



Full Length Article

Structural evolution of oxygen on the surface of TiAlN: Ab initio molecular dynamics simulations

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ARTICLE INFO

Keywords:

TiAlN

Oxidation

Hard coating

Ab initio molecular dynamics

ABSTRACT

We have employed *ab initio* molecular dynamics simulations to study the oxidation behavior of TiAlN hard coatings as a function of Al content and temperature. Results show that for TiAlN with a low Al content (Ti_{0.75}Al_{0.25}N), Ti atoms can always bond with O atoms, while Al atoms bond with O only at a higher temperature. For Ti_{0.5}Al_{0.5}N, both Al and Ti can bond with O atoms, irrespective of temperature. Through analyzing the displacement height of O-bonded metal atoms, we suggest that titanium oxide nucleates at the outermost layer of Ti_{0.75}Al_{0.25}N while the outermost layer after Ti_{0.5}Al_{0.5}N is exposed to oxygen is aluminum oxide. Our simulation results predict, in agreement with experiment, that Ti_{0.5}Al_{0.5}N has superior oxidation resistance in comparison with Ti_{0.75}Al_{0.25}N. This study provides an atomistic insight to the initial stage of the oxidation process, which is else difficult to observe experimentally.

1. Introduction

Due to its high hardness, good wear resistance and oxidation resistance, nitride coatings are widely used for cutting tools to improve their service life time [1–3]. It is reported that the oxidation resistance increases with increasing Al content in the Ti(Al)N coatings [4,5], and the oxidation temperature can reach more than 1000 K for Ti_{0.52}Al_{0.48}N [6,7]. The structure and properties of the TiAlN coatings strongly depend on the Al content. Previous studies have shown that the cubic NaCl-structured TiAlN (Al fraction on the metal sublattice is less than 0.7) exhibits outstanding wear and oxidation resistance [8–11] and even show self-hardening at elevated temperatures. Therefore, cubic TiAlN coatings are industrially widely applied.

TiAlN surface chemistry and kinetics may be radically different for different Al content and temperature. Zhou et al. [12] studied experimentally performance of the Ti_{1-x}Al_xN (x = 0.2, 0.5, 0.6, 0.7) coatings. The results indicated that the oxidation resistance of TiAlN can be significantly improved by increasing the Al content in the coating. McIntyre et al. [13] studied the oxidation of Ti_{0.5}Al_{0.5}N at temperatures between 1023 and 1173 K in pure O₂ atmosphere at ambient pressure. They showed that the oxidation of Ti_{0.5}Al_{0.5}N resulted in the formation of a passive stable double-layer oxide. These consisted of two partially

crystalline sublayers, where the dense upper one was Al-rich and the lower one was Ti-rich, with no measurable N content in either of them. In addition, Joshi [14] found the oxide with similar stratified phenomenon on the surface of the coating. Zhu et al. [15] used cathodic arc evaporation method to investigate high temperature oxidation behavior of a cathodic arc evaporated Ti_{0.5}Al_{0.5}N coating concluding that Ti_{0.5}Al_{0.5}N showed excellent oxidation resistance at 1123 K for 120 min and got destroyed only when oxidized at 1273 K for 15 min. Xu et al. [16] studied the thermal stability and oxidation resistance of V-alloyed TiAlN coatings and found that V reduced the oxidation resistance of TiAlN coatings. However, the traditional experimental methods suffer from spatial resolution and/or in-situ capabilities, and in particular do not provide atomistic description of the oxidation mechanisms [17,18]. Recently, O₂ chemisorption on Ti_{0.5}Al_{0.5}N surface at 300 K was studied using *ab initio* molecular dynamics (AIMD) and it was suggested that O₂ chemisorption on TiAlN resulted in the formation of Ti–O–Ti bridges with Ti₂O₃-like bonding and Ti vacancies [19]. Nevertheless, the study did not take into account the oxidation behavior of TiAlN with different Al contents at high and low temperatures.

