33] , and several theoretical investigations [34-37] found the (0001) surfaces is the most the stable surface of MAX phases, we concentrated our study on this particular orientation. Thus, the purpose of this work is to elucidate the atomistic mechanisms and local bonding that underlie the (0001) surface oxidation of Cr_2AlC once it is exposed to single O atom and O_2 molecule. The study evaluates the adsorption mechanisms of single oxygen atom and single oxygen molecule. In addition, we present a complementary study to describe the progressive surface oxidation based on the evaluation of the energetics of the key atomistic processes involved during the adsorption process. The electronic structure and charge transfer of the final configuration for single oxygen atom and molecular adsorption are calculated and discussed. The findings of the present investigation are not only useful for understanding the high-temperature oxidation mechanism but also important for the technological applications of Cr_2AlC -based coatings.

II. Methodology

To perform efficient surface structure and O adsorption simulations on Cr_2AlC (0001), we employed two well-established DFT-based *ab initio* methods; the plane-wave projector-augmented wave method as implemented in Vienna *ab initio* simulation package (VASP) [38-40] and the orthogonalized linear combination of atomic orbitals methods (OLCAO) [41, 42] as implemented in the OLCAO package. The OLCAO package has been used in many previous studies to analyze electronic structures in complex bulk materials and interfaces [43-49]. The structural relaxation is carried out by using VASP whereas the bonding analysis and electronic structure are calculated using the OLCAO method. For structural

relaxation, the PAW-PBE potential [50] with generalized gradient approximation (GGA) as supplied in the VASP is used for the exchange-correlation potential. It is well known that different exchange correlation approximations could affect the accuracy of the surface energy. The surface energies calculated by the GGA were often lower than the experimental values [51, 52]. For some TM-elements, such as Cr, DFT+ U will be more reliable than GGA. However, reasonable results can be obtained under the GGA when the main objective is to predict the relative stability of various surface configurations by means of comparing surface energy differences[53-56]. We used a cutoff energy of 400 eV, a relatively high accuracy for the ground state electronic convergence criterion (10^{-5} eV) and force convergence limit (10^{-2} eV/Å). The stress level of the final equilibrium structure is less than 0.01 GPa. The relaxation of the present model imposes no restrictions on the volume and lattice vectors of periodic supercell. For the bulk relaxation, the $10 \times 10 \times 2$ k -points mesh was used over VASP. Then, we generated four possible (0001) surface models and relaxed with the $10 \times 10 \times 1$ k -point mesh. Here, we tested the cohesive energy of an 11-layered Ti(C)-terminated surface slab. When increasing the cut off energy to 700 eV and the k -point mesh to $15 \times 15 \times 1$, the cohesive energy difference lies within 0.003 eV/atom. This indicated that the present calculation parameters were sufficiently accurate to describe the surface configurations. To examine the key mechanisms for preferential sites, we map out various hypothetical diffusion pathways for a given molecule of oxygen being adsorbed on the (0001) surface of Cr_2AlC . For this, we employed the climbing Nudged Elastic Band (NEB) analysis using VASP's Transition State Theory (TST) tools [57] to estimate the diffusion barriers. For OLCAO calculation, a full basis set consisting of atomic orbitals of Cr, Al, C and O, and $4 \times 4 \times 2$ k -mesh are used for the self-consistent electronic structure calculation. More details on the OLCAO calculation are provided in the next section.

III. Results and discussion

A. Surface relaxation and surface energy

Prior to evaluating the effect of the adsorption of O atom on Cr_2AlC (0001) surface, we first calculated the energetics on the bare Cr_2AlC (0001) surfaces to assess the effect of terminating layers in the surface energy. By cleaving from the Cr-C and Cr-Al bonds in Cr_2AlC , four possible terminations; Al-, Cr(C)-, C- and Cr(Al)-terminated Cr_2AlC (0001) surfaces can be generated. In this work, we adopted the model from the literature [58] for the surface calculations. For Al- and C-terminated surfaces, 13-layer slabs are considered, while for Cr(C)- and Cr(Al)-terminated surfaces, 11-layer slabs are used here. Following the procedure described by Wang et. al as reported in Ref. [58], the cleavage surfaces are created by breaking the M-A bond in MAX phase ($M = \text{Ti}, \text{V}, \text{Cr}$) using 7-, 11-, 15- and 19-layered M(C)-terminated surface slabs and 9-, 13-, 17- and 21-layered Al-terminated surface slabs. The cleavage energy difference between

the calculation using 11- and 19-layered M(C)-terminated surface slabs was calculated to be only 0.010 J m⁻². This indicated that a slab of 11 atomic layers was thick enough for our purpose. All simulations utilized slabs that were separated by a vacuum of 15 Å thick to avoid unphysical interactions between two adjacent surfaces. To account for a potential surface size effect, three different surface sizes, namely, 1×1, 2×2 and 3×3 supercells were considered. All surface configurations were fully relaxed without any symmetric constraints. Figs. 1(a-d) show that these four Al-, Cr(C)-, C- and Cr(Al)-terminated (0001) surface configurations with 3×3 supercells.

To describe the change in the surface structure after relaxation more clearly along the z axis, the atomic displacement δZ on the different layers are introduced and the results are summarized in Table 1, where the positive values refer to a larger separation distance. As shown in Table 1, relaxation of deeper layers in 3×3 surface is rather small for all cases, because of the surface effect of the big surface size is smaller than small surface (1×1 and 2×2 supercells). In addition, all atom move to vacuum direction (outward) in both Al- and Cr(Al)-terminated cases, while in C-terminated surface, atoms in first and the third layers move inward. For Cr(C)-terminated case, most of atoms move to outward except for the first layer atoms. Moreover, the $\delta Z_{3\times 3}$ with all four surface configurations of 3×3 supercells are smaller than 1×1 and 2×2 supercells surface, which indicates 3×3 supercell surfaces is more stability than the other two supercells surface. This trend is also observed from interlayer distance calculations which will discussion in the next graph.

The relative displacements of the near-surface layers Δd_{ij} are introduced for describing the change in the surface structure after relaxation. The parameter Δd_{ij} is defined as the change in the interlayer distance measured from the ith layer atoms to the nearest layer (jth) atoms along the z-direction. The side view of 3×3/Al-terminated Cr₂AlC (0001) surface with the definition of the relative displacements of the near-surface layers Δd_{12} , Δd_{23} , Δd_{34} , and Δd_{45} are summarized in Table 2. The definition of the relative displacements of the other three cases [Cr(C)-, C- and Cr(Al)- terminations Cr₂AlC (0001) surfaces] is similar with the one for the Al-terminated case. The calculated results of relative displacements of the near-surface layers (as a percentage of the bulk crystal lattice parameter c) for four-terminated Cr₂AlC (0001) surfaces with 1×1, 2×2 and 3×3 supercell are also summarized in Table 2.

