Structure after relaxation

The initial structure of Oxygen above the TiAlZrN(001) surface with 0.11ML coverage

Vacancy generated with one Ti atom near a Zr atom escaped from the surface to bond with oxygen atoms to form TiO₂

More stable surface with no vacancy. Oxygen atoms only interact with Ti atoms

Bond	Length in TiAlZrN (Å)
Ti-O	1.57
Ti-O	1.83
Ti-O	1.83
Ti-O	1.85
Ti-O	1.91
Ti-O	1.96

Bond	Length in TiAlZrN (Å)
Ti-O	1.61
Ti-O	1.65
Ti-O	1.70
Ti-O	1.71

Ab initio Molecular Dynamics studies on effect of Zr on oxidation resistance of TiAlN coatings

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Abstract: It was demonstrated experimentally that doping Zr into TiAlN coatings at room temperature will detriment its oxidation resistance. On the other hand, there are evidences that doping Zr into TiAlN at high temperature will improve coating's oxidation resistance. In the present work, we address the effect of Zr on the oxidation resistance of TiAlN by means of *ab initio* molecular dynamics simulations. The TiAlN and TiAlZrN (1 Zr atom replacing 1 Ti atom) surfaces covered with 4 oxygen atoms at 300K and 1123K were simulated. Based on the analysis of the atomic motion, bond formation after relaxation, and the charge density difference maps we find that at 300K, the addition of Zr induces escape of Ti atoms from the surface, resulting in formation of surface vacancies and subsequently TiO₂. Comparison of metal-oxygen dimers in the vacuum and above the TiAlZrN surface further shows that the addition of Zr in the TiAlN surface will change the lowest bonding energy sequence from Zr-O < Ti-O < Al-O in the vacuum to Ti-O < Zr-O < Al-O above the TiAlZrN surface. From Molecular Dynamics simulations at 1123K, it is find that no Ti vacancies were

1 generated in the surface. Moreover, less charge is transferred from metal to N atoms
2 and the bond lengths between Ti and O atoms become shorter at 1123K as compared
3 with 300K, suggesting that the addition of Zr atom promotes the interaction of Ti and
4 O at TiAlZrN surface at 1123K, leading to a more stable surface. Our simulation
5 explains why Zr-doping at 1123K increases TiAlN coating's oxidation resistance
6 while at 300K reduces its oxidation resistance.

7 **Keyword:** TiAlN; TiAlZrN; Oxidation; *ab initio* Molecular Dynamics

8

1   **1   Introduction**

2   Due to their high hardness and wear resistance as well as good oxidation resistance
3   and thermal stability, TiAlN hard coatings, where Al substitutes for Ti in the
4   TiN-based lattice, are well-established materials used as protective layers for cutting
5   tools [1-5]. It is well-known that the properties of TiAlN coatings strongly depend on
6   the Al content. Experiments show TiAlN exhibits the NaCl structure when the Al:Ti
7   ratio below 3:1 [6]. In particular, the $\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}$ coatings exhibit good wear and
8   oxidation resistance [1]. The ever more demanding industrial applications now require,
9   besides high hardness and wear resistance, also superior performances, such as low
10   friction, oxidation and hot corrosion resistance. For example, an addition of fourth
11   alloying elements (e.g., Cr, Y, Zr, B or Si) yields a better oxidation resistance [7-10].
12   Experimental studies showed that the oxidation resistance of TiAlN coatings cannot
13   meet the specific needs for dry-cutting application above 1000°C [11]. Nevertheless,
14   Chen *et al.* reported that TiAlZrN coatings exhibited a better oxidation resistance than
15   TiAlN coatings at high temperatures [12]. At lower temperatures, however, they
16   found that the TiAlZrN coatings showed a lower oxidation resistance than the TiAlN
17   coatings. Only further increasing temperatures, the Zr-containing coatings then show
18   a better oxidation resistance.

19   This anomalous oxidation behavior of the TiAlZrN coatings need further
20   investigation. Up to now, many experimental investigations on the oxidation of the
21   TiAlN and TiAlZrN coatings have been reported, but only a few theoretical reports
22   deal with the oxidation of TiN [13] or TiAlN [14] coatings. For example, the surface

1 processes on $\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}(0\ 0\ 1)$ interacting with O_2 at 300K were explored using *ab*
2 *initio* molecular dynamics (MD) simulations by Music *et al.* [15]. They found that at a
3 low O_2 coverage, only Ti–O bonds were formed, while increasing the O_2 coverage
4 also lead to a formation of Al–O bonds. Zimmermann *et al.* investigated the early
5 oxidation stages of $\text{TiN}(1\ 0\ 0)$ by *ab initio* MD [13]. They observed selective
6 oxidation of Ti atoms, while Ti vacancies were left behind at the metal/oxide interface.
7 From the simulations they proposed that TiN oxidation may proceed along two
8 possible ways: first adsorbed at the minimum potential energy surface site and then a
9 kinetically driven path that results from the high heat release during the dissociation
10 of O_2 . Holec *et al.* systematically studied alloying trends when early transition metals
11 (Y, Zr, Nb, Hf and Ta) were added in TiAlN with a static energy minimization
12 method [16]. They found that the onset of spinodal decomposition would appear for
13 lower thermal loads when Y, Zr or Nb are alloyed in TiAlN , than for Hf or Ta
14 additions. Nevertheless, no theoretical work about the effect of Zr addition on the
15 oxidation resistance of the TiAlN coatings has been published yet.