In the initial stage of oxidation, O₂ dissociates into isolated O atoms and adsorbed on the surface of nitride coatings [20,21]. In this work, we use AIMD simulations to explore the initial stages of the oxidation

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Received 21 September 2018; Received in revised form 19 November 2018; Accepted 20 November 2018

Available online 22 November 2018

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process on $\text{Ti}_{0.75}\text{Al}_{0.25}\text{N}$ and $\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}$ surface interacting with O. In particular, we focus on describing bonding between metal atoms (Ti and Al) of TiAlN surface and O at different Al contents and temperatures. Furthermore, the temporal evolution of displacement height of metal atoms of TiAlN coating has been investigated. We find that the displacement between metal atoms and O atoms has a decisive effect on the oxidation behavior. The results provide atomistic description for several experimental observations, such as the oxide appeared stratified phenomenon [13,14] and excellent oxidation resistance of TiAlN coatings with high Al content [22].

2. Methodology

The simulations focus on the bonding between O and metal atoms of TiAlN(0 0 1) surface at different Al contents and temperatures. *Ab initio* Molecular Dynamics (AIMD) simulations of TiAlN reacting with oxygen were carried out using the Vienna *ab initio* Simulation Package (VASP) [23] using the generalized-gradient approximation (GGA) and the projector augmented plane-wave (PAW) method [24]. The time step was 1.0 fs and the total simulation time for each simulation was 2000 fs. The description of complex materials at realistic conditions requires a computationally efficient but simultaneously accurate atomistic, structural modeling. The elasticity of TiAlN [10,25] has been successfully predicted using Special Quasi-random Structures (SQS) supercells. Mayrhofer et al. have investigated the impact of the atomic configuration on the structural, elastic properties, and phase stability in TiAlN [26]. We used SQS for the NaCl-structured TiAlN solid solutions generated by the *mcsqs* program, a part of the Alloy-Theoretic Automated Toolkit (ATAT) [27]. The (0 0 1) surface of TiAlN was modeled by periodic slabs consisting of five atomic layers separated by of 15 Å of vacuum. A 3×3 surface unit cell was employed in the AIMD simulation, totaling to 189 atoms in the simulation box (see Fig. 1). The bottom three layers of atoms were fixed to mimic the infinite bulk while other two layers of atoms are free to enable their interactions with incident atoms. The slab is periodic along a-b directions, so it can be regarded as an infinite slab in the a-b plane. Single point (Gamma) was used for sampling the Brillouin zone due to the large dimensions of the supercell. The plane wave energy cut-off was set to 400 eV. Considering that the onset of the TiAlN coatings oxidize had been reported at 773 K (500 °C) and 1123 K (850 °C) [28,29], we set the Nosé-Hoover

thermostat controlling the temperature, to 773 K and 1123 K to simulate TiAlN(0 0 1) surfaces interacting with O as a function of time, respectively, within the canonical ensembles (NVT) [30]. We initialized our calculations with the O atoms coverage of 0.25 monolayer (the ratio of the number of O atoms to the number of surface atoms) and O atoms were initially placed 3 Å above the (0 0 1) surface at random positions. When the distance between an O atom and a neighboring atom was smaller than 2 Å, it was considered a bond had been formed.

3. Results and discussions

3.1. Structural evolution

Oxidation is a dynamic and rapid process, which is thus difficult to observe experimentally. All these interaction processes occur during the impact of O atoms with TiAlN(0 0 1) surface, so the investigation of bonding between O and surface atoms is very meaningful. Evolution of the TiAlN–O bonding in the initial stage of oxidation is illustrated for 773 K and 1123 K by the structure snapshots shown in Fig. 2. At low temperature and low Al content (Fig. 2(a)), O atoms tend to bond with Ti atoms, but not with Al and N. This is in agreement with the prediction reported by Music and Schneider [31], who ran their AIMD simulation at 300 K (room temperature). They obtained preferred O bonding with Ti atoms, whereas Al–O bonds were formed only for O coverages equal or greater than 0.22 monolayer. Although the O coverage is greater than 0.22 monolayer in the present work, no Al–O bonds are formed. This can be rationalized by the fact that the Al fraction is only 0.25, rather than the 0.5 as the Ref. [32]. When the temperature is increased to 1123 K, Al also serves as an active species, hence the O atoms are bonded to both Ti and Al atoms on the surface, as shown in Fig. 2(b).