As listed in Table 2, for 3×3 supercells surface, the percentage change of the interlayer distances increases in the order Δd_{12} (Al-terminated) < Δd_{12} (CrC-terminated) < Δd_{12} (CrAl-terminated) < Δd_{12} (C-terminated). In more general terms, we may tie the amount of relaxation to the “surface roughness,” which is defined [59] as the inverse of the fraction of the area in z-plane occupied by atoms of radii equal to one-half the bulk nearest-neighbor distance. For the Al-, CrC-, CrAl- and C-terminated (0001) surfaces of Cr₂AlC, the rough nesses so defined are 1.20, 1.70, 2.08 and 2.94, respectively. We hence have a simple picture that the “rougher” surfaces have bigger percentage relaxation of interlayer distances.

In the present work, surface energy E_{surf} (J/m²) of Cr₂AlC (0001) surface calculations were carried out according to Wang et. al definition [58], and the results are summarized in Table 3 with the relaxation energies E_{rel} (J/m²). The previous reported surface energy of Cr₂AlC (0001) surface [58] are also enclosed here for a comparative study. As is seen in Table 3, for 1×1 and 2×2 supercells surface, our calculated surface energies are consistent with results in Ref. [58, 60] confirming the reliability of our approach. For 3×3 supercells surface, the calculated surface energies of four terminated cases using 3×3 supercell surfaces are in general smaller than those in 1×1 and 2×2 surface supercells indicating large surface size is more stable than the other two cases. Moreover, a larger surface area provides more contact opportunities between sorbents and sorbates. This consequently results in higher sorption capacity for many sorbents. Thus, larger surface size in the 3×3 supercell is adopted here for the oxygen adsorption analysis. Nevertheless, in each case, the calculated surface energy of Al-terminated Cr₂AlC (0001) surface is always smaller than the other three terminated surface indicating that the Al-terminated Cr₂AlC (0001) surface is the most stable. Based on the above surface energy discussion, therefore, the rest of the discussion will focus only on the Al-terminated Cr₂AlC (0001) surface with 3×3 surface supercells with single oxygen atom and molecular adsorption.

B. Adsorption structure and adsorption energy

(a) Single oxygen atom adsorption on Cr₂AlC (0001)

The single O atom is initially placed on four different sites: Top (T), Bridge (B), FCC (F)- and HCP (H)- hollow sites of the relaxed Al-terminated Cr₂AlC (0001) surface, which is comprised of 13 atomic layers of 3×3 supercell separated by a vacuum of 15 Å. The first Cr layer is positioned underneath the Al layer and C layer is sandwiched between the two consecutive Cr layers forming layered “CrC clusters”, then the pattern is repeated back to the Al layer (see Fig. 2). Our use of terminology “HCP-hollow (H)” as well as “FCC-hollow (F)” terms here is only meant for convenience for discussions as they are related to oxidation mechanisms on the (001) surface of pure Al-FCC. The layer sequence of “FCC-like” ABC for the MAX phase implies the “A” layer being the Aluminum layer, “B” layer as the Chromium layer and “C” as the Carbon layer (Fig. 2). The adsorbed structures are also relaxed and the absorbed O atom resides to its relaxed z position on each specific sites. The oxygen-surface interactions on the (3×3)/Al-terminated Cr₂AlC (0001) surface is performed by exploring thoroughly the adsorption energetics (E_{ads}) as defined by subtracting the sum of total energy of half optimized O₂ ($\frac{1}{2} E_{\text{O}_2}$) and bare surface (E_{surf}) from total energy of adsorption system (E_{ads}) [61]

$$\Delta E_{\text{ads}} = (E_{\text{ads}} - E_{\text{surf}} - \frac{1}{2} E_{\text{O}_2}) \quad (1)$$

where E_{ads} and E_{surf} are the total energies of the final adsorbate system and the bare (3×3)/Cr₂AlC(0001) surface, respectively, and E_{O_2} is the total energy of a free O₂ molecule in its ground state, computed in a box of side 20 Å. Here, it should be addressed that there is an overestimated exchange energy in the over binding of O₂ in DFT due to the absence of over binding in density functional theory (DFT). Thus, GGA functionals are adopted in the present work owing to the over binding of the oxygen molecule is will reduced when GGA functionals are used. But there is still a significant over binding is present for the oxygen molecule even within the GGAs. However, there is over binding of O₂ molecular, our discussions on the adsorption energy are reliable due to the same method for the computed adsorption energy of the four adsorption configurations. With this sign convention, a positive value of the adsorption energy corresponds to the energetic gain of an exothermic reaction. In general, a negative E_{ads} indicates that the oxygen adsorption is exothermic and thus the adsorption system is energetically stable. The relative comparison quantitatively between calculated E_{ads} for different atomic geometries of the same adsorption system is the focus of our study.

The adsorption energy of the corresponding geometrical structures is presented in Table 4. One can clearly see that from Table 4, the FCC-hollow (F) site is the most stable binding site for single O atom with adsorption energy of -5.696 eV. The second most favorable adsorption energy, -5.233 eV of O is for the HCP-hollow (H) site. The top (T) and bridge (B) sites exhibit much less favorable adsorption energy of -3.179 and -3.292 eV respectively. These sites may be considered as transition states the O to diffuse on Cr₂AlC (0001) surface between the two more preferred FCC and HCP-hollow sites. Similar to that observed in the Al FCC phase, these two sites are the more favorable sites on the Al layer despite the fact that in MAX phases the atom types constructing the “B” and “C” layers structure placed underneath the Al layer are not made of Al. In the case of FCC Al, the FCC hollow site is actually the one with the lowest binding energy followed by the HCP-site with slightly lower binding energy. In addition, the magnitude of the binding energy is 1 ~ 2 eV higher (e.g. FCC site = -7.65 eV [62]) than our results for the MAX phase. To some extent this can be explained by the nature of the bonding mechanism that within the MAX phase.

The interlayer directional bonding between the A layer and the (Cr+C) layer is typically weaker than the strong Cr-C bonds exist within the “CrC clustered” layer [1]. As results, the A layer’s response to the oxidation, at least at the initial stage, may be quite similar to that observed on Al-FCC with the (111) terminating plane meaning that the oxygen adsorption may be governed mostly by the interaction with the top Al layer and its interaction with the oxygen. Nevertheless, there is indeed a difference in terms of the nature of the interlayer bonding between the FCC and the layered Cr₂AlC as for the MAX phase, there is a directional bonding connecting the Al layer and the Cr and C atoms resided in the layers underneath it. These directional bonds are much stronger than that of Al-Al metallic bonding present within the FCC metal [63]. It is thus reasonable to assume that as a consequence, the Al-O binding energy on the Cr₂AlC

(0001) surface should be less in magnitude than of that of Al-O on Al-FCC. Nevertheless, this suggests there is a linkage between the oxidation response of the FCC Al and Al-containing MAX. In addition, the additional contribution from the additional ionic bonding between Cr and O could not be neglected and quite possibly skews the site preference toward the FCC site.