16 In this paper, we use *ab initio* MD simulations to investigate the $\text{TiAlN}(0\ 0\ 1)$ and
17 $\text{TiAlZrN}(0\ 0\ 1)$ surface interacting with O atoms at low and high temperatures,
18 respectively. Former first-principles study shows the $(1\ 0\ 0)$ surface has the lowest
19 surface energy between $\text{TiN}(1\ 0\ 0)$, $(1\ 1\ 0)$ and $(1\ 1\ 1)$ surface [17]. They also found
20 surfaces with higher energies typically lead to stronger adsorption and bad oxidation
21 resistance. The comparison between them should sheds light on the differences in
22 oxidation of these coatings.

2 Methodology

The *ab initio* MD simulations of TiAlN and TiAlZrN reacting with oxygen were carried out using the Vienna Ab initio Simulation Package (VASP) [18, 19], based on the Density Functional Theory [20, 21]. The exchange-correlation functional parametrized by Perdew, Burke and Ernzerhof, and the ion-electron interactions as described with the projector augmented wave method were used [22, 23]. Ti $3s^2 3p^4 3d^3 4s^1$, Al $3s^2 3p^1$, N $2s^2 2p^3$, Zr $4s^2 4p^6 4d^2 5s^2$ electrons were treated as valence electrons. The MD time step was 1.0 fs and the total simulation time of each simulation was 8000 fs. Single point (Gamma) was used for sampling the Brillouin zone since the number of atoms was larger than 100. The plane wave energy cut-off was set to 300 eV.

The present *ab initio* MD simulations used the Nosé–Hoover thermostat to control the temperature of the simulation at 300K and 1123K, respectively, within the canonical ensembles (NVT) [24]. The temperatures were adopted according to the experiments by Chen *et al.* In their report, Chen *et al.* studied the oxidation resistance of Zr-free and Zr-containing TiAlN coatings at different temperatures [12]. They found that the Zr-free coatings exhibited a better oxidation than the Zr-containing at the room temperature, but the oxidation resistance ability reversed at 1123K.

According to the OpenMX-based [25] study of Music *et al.* [15], Al-O bonds formed when the coverage of O₂ was equal or larger than 0.22 monolayers; at the same time, Ti atoms were predicted to escape from the surface. Therefore, in the present work we focused on Ti_{0.5}Al_{0.5}N interaction with O₂ at the O₂ coverages of

0.22 and 0.33 monolayers. Fig. 1 shows snapshots of the final configuration after the 8000 fs simulations. We conclude that our results are in a good agreement with the simulations results of Music *et al.* [15], as Al-O bonds formed at both of O₂ coverages and simultaneously Ti atoms escaped from the surface layer. Thereafter, to reduce the impact of Al and to concentrate on the effect of Zr, we use the O coverage of 0.11 monolayers of the $\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}(0\ 0\ 1)$ surface in the following simulations. The used simulation box of $\text{TiAlZrN}(0\ 0\ 1)$ surface slab model is shown in Fig. 2. The simulation box contained 144 atoms, out of which half of the Ti atoms were randomly replaced with Al atoms in the initial TiN supercell of four atomic layers. The TiAlZrN supercell was constructed by replacement of 1 Ti atom with 1 Zr atom in the surface layer. 4 O atoms were initially placed on top of the 3 Ti atoms and 1 Al atom in the distance of 3 Å from the surface, while the total vacuum space was set to 15 Å to avoid interaction between periodic boundary images of the slabs.

3 Results and discussion

3.1 Simulations at 300K

3.1.1 Structure of the surface after relaxation

Fig. 3 shows the interaction of the $\text{TiAlN}(0\ 0\ 1)$ surface with 4 O atoms, as obtained after the 8000 fs simulation at 300K. We observe that the individual O atoms interact with the Ti atoms in surface layer, but never with either Al or N. We also find that the Ti atoms do not escape from the surface but move about 0.65 Å from the TiAlN/O interface closer to the O atoms, suggesting the O atoms prefer to interact

1 with Ti over Al atoms. These findings agree well with the predictions reported by
2 Music *et al.* [15], in which they observed that O preferred to bind with Ti atoms, and
3 Al-O bonds formed only for O₂ coverages equal or larger than 0.22 monolayers. From
4 the displacement vector of O atoms (Fig. 4 (a)) and the coordination of the Ti and O
5 atoms in the TiAlN/O interface, we find that O leaves the position on top of the Al
6 atom, and that each O atom only binds with Ti atom(s). The measured Ti-O bond
7 lengths are listed in Table 1; Ti-O bond lengths are about 1.59-1.80 Å, which is
8 shorter than the Ti-O bond length in TiO₂ (about 1.87-1.96 Å) [15].