Another important finding is that some Ti atoms escape from the surface. These escaped Ti atoms interact with O atoms and eventually lead to a formation of TiO_2 or Ti_2O_3 . As a consequence of the created Ti vacancy right at the surface of $\text{Ti}_{0.75}\text{Al}_{0.25}\text{N}$, O atoms can further oxidize the TiAlN coating from the Ti vacancy into the interior. This is in agreement with the experimental observation that the growth of oxide scales on TiAlN coatings is driven by an Al diffusion towards the oxide/O interface and a simultaneous inward diffusion of O to the oxide/nitride interface where Ti is oxidized [32]. This latter process is indeed

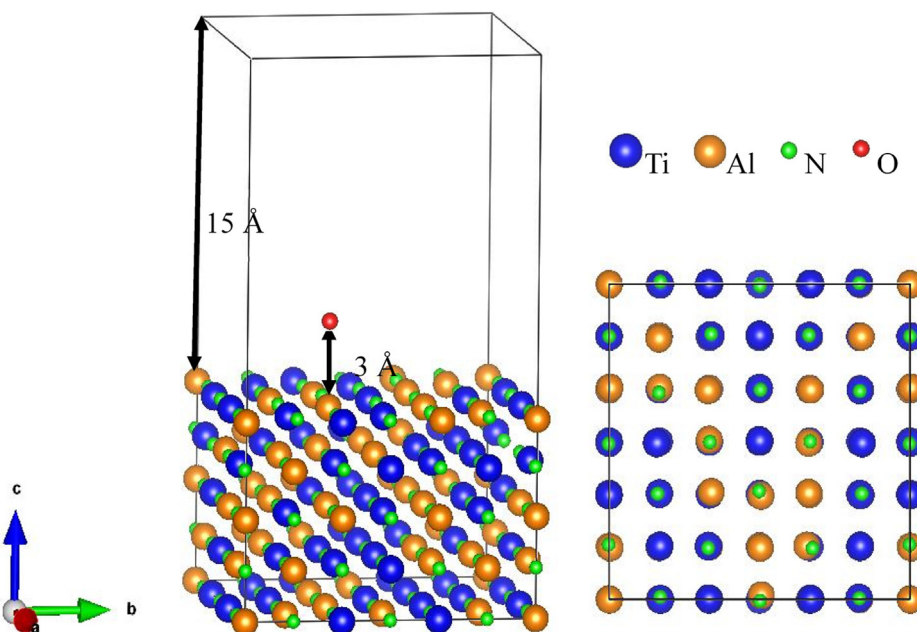


Fig. 1. Side view (left panel) and top view (right panel) of $\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}$ (0 0 1) model.