(b) Single oxygen molecular (O_2) adsorption on Cr_2AlC (0001)

To study the O_2 adsorption on the Cr_2AlC (0001), four possible configurations are selected for the perpendicular approach of the molecule to the Cr_2AlC (0001) surface as shown in Fig. 4 (a-d). In the present work, initially, the O_2 was placed away from the surface at a distance of 1.806 Å, which is comparable to the distance (1.807 Å) reported in the Ref. [64]. To find the approximate stable adsorption configuration and obtain the system energy as a function of the separation, the structure of the Cr_2AlC and the O-O bond lengths (1.238 Å) of the O_2 molecule, and the distance between the Cr_2AlC (0001) surface and the molecule all are relaxed. In each full relaxation process, the O_2 molecular bond breaks readily forming two single oxygen atoms ($O_2 \rightarrow 2O^*$), and then the two O atoms occupied FCC-hollow or HCP-hollow sites creating Al-O ionic bonds with the surrounding Al atoms on the (0001) surface. For the two separate oxygen atoms adsorption cases, six configurations of two oxygen atoms adsorptive on 3×3 /Al-terminated (0001) surface are considered, and total energies of these configurations are calculated and depicted in Fig. 5. As shown in Fig. 5, we know that the most stable configuration of O_2 molecular adsorption on Cr_2AlC (0001) is the case that two oxygen atoms ride on FCC-FCC sites, and form “O-Al-O” cluster with the total energy - 924.765 eV. In the configuration, as we know, the molecule is able to fit optimally into the electron density valley that exists around the “Al+C” hexagon center suggesting oxygen prefer to form cluster in the Cr_2AlC (0001) surface.

For further explored the minimum energy path (MEP) between a given initial and final state of a transition, the total energy associated with the adsorptions sites are plotted in Fig. 4. We chose this process because it is complex and the saddle point is quite far removed from a straight line interpolation between the initial and final states. The evaluation on the surface adsorption of oxygen allows us the opportunity to gain a more in-depth analysis on the diffusion mechanism of oxygen molecules on the surface. This understanding has a direct and profound impact to the overall mechanisms of the oxygen layer formation on the surface of Cr_2AlC . It is well understood that the key to the excellent oxidation resistance of MAX phase such as Cr_2AlC is the ready formation of a continuous later of alumina on the surface[26, 65-68]. We have established in the previous section (Section A) that the Al -only (0001) layer has the lower surface energy and thus is more likely to be the most stable terminating surface. This is one of the main reasons as to why the formation of an aluminum oxide can readily take place upon exposure. However, it was still

unclear as to why a continuous layer of alumina can form. Please note maintaining a full contiguity of the oxide scale is very critical since in the absence of such a continuous layer of alumina, a possible direct access of oxygen onto MAX surface may result in the formation of metal oxides and/or gaseous products such as CO/CO₂, none of which will be a viable strategy for a good high-temperature oxidation resistant phase. Thus, there must be a mechanism by which a clustering of aluminum oxide to take place. We examined this key mechanism more carefully by mapping the whole diffusion pathways for a given molecule of oxygen being adsorbed on the (0001) surface of Cr₂AlC. For this purpose, we employed the Nudged Elastic Band (NEB) analysis using VASP's Transition State Theory (TST) tools [57] to estimate the diffusion barriers. Fig. 4 below shows the relative energy barrier of various configurations (R1-R6) of the molecule on the surface. We note of the following important findings:

1. The most preferred site turns out to be the short-range cluster of alumina wherein the two adjacent oxygen atoms sit on the FCC site (i.e. R1) or (FCC-FCC)_s. The cluster formation has an energy formation that is 0.2 eV lower than that of a long-range FCC-FCC cluster (namely R2)
2. The energy landscape on the various movements of two oxygen atoms on the surface give a much clearer picture now of the potential challenge in establishing a short-range cluster in R1 which is a precursor to a continuous later of alumina. This is despite the fact that R1 actually does possess the lowest energy. For example, to migrate from a long-range FCC-FCC clusters (i.e R2), the oxygen molecule will have to overcome two subsequent barriers; one is to migrate from its position R2 into a short-range FCC-HCP position (R3) and then to move from R3 to R1. The same can be said to move from a long cluster of HCP-HCP (R6) to a short-range cluster of HCP-HCP (R5). Nevertheless, with a higher temperature, more likely these barriers will be overcome and a short-range cluster can be established. This partly explains as to why a continuous layer formation of alumina is much more stable at higher temperature.
3. The revelation of this complex energy landscape nevertheless allows us to now to construct a better strategy/criteria to enhance the oxidation resistance in Cr₂AlC, namely; 1) stabilization of (0001) Al should be encouraged to ensure the initiation of alumina cluster and 2) the various energy barriers to migrate the oxygen molecule on the (0001) Al surface must be minimized as low as possible so as to allow the formation of alumina clustering. Further, these strategies should have been applicable to the other MAX phases and we are evaluating this in the current quarter.

(c) Surface relaxations of adsorption system

The calculated surface geometries of the bare (3×3)/Al-terminated (0001) surface, O@FCC (single O atom), and O₂ @ (FCC-FCC)_s (single O₂ molecular) are shown in Fig. 5. The figure shows that for both single O atom and O₂ molecular adsorption cases, the presence of oxygen pushes its three Al neighbors

radially away (0.03 Å and 0.01 Å) but at the same time it attracts the Al atoms as evidenced by Al atoms being lifted up [see Fig. 5 (d-f)]. For O @ FCC and O₂ @ (FCC-FCC)_s (R1), there are also a counteracted downward movement of the non-O-coordinated Al atom, leading to a modest first and second layer buckling of 0.05 Å and 0.01 Å, respectively. For the O @ FCC, the oxygen-induced increase of d_{12} and results in a +2.0% expansion with respect to the clean surface interlayer distance. Also, d_{23} is expanded (+0.9%). Going to O₂ @ (FCC-FCC)_s (R1) structure, the buckling is less pronounced than O @ FCC case. We now find a buckling of 0.01 Å for the first Al layer and of 0.02 Å for the second one [see Fig. 5(f)]. The overall relaxation pattern remains very much the same as before: The oxygen adatoms are slightly pushed away from the highest coordinated Al atoms, and the first and second interlayer spacing are slightly expanded (now by +0.5% and +1.8%). It therefore comes as a surprise that this layer relaxation trend is not continued, and it is even reversed, for O₂ @ (FCC-FCC)_s (R1). We find that the d_{12} distance is reduced (compared to the interlayer spacing of O @ FCC) by -1.9%, while concerning d_{23} , we obtain an expansion of +1.0%.

C. Charge transfer, and interatomic bonding

To quantitatively investigate the charge transfer and interatomic bonding of bare surface and oxygen adsorption systems, we have calculated the effective charge (Q^*) and bond order (BO) values of O @ FCC and O₂ @ FCC-FCC cases according to Eqs. (2) - (3):

$$Q_{\alpha}^* = \sum_i \sum_{n,occ} \sum_{j,\beta} C_{i\alpha}^{*n} C_{j\beta}^n S_{i\alpha,j\beta} \quad (2)$$

$$\rho_{\alpha\beta} = \sum_{n,occ} \sum_{i,j} C_{i\alpha}^{*n} C_{j\beta}^n S_{i\alpha,j\beta} \quad (3)$$

Where i and j label the orbital quantum numbers of atoms α and β , and n is the band index. $S_{i\alpha,j\beta}$ is the overlap matrix and $C_{j\beta}^n$ is an eigenvector coefficient of the wave function. In this work, the effective charge of the atom is defined as the number of the valence electrons on this atom based on the Mulliken scheme [69] which requires the use of more localized orbital. Hence a minimal basis is used for this purpose. Based on the adsorption energy calculation, we concluded that the FCC and (FCC-FCC)_s (R1) sites are the preferred site for single O atom and O₂ molecular cases. We then performed the Mulliken effective charge and interatomic bonding of these two adsorption systems to shed some lights on the mechanism of electron transfer and adsorption process for a single O atom and single O₂ molecular qualitatively. Those of pure Al-terminated (0001) surfaces are also presented here for comparison (see Table. 5).

The calculated Mulliken effective charge Q^* (electron) for the Al-terminated Cr₂AlC (0001) surface with and without single oxygen atom (FCC site) are also presented in Table 5. From Table 5, one can clearly see that, for bare Al-terminated Cr₂AlC (0001) surface, Q^* on Al_s and Cr_{subS} are smaller than their

counterparts in the crystalline case indicating a larger charge transfer from Al_S and Cr_subs ions in the surface model. While for Al_NB and Cr_B are just slightly larger than their counterparts in the bulk suggesting there are a lit bit of change in Q^* of their of the crystalline. The same is true for C_subs and C_B ions. The Q^* for all ions in $\text{O-3}\times\text{3/Cr}_2\text{AlC}$ (0001) follow a similar pattern but with a much larger and complex variation from the pure surface case and, for the all ions in $\text{O-3}\times\text{3/Cr}_2\text{AlC}$ (0001), the change in Q^* from the crystalline value is not large except for Al_S . An interesting observation is that Q^* for all ions in $\text{O-3}\times\text{3/Cr}_2\text{AlC}$ (0001) are different between the two layers (higher part and lower part). The general picture that emerges from the above analysis is that there are larger charge transfers in the surface models with single oxygen atom adsorption than in bare surface and in bulk crystals, or that the adsorption system as a whole is more ionic. The charge transfer is generally larger in $\text{O-3}\times\text{3/Cr}_2\text{AlC}$ (0001) than in pure $3\times 3/\text{Cr}_2\text{AlC}$ (0001).

The calculated BO values for Al-Al, Cr-Al, Cr-Cr, and Cr-C pairs of pure $3\times 3/\text{Al}$ -terminated Cr_2AlC (0001) surface with and without oxygen adsorption models are summarized in Table 6. The BO value of $\text{Al}_\text{S}-\text{O}_\text{ads}$ pair of two adsorption systems are also list in here. As Table 6 shows that all the BO values for Al-Al, Cr-Al, Cr-Cr, and Cr-C pairs in $(3\times 3)/\text{Al}$ -terminated Cr_2AlC (0001) without and with oxygen are slightly difference except for $\text{Cr}_\text{subs}-\text{Al}_\text{S}$ pair. For crystalline Cr_2AlC , from Table 6, one can clearly see that Cr-C bond order value is 0.175, Cr-Al bond order value is 0.112, and the bond other for the other two cases (Al-Al and Cr-Cr) are 0.077 and 0.014, respectively, suggesting Cr-C is the most strongest bond, and Cr-Al bond is also strong bond while Al-Al bond and Cr-Cr bond are relatively week bonds in bulk Cr_2AlC . For pure $3\times 3/\text{Al}$ -terminated Cr_2AlC (0001) surface, a careful inspection of Table 6 reveals that the Al ions at the surface have fairly large BO values ($\text{Al}_\text{S}-\text{Al}_\text{S}$ bond) compared with those in the crystal and at the interior portion ($\text{Al}_\text{NB}-\text{Al}_\text{NB}$) of the surface model. The relatively strong $\text{Al}_\text{S}-\text{Al}_\text{S}$ bonds at the surface is one of the reasons for the stability of this (0001) model compared to other models with different terminations. While for $\text{O-(3}\times\text{3)/Cr}_2\text{AlC}$ (0001) system, as shown in Table 6, the bond order value of the $\text{Al}_\text{S}-\text{Al}_\text{S}$ pair (0.139) in $\text{O-(3}\times\text{3)/Cr}_2\text{AlC}$ (0001) is larger than it (0.121) in pure $(3\times 3)/\text{Cr}_2\text{AlC}$ (0001) surface suggesting adsorption oxygen atom effect on the geometry structure of surface model resulting $\text{Al}_\text{S}-\text{Al}_\text{S}$ bond more stronger. The bond order value of $\text{Al}_\text{S}-\text{O}_\text{ads}$ in $\text{O-(3}\times\text{3)/Cr}_2\text{AlC}$ (0001) system is 0.165, indicating $\text{Al}_\text{S}-\text{O}_\text{ads}$ bonding is the very strong in adsorption system and highly covalent binding strength with Cr_2AlC (0001) surface. However, the bond order of $\text{Cr}_\text{subs}-\text{O}_\text{ads}$ bond is negative (-0.071), which suggests $\text{Cr}_\text{subs}-\text{O}_\text{ads}$ bond is unstable or not exists in here. The above bond order analyses are also supported by the bond length analysis of the pure surface and oxygen adsorption systems [see Table 6]. As shown in Table 6, all bond lengths in surface model are relatively smaller than it in crystalline case, as a result the bond order value are larger than those in bulk.

D. Electronic structure

To gain insight into how it evolves as single O and O₂ molecule is adsorbed, the total density of states (DOS) of Al atom of bulk, pure surface, and single O atom/ or single O₂ molecular adsorption systems are plotted in Fig. 6(a-b). The DOS of O adsorption atom for two adsorption cases are also presented here. Compared the DOS of Al in bulk Cr₂AlC [as shown in Fig. 6(a)] and the pure (3×3)/Al-terminated Cr₂AlC (0001) surface [as shown in Fig. 6(b)], the most significant change is mostly the higher number of states at the Fermi level which suggests that by forming a (0001) Al surface, the change in chemical bonding compared to the bulk is quite small. Once again it suggests that it is more likely to form a surface with Al atoms as the top layer. For the two oxygen atoms adsorption cases [see Fig. 6(c-d)], the effect of the oxygen adatoms on the DOS with respect to the bulk is the introduction of additional states represented by small peaks around the energy region from -10 eV to -4 eV and also the higher number of states at the Fermi level. Moreover, after the adsorption of O atom, in the valence band below Fermi level, the Al DOS overlap with the DOS of the adsorbed O atoms, indicating the hybridization of the Al with O atoms [70].