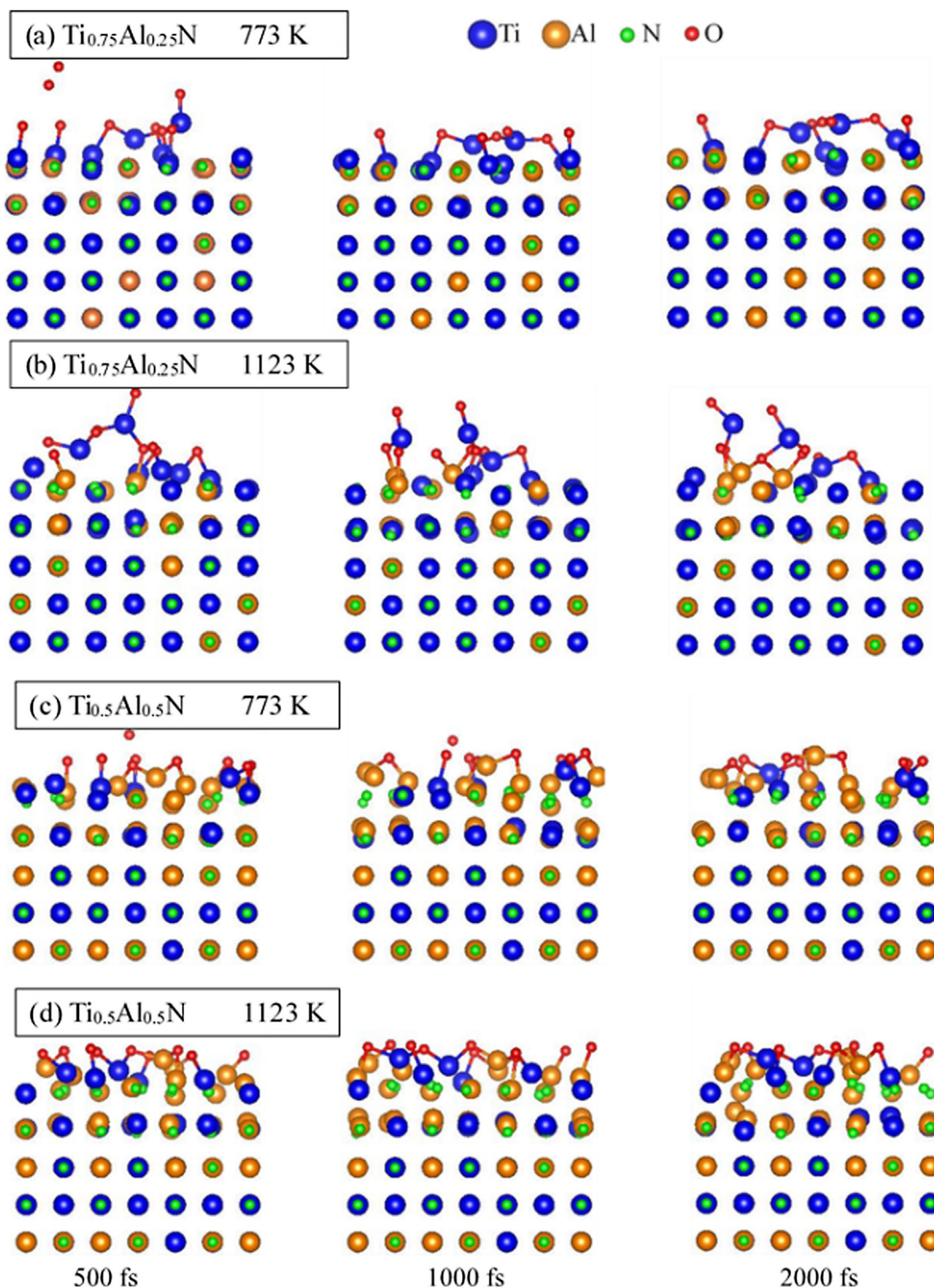


Fig. 2. MD snapshots of TiAlN(001) interacting with O atoms after 500 fs, 1000 fs and 2000 fs for (a) $\text{Ti}_{0.75}\text{Al}_{0.25}\text{N}$ at 773 K, (b) $\text{Ti}_{0.75}\text{Al}_{0.25}\text{N}$ at 1123 K, (c) $\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}$ at 773 K, and (d) $\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}$ at 1123 K.

corresponding to forming a Ti vacancy and its subsequent filling with O, although it should be noted, that, in particular at low temperatures, O diffusion along grain boundaries rather than bulk diffusion is likely to be the decisive parameter [33]. In addition, previous studies have shown that Ti vacancies also formed in the initial oxidation stages of the TiN surface [34,35]. Zimmermann et al. [34] investigated the early oxidation stages of TiN(100) by AIMD and suggested that the localization of Ti vacancies in the thin oxide layer and at the TiN/oxide interface is thermodynamically stable.

Fig. 2(c) and (d) show that in the case of $\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}$, O atoms

interact with both Ti and Al metals, while no obvious Ti vacancies can be observed. Because of the increased of Al content, O atoms tend to combine stronger with Al atoms to form a dense layer of oxide. Furthermore, Vaz et al. [32] reported that the oxidation resistance meliorates with high Al contents. The MD snapshots of TiAlN(001) interacting with O atoms at different temperatures clearly show that there is no apparent escape of Ti atoms with increasing Al content.

Qualitatively, there is an obvious difference in the positions of surface atoms of $\text{Ti}_{0.75}\text{Al}_{0.25}\text{N}$ at different temperatures, but hardly any difference is noticeable for $\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}$. Therefore, to highlight the

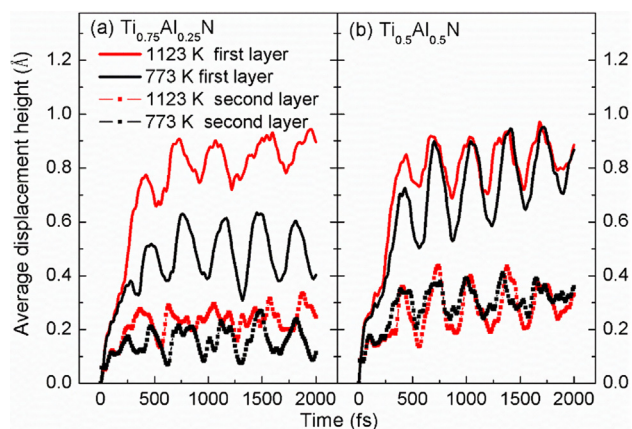


Fig. 3. Average displacement of surface atoms (first and second layers) as a function of temperature and time: (a) $\text{Ti}_{0.75}\text{Al}_{0.25}\text{N}$, (b) $\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}$.

structural characteristics of surface atoms as a function of time, the temporal evolution of displacement height of the metal atoms of TiAlN coating is evaluated in the next section.