To further understand the bonding of the O atom with the Al-terminated Cr₂AlC (0001) surface, the differences of the DOS of Al atom in different systems are presented in Fig. 7. As shown in Fig. 7(a), one can see that by forming a (0001) Al surface, the change in chemical bonding is notable compared that to the bulk. Once again it suggests that it is more likely to form a surface with Al atoms as the top layer. After the adsorption of O atom, as shown in Fig. 7(b-c), the general features at the around Fermi level are similar with the Fig. 7(a), except for the order of magnitude. From Fig. 7(b-c), one can clearly see that the DOS of Al is smaller than that in clean surface near Fermi level suggesting that after the adsorption of O atom, the apparent electron accumulation on the adsorbed O atom and the electron depletion on the Al surface atom not surprisingly indicate the ionic bond characteristics between the Al and O atoms. It also indicates that the charge is transferred from the Al surface atom to the O atom, which has been supported by the above Milliken effective charge analysis. On the other hand, there is almost no electron transfer detected between the adsorbed and subsurface Cr atoms, indicating that there is little interaction between them. Moreover, the difference DOS (DDOS) between the clean and the two adsorption systems are also presented in Fig. 7(d-e), which clearly show that the most significant difference is the curvature at the Fermi level. In the Fermi Level, the DDOS of both single oxygen atom and single oxygen molecular adsorption on the surface has big sharp peak. This can be explained by the fact that electrons in the adsorption cases form stronger bonds with Al in the top layer, and hence have a higher binding energy.

IV. Summary and conclusions

In this paper, density-functional calculations have been performed on Cr_2AlC (0001) surface and in contact with oxygen adsorption, which is a very important step towards understanding the oxidation processes on the MAX phases. In order to determine the convergence of surface energy with respect to surface size and thickness, we tested full relaxations for the (1×1), (2×2) and (3×3) (0001) surface configurations without any symmetric constraint. According to the cleavage energy created by breaking the Cr-Al bond and Cr-C bonds in Cr_2AlC , four possible terminations of Cr_2AlC (0001) surface, Al-, C-, Cr(Al)- and Cr(C)-terminated surface, were considered, and the corresponding surface energies were computed and compared. For the Al- and C-terminated surface, 13-layerer atoms are used, while for Cr(Al)- and Cr(C)-terminated cases, 11-layered atoms are considered in the modeling. The surface energy calculations indicated that the Al- and Cr(C)-terminated surfaces are more stable than the C- and Cr(Al)-terminated surfaces.

For the most stable terminated surface, a detailed model describing the oxygen-surface and oxygen-oxygen interactions is developed by exploring thoroughly the geometrical structure, bonding character, and electronic structure. For the study of the single O atoms adsorption, we observed the site preferences that partly resemble that of (111) of FCC-Al. The energy barriers for various diffusion paths to form a pair of Al-O clusters are identified and calculated. In both cases of the adsorption systems (O and O_2), the general picture are the quite similar, namely, the adatom O strongly bonds to the surface Al and formed Al-O bond resulting in the redistribution of the Mulliken charges and the charge transfer from the Cr_2AlC (0001) surface to the adsorbed O atom.

Acknowledgements

This work is supported by U.S. DOE-NETL, the award FE0005865. This research used the resources of the National Energy Research Scientific Computing Center supported by DOE under Contract No. DE-AC03-76SF00098. This work was also supported by the Natural Science Foundation of Shenzhen under Grant No. JCYJ20130402113127530.

TABLES

Table 1

Atom displacements of the different layers for Al-, C-, CrAl- and CrC-terminated Cr_2AlC (0001) surface with 1×1 , 2×2 , and 3×3 supercells (as a percentage of the bulk crystal lattice parameter c).

Layer	Al-termination				C-termination			
	Atom	$\delta Z_{1\times 1}$	$\delta Z_{2\times 2}$	$\delta Z_{3\times 3}$	Atom	$\delta Z_{1\times 1}$	$\delta Z_{2\times 2}$	$\delta Z_{3\times 3}$
1	Al	0.559	0.687	0.557	C	-1.799	-1.618	-1.524
2	Cr	0.688	0.651	0.646	Cr	1.297	1.211	1.209
3	C	0.446	0.410	0.421	Al	-0.366	-0.239	-0.155
4	Cr	0.295	0.252	0.211	Cr	0.061	0.116	0.114
5	Al	0.128	0.127	0.125	C	0.034	0.097	0.045
Layer	Cr(Al)-termination				Cr(C)-terminaton			
	Atom	$\delta Z_{1\times 1}$	$\delta Z_{2\times 2}$	$\delta Z_{3\times 3}$	Atom	$\delta Z_{1\times 1}$	$\delta Z_{2\times 2}$	$\delta Z_{3\times 3}$
1	Cr	1.738	1.667	1.319	Cr	-0.257	-0.211	-0.175
2	Al	2.376	2.208	1.767	C	0.895	0.648	0.621
3	Cr	1.669	1.584	1.100	Cr	0.269	0.230	0.216
4	C	1.027	0.967	0.665	Al	0.236	0.124	0.105
5	Cr	0.362	0.323	0.217	Cr	0.156	0.085	0.082

Table 2

Atom relative displacements of the near-surface layers for Al-, C-, CrAl- and CrC-terminated Cr_2AlC (0001) surface with 1×1 , 2×2 , and 3×3 supercell (as a percentage of the bulk crystal lattice parameter c).

Al-termination				C-termination			
$\Delta d/\text{supercell}$	1×1	2×2	3×3	$\Delta d/\text{supercell}$	1×1	2×2	3×3
Δd_{12}	-0.046	-0.030	-0.025	Δd_{12}	-1.403	-1.387	-1.384
Δd_{23}	0.169	0.123	0.121	Δd_{23}	0.739	0.719	0.686
Δd_{34}	0.098	0.079	0.075	Δd_{34}	-0.185	-0.174	-0.162
Δd_{45}	0.020	0.019	0.015	Δd_{45}	0.040	0.039	0.012
Cr(Al)-termination				Cr(C)-terminaton			
$\Delta d/\text{supercell}$	1×1	2×2	3×3	$\Delta d/\text{supercell}$	1×1	2×2	3×3
Δd_{12}	-0.412	-0.319	-0.271	Δd_{12}	-0.319	-0.416	-0.224
Δd_{23}	0.354	0.334	0.312	Δd_{23}	0.313	0.209	0.203
Δd_{34}	0.321	0.308	0.218	Δd_{34}	0.055	0.053	0.040
Δd_{45}	0.333	0.322	0.224	Δd_{45}	0.042	0.041	0.016

Table 3

The calculated cleavage energies E_{cle} (J/m²), relaxation energies E_{rel} (J/m²) and surface energies E_{surf} (J/m²) of Al-, C-, CrAl- and CrC-terminated Cr₂AlC (0001) surface with 1×1, 2×2, and 3×3 supercells.

	Bond	E_{cle}	Termination	E_{rel}	E_{surf}	Ref. 47
1×1	Cr-Al	2.479	Al(CrC)	0.102	2.337 (2.321)	2.479 (2.420)
	Cr-C	5.923	C(CrAl)	0.724	5.199 (5.278)	5.093 (5.770)
2×2	Cr-Al	2.385	Al(CrC)	0.001	2.374 (2.377)	
	Cr-C	5.786	C(CrAl)	0.011	5.185 (5.329)	
3×3	Cr-Al	2.382	Al(CrC)	0.081	2.301 (2.375)	
	Cr-C	5.806	C(CrAl)	0.796	5.010 (5.336)	

Table 4

Adsorption energy of an oxygen atom onto different sites at (3×3)/Al-terminated Cr₂AlC (0001) surface.

Adsorption Site	Top	Bridge	HCP-Hollow	FCC-Hollow
E_{ads} (eV)	-3.179	-3.292	-5.233	-5.696

Table 5

Calculated Mulliken effective charge Q^* (electron) of atoms in the different layers of pure $3\times 3/\text{Al}$ -terminated Cr_2AlC (0001) surface and single oxygen atom adsorption on FCC-hollow site of $3\times 3/\text{Al}$ -terminated Cr_2AlC (0001) surface. The “*” indicates the value for the lower surface.

Atomic Layer	bulk	(3×3)/ Cr_2AlC (0001)	O-(3×3)/ Cr_2AlC (0001)	O_2 -(3×3)/ Cr_2AlC (0001)
O	--- --- ---	--- --- ---	6.744	6.715
Al _S	3.127	2.837	2.747, 2.785*	2.664, 2.760*
Cr _{subS}	5.582	5.321	5.694, 5.631*	5.684, 5.637*
C _{subS}	4.709	4.727	4.731, 4.720*	4.737, 4.715*
Cr _{NB}	5.582	5.988	5.577, 5.582*	5.632, 5.626*
Al _{NB}	3.127	3.201	3.172, 3.174*	3.177, 3.180*
Cr _B	5.582	5.484	5.632, 5.649*	5.619, 5.572*
C _B	4.709	4.721	4.727, --- ---	4.726, --- ---

Table 6

Calculated bond order (BO) and bond length (BL) of pure 3×3/Al-terminated Cr₂AlC (0001) surface with single O atom and O₂ molecular adsorption on FCC-hollow site. The numbers of Al_s-O_{ads} in parentheses is the corresponding values in α -Al₂O₃ bulk crystal.

BO	bulk	(3×3)/Cr ₂ AlC(0001)	O-(3×3)/Cr ₂ AlC(0001)	O ₂ -(3×3)/Cr ₂ AlC(0001)
Al _s -O _{ads}	--- ---- ---	--- ---- ---	0.171 (0.165)	0.171
Al _s -Al _s	0.110	0.121	0.139	0.110
Al _s -Cr _{subS}	0.324	0.101	0.092	0.136
C _{subS} -Cr _{subS}	0.043	0.018	0.017	0.016
Cr _{subS} -C _{NB}	0.523	0.180	0.172	0.177
BL(Å)	bulk	(3×3)/Cr ₂ AlC(0001)	O-(3×3)/Cr ₂ AlC(0001)	O ₂ -(3×3)/Cr ₂ AlC(0001)
Al _s -O _{ads}	--- ---- ---	--- ---- ---	1.874 (1.928)	1.855
Al _s -Al _s	2.844	2.828	2.733	2.707
Al _s -Cr _{subS}	2.665	2.656	2.721	2.660
C _{subS} -Cr _{subS}	2.844	2.828	2.980	2.835
Cr _{subS} -C _{NB}	1.962	1.962	1.970	1.960

References

- [1] M.W. Barsoum, M. Radovic, Elastic and Mechanical Properties of the MAX Phases, *Annual Review of Materials Research*, 41 (2011) 195-227.
- [2] Y. Mo, P. Rulis, W.Y. Ching, Electronic structure and optical conductivities of 20 MAX-phase compounds, *Physical Review B*, 86 (2012) 165122.
- [3] Z. Sun, Progress in research and development on MAX phases: a family of layered ternary compounds, *International Materials Reviews*, 56 (2011) 143-166.
- [4] J. Wang, Y. Zhou, Recent Progress in Theoretical Prediction, Preparation, and Characterization of Layered Ternary Transition-Metal Carbides, *Annual Review of Materials Research*, 39 (2009) 415-443.
- [5] X. Qian, Y. Li, X. He, H. Fan, S. Yun, First-principle study of structural and electronic properties of ternary layered Ta₂AlC, *Journal of Physics and Chemistry of Solids*, 72 (2011) 954-956.
- [6] Y. Medkour, A. Bouhemadou, A. Roumili, Structural and electronic properties of M₂InC (M = Ti, Zr, and Hf), *Solid State Communications*, 148 (2008) 459-463.
- [7] D. Music, Z. Sun, J.M. Schneider, Electronic structure of Sc₂AC (A=Al, Ga, In, Tl), *Solid State Communications*, 133 (2005) 381-383.
- [8] C. Li, Z. Wang, C. Wang, Phase stability, mechanical properties and electronic structure of hexagonal and trigonal Ti₅Al₂C₃: An ab initio study, *Intermetallics*, 33 (2013) 105-112.
- [9] J. Frodelius, J. Lu, J. Jensen, D. Paul, L. Hultman, P. Eklund, Phase stability and initial low-temperature oxidation mechanism of Ti₂AlC thin films, *Journal of the European Ceramic Society*, 33 (2013) 375-382.
- [10] M. Dahlqvist, B. Alling, I.A. Abrikosov, J. Rosén, Phase stability of Ti₂AlC upon oxygen incorporation: A first-principles investigation, *Physical Review B*, 81 (2010) 024111.
- [11] J. Wang, Y. Zhou, T. Liao, J. Zhang, Z. Lin, A first-principles investigation of the phase stability of Ti₂AlC with Al vacancies, *Scripta Materialia*, 58 (2008) 227-230.
- [12] J. Wang, J. Wang, Y. Zhou, C. Hu, Phase stability, electronic structure and mechanical properties of ternary-layered carbide Nb₄AlC₃: An ab initio study, *Acta Materialia*, 56 (2008) 1511-1518.
- [13] S. Cui, D. Wei, H. Hu, W. Feng, Z. Gong, First-principles study of the structural and elastic properties of Cr₂AlX (X=N, C) compounds, *Journal of Solid State Chemistry*, 191 (2012) 147-152.
- [14] M.G. Brik, N.M. Avram, C.N. Avram, Ab initio calculations of the electronic, structural and elastic properties of Nb₂InC, *Computational Materials Science*, 63 (2012) 227-231.
- [15] M.A. Ghebouli, B. Ghebouli, M. Fatmi, A. Bouhemadou, Theoretical prediction of the structural, elastic, electronic and thermal properties of the MAX phases X₂SiC (X = Ti and Cr), *Intermetallics*, 19 (2011) 1936-1942.
- [16] S. Cui, W. Feng, H. Hu, Z. Lv, G. Zhang, Z. Gong, First-principles studies of the electronic and elastic properties of Ti₂GeC, *Solid State Communications*, 151 (2011) 491-494.
- [17] Y. Bai, X. He, M. Li, Y. Sun, C. Zhu, Y. Li, Ab initio study of the bonding and elastic properties of Ti₂CdC, *Solid State Sciences*, 12 (2010) 144-147.
- [18] M.B. Kanoun, S. Goumri-Said, A.H. Reshak, Theoretical study of mechanical, electronic, chemical bonding and optical properties of Ti₂SnC, Zr₂SnC, Hf₂SnC and Nb₂SnC, *Computational Materials Science*, 47 (2009) 491-500.
- [19] A. Bouhemadou, Structural, electronic and elastic properties of MAX phases M₂GaN (M=Ti, V and Cr), *Solid State Sciences*, 11 (2009) 1875-1881.
- [20] Z. Sun, S. Li, R. Ahuja, J.M. Schneider, Calculated elastic properties of M₂AlC (M=Ti, V, Cr, Nb and Ta), *Solid State Communications*, 129 (2004) 589-592.
- [21] C.L. Yeh, W.J. Yang, Formation of MAX solid solutions (Ti,V)₂AlC and (Cr,V)₂AlC with Al₂O₃ addition by SHS involving aluminothermic reduction, *Ceramics International*, (2013).
- [22] T. Rampai, C.I. Lang, I. Sigalas, Investigation of MAX phase/c-BN composites, *Ceramics International*, 39 (2013) 4739-4748.