3.2. Average displacement

The average vertical (z direction, perpendicular to the surface) displacements plotted in Fig. 3 represent the average displacement of all atoms in either the top-most (surface) or the second top-most layer with respect to their initial (ideal NaCl) positions. The thermal equilibrium is achieved after approx. 500 ps for both systems and both temperatures. The average displacement of the first layer of $\text{Ti}_{0.75}\text{Al}_{0.25}\text{N}$ increased from $\sim 0.4\text{--}0.6\text{ \AA}$ at 773 K to $\sim 0.7\text{--}0.9\text{ \AA}$ at 1123 K (Fig. 3(a)). The second layer of atoms exhibits a similar behavior, i.e., the higher the temperature, the larger of the displacement, nonetheless the average displacement height of the second layer atoms is relative small (within $0.1\text{--}0.3\text{ \AA}$). Our simulations suggest that the mean displacement is distinctly different between 773 K and 1123 K in the case of $\text{Ti}_{0.75}\text{Al}_{0.25}\text{N}$. On the contrary, it is practically the same for both temperatures in the $\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}$ case. For the $\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}$ coating, the average displacement height of the first and the second layer atom is $\sim 0.6\text{--}0.9\text{ \AA}$ and $\sim 0.1\text{--}0.4\text{ \AA}$, respectively (see Fig. 3(b)).

An interesting question is whether both metals, Ti and Al, are influenced in the same way by the presence of O or not. Therefore, we plot in Fig. 4 separately the displacement of Ti and Al atoms as a function of time and temperature. Moreover, we distinguish between O-bonded atoms (distance to O smaller than 2.5 \AA) and non-bonded ones. For $\text{Ti}_{0.75}\text{Al}_{0.25}\text{N}$ at 773 K, O atoms bond only with Ti atoms; all the surface Al atoms have no bonds with O, and thus the average displacement of Al is $\sim 0\text{ \AA}$. The displacement height of the O-bonded Ti atoms is approximately $0.6\text{--}1.2\text{ \AA}$, whereas the non-bonded ones remain almost undispaced. At the higher temperature of 1123 K, some O atoms begin to bond also with Al (Fig. 4(b)). Owing to the fact that the Ti atoms escape from the surface to bond with the O atoms, the average displacement height of the Ti atoms increases to $\sim 1.6\text{--}2.0\text{ \AA}$ and it is obviously higher than that of the bonded Al atoms.

Kunze et al. discussed the oxidation kinetics based on analyzing the surface atoms displacements, and indicated that the kinetics of the initial oxidation of $\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}$ coatings is governed by the Ti–O bond and the Ti-vacancy formation at room temperature [19]. They also suggested that the larger the displacement, the faster the initial oxidation process. In a line with this concept, the kinetics of the initial chemisorption of O on $\text{Ti}_{0.75}\text{Al}_{0.25}\text{N}$ is governed by Ti–O bonds at 773 K. At high temperature, the kinetics is governed by both Ti–O bond and Al–O bond, and the process of Ti–O bond is faster than Al–O bond. Interestingly, the result is totally different for $\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}$. Although the kinetics is governed by both Ti–O and Al–O bonds, the process of the

Al–O bond is faster than Ti–O bond. This may be understood based on the electronic structure argumentation presented in the next section. In addition, our results imply that for low Al content, the outermost layer of the oxide on $\text{Ti}_{0.75}\text{Al}_{0.25}\text{N}$ is expected to be Ti-rich. Furthermore, the present results suggest that only a single layer oxide is formed at the lower temperature, while a double layer oxide can be expected at the higher temperature. Additionally, the formation of titanium oxide is connected with a volume expansion and thus an increase of the internal stresses, which can lead to crack formation within the oxide scale [29]. For $\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}$, the influence of temperature on the displacement of Ti and Al is not so pronounced, but the average displacement of bonded Al is larger than that of bonded Ti, as can be seen from Fig. 4(c) and (d). The average displacement of bonded Ti is $\sim 0.6\text{--}1.2\text{ \AA}$ at 773 K and $\sim 0.8\text{--}1.3\text{ \AA}$ at 1123 K, while the average displacement for bonded Al is $\sim 0.8\text{--}1.5\text{ \AA}$ and $\sim 1.2\text{--}1.6\text{ \AA}$ at 773 K and 1123 K, respectively.

By comparing $\text{Ti}_{0.75}\text{Al}_{0.25}\text{N}$ with $\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}$, we find that the O atoms are mainly bonded to Ti atoms to form the oxide at low temperature in the former case, while in the latter case of $\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}$ the O atoms are bonded to both Ti and Al atoms, and the displacement height of Al is larger than that of Ti. This implies that the top-layer of oxide is likely to be Ti-rich at low Al content ($\text{Ti}_{0.75}\text{Al}_{0.25}\text{N}$), whereas the top-layer is Al-rich for higher Al content ($\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}$). This is in agreement with the results of EDX measurements showing that when the Al metal fraction is above 0.5 and the temperature is 1123 K, the top-layer is Al-rich [5]. Especially at temperatures above 1073 K, the Al atoms diffuse outwards rapidly [32,36]. The formation of a dense layer of aluminum oxide retards the inward diffusion of O atoms during the oxidation process of TiAlN coatings and is thus beneficial for their oxidation protection. These results provide atomic scale explanation for, and insight into the experimental observations on oxidation of TiAlN coatings [13,14,37].

3.3. Electronic structure

In this section we will discuss electronic density of states (DOS) in order to rationalize the observations described in the previous sections. Fig. 5 presents the total density of states (TDOS) of TiAlN as a function of the Al content and temperature (773 K and 1123 K). Apparently, the temperature-induced structural modification are unimportant for TDOS (calculated at 0 K), and only differences based on the Al content can be observed. The TDOS of $\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}$ at the Fermi level is lower than that of $\text{Ti}_{0.75}\text{Al}_{0.25}\text{N}$. Compared with $\text{Ti}_{0.75}\text{Al}_{0.25}\text{N}$, the TDOS of $\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}$ flattens and shifts towards lower energies to make system stable, similarly to the argumentation in Ref. [31].

In order to further clarify the role of the Al content on the oxidation resistance, we explore the electronic density of states (DOS) of only the bonded surface atoms at 1123 K. We plot the DOS of O atoms and Al or Ti atoms bonded to it, as shown in Fig. 6. For $\text{Ti}_{0.75}\text{Al}_{0.25}\text{N}$ (Fig. 6(a)), orbital hybridization mainly occurs between the O- p and Ti- p and d orbitals within -6 to -2 eV (occupied bonding states) and 0 to 2 eV (unoccupied anti-bonding states) for O adsorbed on Ti sites, and between the O- p and Al- p orbitals within -6 to -1 (occupied bonding states) and near to 2 eV (unoccupied states) for O adsorbed on Al sites. The interaction between O and Ti states is quite strong as visualized by the ‘overlap’ curve (a simple product of Ti(Al) and O DOS). This is why O tends to combine with Ti atoms on $\text{Ti}_{0.75}\text{Al}_{0.25}\text{N}$ surface. In contrast, DOS overlap between O and Ti is much less pronounced and flattens out for $\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}$ system, suggesting a weaker bonding interaction. However, when O adsorbs on Al sites in the $\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}$ case (Fig. 6(b)), there is a significant overlap between the O- p and Al- s near -8 eV, and an obvious shift towards lower energies to reach a more stable bonding.

At low Al content, surface oxides tend to form oxides of Ti. As the content of Al increases, the chance of Al bonding with O increases. The above analysis and discussion indicate that O and Al atoms exhibit a strong bonding interaction, and that the oxidation structure of Al becomes stable with increasing Al content. At the same time, the