- [23] T.F. Zhang, Q.M. Wang, J. Lee, P. Ke, R. Nowak, K.H. Kim, Nanocrystalline thin films synthesized from a Ti_2AlN compound target by high power impulse magnetron sputtering technique, *Surface and Coatings Technology*, 212 (2012) 199-206.
- [24] J. Yang, L.M. Pan, W. Gu, X.B. Gu, K. Song, T. Qiu, S.M. Zhu, Oxidation behavior and kinetics of in situ $(\text{TiB}_2+\text{TiC})/\text{Ti}_3\text{SiC}_2$ composites in air, *Ceramics International*, 38 (2012) 159-168.
- [25] S. Li, X. Chen, Y. Zhou, G. Song, Influence of grain size on high temperature oxidation behavior of Cr_2AlC ceramics, *Ceramics International*, 39 (2013) 2715-2721.
- [26] Z.J. Lin, M.S. Li, J.Y. Wang, Y.C. Zhou, High-temperature oxidation and hot corrosion of Cr_2AlC , *Acta Materialia*, 55 (2007) 6182-6191.
- [27] D.B. Lee, T.D. Nguyen, J.H. Han, S.W. Park, Oxidation of Cr_2AlC at 1300°C in air, *Corrosion Science*, 49 (2007) 3926-3934.
- [28] D. Lee, S.W. Park, Oxidation of Cr_2AlC between 900 and 1200 C in air, *Oxidation of Metals*, 68 (2007) 211-222.
- [29] D.B. Lee, T.D. Nguyen, Cyclic oxidation of Cr_2AlC between 1000 and 1300°C in air, *Journal of Alloys and Compounds*, 464 (2008) 434-439.
- [30] W. Tian, P. Wang, Y. Kan, G. Zhang, Oxidation behavior of Cr_2AlC ceramics at 1,100 and $1,250^\circ\text{C}$, *J Mater Sci*, 43 (2008) 2785-2791.
- [31] Z. Lin, M. Zhuo, Y. Zhou, M. Li, J. Wang, Atomic scale characterization of layered ternary Cr_2AlC ceramic, *Journal of Applied Physics*, 99 (2006) 076109-076103.
- [32] R. Mertens, Z. Sun, D. Music, J.M. Schneider, Effect of the Composition on the Structure of Cr-Al-C Investigated by Combinatorial Thin Film Synthesis and ab Initio Calculations, *Advanced Engineering Materials*, 6 (2004) 903-907.
- [33] O. Wilhelmsson, J.-P. Palmquist, T. Nyberg, U. Jansson, Deposition of Ti_2AlC and Ti_3AlC_2 epitaxial films by magnetron sputtering, *Applied Physics Letters*, 85 (2004) 1066-1068.
- [34] M. Denis, S. Zhimei, A. Rajeev, M.S. Jochen, Electronic structure of $\text{M}_2\text{AlC}(0001)$ surfaces ($\text{M} = \text{Ti}, \text{V}, \text{Cr}$), *Journal of Physics: Condensed Matter*, 18 (2006) 8877.
- [35] D. Music, Z. Sun, R. Ahuja, J.M. Schneider, Surface energy of $\text{M}_2\text{AlC}(0001)$ determined by density functional theory ($\text{M} = \text{Ti}, \text{V}, \text{Cr}$; $\text{A} = \text{Al}, \text{Ga}, \text{Ge}$), *Surface Science*, 601 (2007) 896-899.
- [36] Z. Sun, R. Ahuja, Ab initio study of the $\text{Cr}_2\text{AlC}(0001)$ surface, *Applied Physics Letters*, 88 (2006) -.
- [37] H.Z. Zhang, S.Q. Wang, First-principles study of Ti_3AlC_2 surfaces, *Acta Materialia*, 55 (2007) 4645-4655.
- [38] G. Kresse, J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, *Computational Materials Science*, 6 (1996) 15-50.
- [39] G. Kresse, J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, *Physical Review B*, 54 (1996) 11169-11186.
- [40] G. Kresse, J. Hafner, Ab initio molecular dynamics for liquid metals, *Physical Review B*, 47 (1993) 558-561.
- [41] W.-Y. Ching, P. Rulis, *Electronic Structure Methods for Complex Materials: The Orthogonalized Linear Combination of Atomic Orbitals*, Oxford University Press, 2012.
- [42] M. Dahlqvist, B. Alling, I.A. Abrikosov, J. Rosen, Magnetic nanoscale laminates with tunable exchange coupling from first principles, *Physical Review B*, 84 (2011) 220403.
- [43] W.Y. Ching, P. Rulis, L. Ouyang, S. Aryal, A. Misra, Theoretical study of the elasticity, mechanical behavior, electronic structure, interatomic bonding, and dielectric function of an intergranular glassy film model in prismatic $\beta\text{-Si}_3\text{N}_4$, *Physical Review B*, 81 (2010) 214120.
- [44] S. Aryal, P. Rulis, L. Ouyang, W.Y. Ching, Structure and properties of the low-density phase $\epsilon\text{-Al}_2\text{O}_3$ from first principles, *Physical Review B*, 84 (2011) 174123.