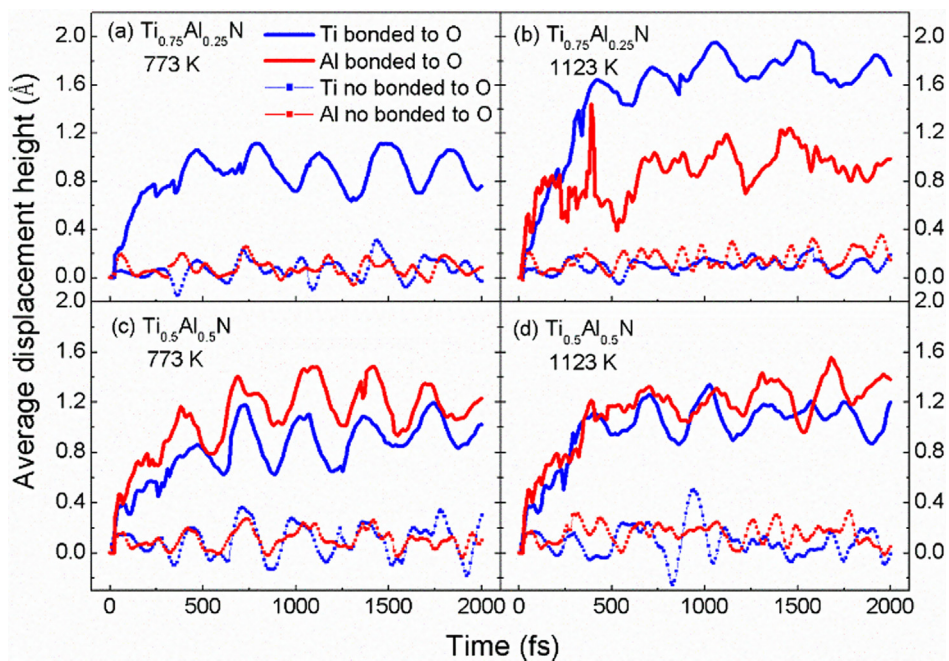


Fig. 4. Displacement of Ti and Al atoms, bonded and non-bonded to O, as a function of time for $Ti_{0.75}Al_{0.25}N$ at (a) 773 K and (b) 1123 K, and for $Ti_{0.5}Al_{0.5}N$ at (c) 773 K and (d) 1123 K, respectively.

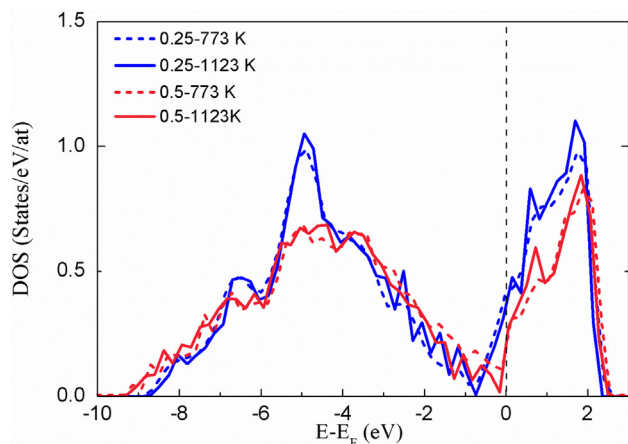


Fig. 5. Total density of states (of the whole simulation box) for $Ti_{0.75}Al_{0.25}N$ and $Ti_{0.5}Al_{0.5}N$ after annealing at 773 K and 1123 K and interaction with O atoms. Vertical dotted line denotes the Fermi level (E_F).

increasing Al content aggregates more electronegative O atoms, thus contributing to forming a dense Al_2O_3 oxide layer.

Temperature and Al content have a great influence on forming the precursors later leading to the formation of the oxide itself. The kinetics of oxidation as well as the final structure of the oxide are determined by the rate of diffusion of O and metal atoms in the oxide layer [38]. The mobility of metal atoms and O through the Ti-rich oxide layer are considerably higher than in the Al-rich layer [39]. At high temperatures (above 800 °C), Al diffuses readily through the nitride and the TiO_2 layers [14]. Traces of such behavior can be attributed to the formation of Al–O bonds formed at high temperatures in $Ti_{0.75}Al_{0.25}N$. In addition, the diffusion rate of Ti atoms is hampered by the Al-rich layer, so the displacement height of $Ti_{0.5}Al_{0.5}N$ is obviously smaller than that of $Ti_{0.75}Al_{0.25}N$ in 1123 K. These are in excellent agreement with our displacement data, which eventually leads to the stratified character of the formed oxide.

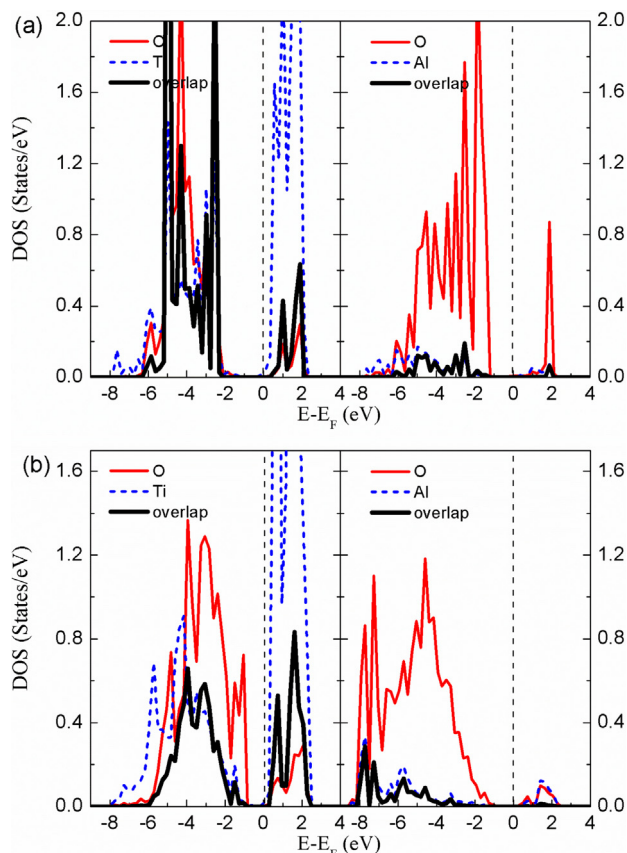


Fig. 6. Density of states (red solid line and blue dashed line) and ‘overlap’ (thick black solid line) for O adsorbed on Ti and Al sites at 1123 K: (a) $Ti_{0.75}Al_{0.25}N$, (b) $Ti_{0.5}Al_{0.5}N$. Vertical dotted line denotes the Fermi level (E_F).

4. Conclusion

In conclusion, we have investigated the structural evolution of TiAlN(0 0 1) surface interacting with O atoms at 773 K and 1123 K by means of *ab initio* molecular dynamics simulation. It was found that for Ti_{0.75}Al_{0.25}N at 773 K, the O atoms bond preferably with Ti atoms and no bonds with Al or N atoms were obtained, while O atoms can bond with both Al and Ti atoms at 1123 K. Besides, Ti atoms escape from the surface, leading to a formation of Ti vacancies. Contrarily, both Al and Ti atoms bond with O at 773 K and 1123 K for Ti_{0.5}Al_{0.5}N. To further gain an insight into the formation of oxide, the displacement of metal atoms was analyzed. Through examining the displacements of bonded metal atoms, we suggest that the surface oxide of Ti_{0.75}Al_{0.25}N consists of a Ti-rich top-layer at 773 K, as well as a Ti-rich top-layer and an Al-rich bottom-layer at 1123 K. In the case of Ti_{0.5}Al_{0.5}N, the average displacement height of Al atoms is larger than that of Ti atoms, irrespective of temperature, hence suggesting that the surface oxide consists of an Al-rich top-layer and a Ti-rich bottom-layer. The electronic structure analysis indicate that O and Al atoms have a strong bonding interaction and the interface structure becomes more stable with increasing of Al content. The formation of a dense Al oxide retards the inward diffusion of O atoms during the oxidation process of TiAlN coatings, and thus protects the underlying nitride from a further oxidation. The upper Al-rich layer impedes the diffusion of metal and O atoms. Consequently, Ti_{0.5}Al_{0.5}N shows a better oxidation resistance than Ti_{0.75}Al_{0.25}N. These results are relevant for basic understanding of the initial stages of oxidation, during which first bonds between metal and O atoms are formed. This study corroborates the previous experimental observations, while it provides a novel, atomistic perspective on the very fundamental processes governing the initial stages of oxidation of TiAlN.

Acknowledgements

This work is supported by the National Key Research and Development Program of China (Grant No. 2016YFB0701301) and the Ministry of Industry and Information Technology of China (Grant No. 2015ZX04005008). We acknowledge the computational resources of the Vienna Scientific Cluster (VSC).

Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apsusc.2018.11.158>.

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