- [45] W.Y. Ching, L. Ouyang, P. Rulis, H. Yao, Ab initio study of the physical properties of $\gamma\text{Al}_2\text{O}_3$: Lattice dynamics, bulk properties, electronic structure, bonding, optical properties, and ELNES/XANES spectra, *Physical Review B*, 78 (2008) 014106.
- [46] W.Y. Ching, P. Rulis, A. Misra, Ab initio elastic properties and tensile strength of crystalline hydroxyapatite, *Acta Biomaterialia*, 5 (2009) 3067-3075.
- [47] W.Y. Ching, P. Rulis, L. Ouyang, S. Aryal, A. Misra, Theoretical study of the elasticity, mechanical behavior, electronic structure, interatomic bonding, and dielectric function of an intergranular glassy film model in prismatic $\beta\text{-Si}_3\text{N}_4$, *Physical Review B*, 81 (2010) 214120.
- [48] W.-Y. Ching, P. Rulis, *Electronic Structure Methods for Complex Materials: The orthogonalized linear combination of atomic orbitals*, Oxford University Press, Oxford, 2012.
- [49] C.C. Dharmawardhana, A. Misra, S. Aryal, P. Rulis, W.Y. Ching, Role of interatomic bonding in the mechanical anisotropy and interlayer cohesion of CSH crystals, *Cement and Concrete Research*, 52 (2013) 123-130.
- [50] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized Gradient Approximation Made Simple, *Physical Review Letters*, 77 (1996) 3865-3868.
- [51] A.E. Mattsson, D.R. Jennison, Computing accurate surface energies and the importance of electron self-energy in metal/metal-oxide adhesion, *Surface Science*, 520 (2002) L611-L618.
- [52] D. Yu, M. Scheffler, First-principles study of low-index surfaces of lead, *Physical Review B*, 70 (2004) 155417.
- [53] J. Ho, E. Heifets, B. Merinov, Ab initio simulation of the $\text{BaZrO}_3(0001)$ surface structure, *Surface Science*, 601 (2007) 490-497.
- [54] D.E. Jiang, E.A. Carter, Prediction of strong adhesion at the MoSi_2/Fe interface, *Acta Materialia*, 53 (2005) 4489-4496.
- [55] K. Reuter, M. Scheffler, Composition, structure, and stability of $\text{RuO}_2(110)$ as a function of oxygen pressure, *Physical Review B*, 65 (2001) 035406.
- [56] X.G. Wang, W. Weiss, S.K. Shaikhutdinov, M. Ritter, M. Petersen, F. Wagner, R. Schlögl, M. Scheffler, The Hematite (Fe_2O_3) (0001) Surface: Evidence for Domains of Distinct Chemistry, *Physical Review Letters*, 81 (1998) 1038-1041.
- [57] D. Sheppard, P. Xiao, W. Chemelewski, D.D. Johnson, G. Henkelman, A generalized solid-state nudged elastic band method, *The Journal of Chemical Physics*, 136 (2012) -.
- [58] J. Wang, J. Wang, Y.C. Zhou, Stable $\text{M}_2\text{AlC}(0001)$ surfaces ($\text{M} = \text{Ti}, \text{V}$ and Cr) by first-principles investigation, *Journal of Physics: Condensed Matter*, 20 (2008) 225006.
- [59] J. Sokolov, F. Jona, P.M. Marcus, Trends in metal surface relaxation, *Solid State Communications*, 49 (1984) 307-312.
- [60] Z. Sun, R. Ahuja, Ab initio study of the $\text{Cr}_2\text{AlC}(0001)$ surface, *Applied Physics Letters*, 88 (2006) 161913-161913.
- [61] C.R. Ashman, G. Pennington, First-principles study of oxygen adsorption on the nitrogen-passivated $4\text{H-SiC}(0001)$ silicon face, *Physical Review B*, 80 (2009) 085318.
- [62] C. Lanthony, J.M. Ducre, M.D. Rouhani, A. Hemeryck, A. Estve, C. Rossi, On the early stage of aluminum oxidation: An extraction mechanism via oxygen cooperation, *J Chem Phys*, 137 (2012) 094707.
- [63] J.-C. ZHENG, H.-Q. WANG, A.T.S. WEE, C.H.A. HUAN, STRUCTURAL AND ELECTRONIC PROPERTIES OF AL NANOWIRES: AN AB INITIO PSEUDOPOTENTIAL STUDY, *International Journal of Nanoscience*, 01 (2002) 159-169.
- [64] J. Behler, Dissociation of Oxygen Molecules on the $\text{Al}(111)$ Surface, in, TU Berlin, Berli, 2004, pp. 246.
- [65] H.J. Yang, Y.T. Pei, J.T.M. De Hosson, Oxide-scale growth on Cr_2AlC ceramic and its consequence for self-healing, *Scripta Materialia*, 69 (2013) 203-206.
- [66] D.B. Lee, T.D. Nguyen, J.H. Han, S.W. Park, Oxidation of Cr_2AlC at 1300°C in air, *Corrosion Science*, 49 (2007) 3926-3934.

- [67] D.E. Hajas, M. to Baben, B. Hallstedt, R. Iskandar, J. Mayer, J.M. Schneider, Oxidation of Cr₂AlC coatings in the temperature range of 1230 to 1410 °C, *Surface and Coatings Technology*, 206 (2011) 591-598.
- [68] Q.M. Wang, A. Flores Renteria, O. Schroeter, R. Mykhaylonka, C. Leyens, W. Garkas, M. to Baben, Fabrication and oxidation behavior of Cr₂AlC coating on Ti6242 alloy, *Surface and Coatings Technology*, 204 (2010) 2343-2352.
- [69] R.S. Mulliken, Electronic Population Analysis on LCAO [Single Bond] MO Molecular Wave Functions. I, *The Journal of Chemical Physics*, 23 (1955) 1833.
- [70] G.G. Khan, N.R. Bandyopadhyay, A. Basumallick, Ab-initio pseudopotential study of electronic structure and chemisorption of oxygen on aluminium surface, *Journal of Physics and Chemistry of Solids*, 70 (2009) 298-302.

FIGURES

Fig. 1. Four possible surface configurations: (a) Al-terminated surface, (b) C-terminated surface, (c) Cr(C)-terminated surface, (d) the Cr(Al)-terminated surface. For the Al- and C-terminated surface, 13-layerer atoms are used, while for Cr(Al)- and Cr(C)-terminated cases, 11-layered atoms are considered in the modeling.

Fig. 2. Illustration of adsorption of an oxygen atom on $(3 \times 3)/\text{Al}$ -terminated- Cr_2AlC (0001) surface: (a) Bare surface, (b) Four adsorption sites: Top (T) site, Bridge (B) site, FCC-hollow (F) site, and HCP-hollow (H) site.

Fig. 3. Four different adsorption sites of single oxygen molecular on (3×3)/Al-terminated Cr_2AlC (0001) surface: (a) Top site, (b) Bridge site, (c) FCC site, (d) HCP site. The

Fig. 4 Six configurations of an oxygen molecule being adsorbed onto the (0001) Al surface with the corresponding energy barriers to migrate into the adjacent configuration. A short-range cluster of alumina oxide with both oxygen atoms which are positioned on the FCC site is the most preferred site (R1).

Fig. 5. Top and side view of the atomic layers for the stable surface of the (3×3)/Al-terminated Cr₂AlC (0001) surface structure, after ionic relaxation. The interatomic distances for three structures indicate the large relaxation found in the Cr₂AlC (0001) surface. (a)-(b) bare surface, (c)-(d) single O atom adsorption system, (e)-(f) single O₂ molecular adsorption case.

Fig. 6. (a) DOS of Al atom in bulk Cr_2AlC unit cell, (b) total DOS of surface layer Al atoms (Al_S) of pure $(3\times 3)/\text{Al}$ -terminated Cr_2AlC (0001) surface, (c) partial DOS of Al and O atoms in single O adsorption on Cr_2AlC (0001), and (d) partial DOS of Al and O in single O_2 molecular adsorption Cr_2AlC (0001) surface.

Fig. 7. The corresponding differences of the DOS of Al atom in different system. The inset is the zoom in view of the corresponding differences of the DOS of Al atom in different system. In the inset figure, the range of X axis is from -1.0 eV to 1.0 eV.