9 In order to understand the reason, dependence of the bonding energies of Ti-O,
10 Zr-O, and Al-O dimers in the vacuum on the bond length was calculated from the
11 Molecular Static (MS) calculations with conjugated gradient method at 0 K and is
12 presented in Fig. 5. The lowest bonding energies and the corresponding bond lengths
13 are listed in Table 2, where the lowest bonding energy of Al-O is used as the reference
14 state. It may be concluded that the bonding energies of Ti-O and Zr-O are lower than
15 that of Al-O when the bond length is larger than 1.48 Å, suggesting that the much
16 higher Ti-O and Zr-O bond strengths lead to the preferred formation of the Ti-O and
17 Zr-O bonds. Moreover, for bond lengths larger than 1.6 Å, Zr-O yields lower bonding
18 energy and Al-O and Ti-O, and reaches the lowest bonding energy at 1.75 Å.

19 Fig. 6 shows the interaction of the TiAlZrN(0 0 1) surface with 4 O atoms, as
20 obtained after the 8000 fs simulation at 300K. Similarly to the case of TiAlN(0 0 1)
21 surface, O do not interact with Al or N, but interact with Ti and Zr atoms instead.
22 Moreover, one Ti atom near a Zr atom escapes from the TiAlZrN/O interface layer,

1 thus generating a Ti vacancy in the interface layer. This escaped Ti atom bonds with
2 the three nearest O atoms. Fig. 4 (b) clearly shows the O atoms leave the original
3 locations and gathered to the escaped Ti atom. The measured Ti-O bond lengths are
4 listed in Table 1. Apart from one with 1.57 Å, the most Ti-O bonds adopt lengths of
5 1.83-1.96 Å, consistent with TiO₂ [15] The distance between the nearest Zr and O
6 atoms is 2.07 Å, however, much larger than 1.75 Å, which is the equilibrium bond
7 length of Zr-O dimer in the vacuum.

8 Considering the presence of the TiAlZrN surface affects the bonding nature
9 between atoms, we have also calculated the bonding energy for O above Al, Ti and Zr
10 atoms in the constructed TiAlZrN surface as a function of the distance between the O
11 and the metal atoms from MS method at 0K (Fig. 7). The lowest bonding energies and
12 the corresponding bond lengths are also listed in Table 2, where the lowest bonding
13 energy of Al-O is used as the reference state. From Table 2, one can find that the
14 lowest bonding energy sequence among Ti-O, Zr-O, and Al-O is different with that in
15 the vacuum situation. Specifically, when O is above the TiAlZrN surface, the lowest
16 bonding energy sequence is Ti-O < Zr-O < Al-O, instead of Zr-O < Ti-O < Al-O in the
17 vacuum. This sequence explains why O bonds preferentially to Ti, since the Ti-O
18 bond has the lowest bonding energy above the TiAlZrN surface. It needs to note that,
19 as shown in Table 1, at 300K, the Ti-O bond length in TiAlZrN is 1.83-1.96 Å, larger
20 than that in TiAlN (1.75-1.80 Å). It is because the escaped Ti atom in TiAlZrN surface
21 observed in MD binds with O atoms to form TiO₂, thus the measured bond lengths
22 (1.83-1.96 Å) of Ti-O in this situation agree with the equilibrium length of TiO₂

(1.87-1.96 Å [15]). For TiAlN at 300K, the Ti is not escaped from the surface, so that the Ti-O bond length (1.75-1.80 Å) is close to the equilibrium length of Ti-O when O above TiAlZrN surface (1.78 Å at 0 K).

In short, from the comparison of TiAlN(0 0 1) and TiAlZrN(0 0 1) surface interactions with 4 O atoms at 300K, it is possible to conclude that the addition of Zr promotes Ti atom to escape from the surface, thus promoting the formation of a surface vacancy and TiO₂.

3.1.2 Charge density difference

To further clarify the role of Zr doping, the charge density difference maps were calculated to study the charge transfer among atoms in the surfaces. The sliced position is at the surface of TiAlN (average position of surface atoms) for the charge density difference maps. The charge density difference of a system AB is defined as: $\Delta\rho = \Delta\rho_{AB} - \rho_A - \rho_B$, where in calculations of the latter two quantities, the atomic positions are fixed to those in the AB system.

Fig. 8 (a) and (b) show the charge density difference of TiAlN and TiAlZrN surface at 300K, respectively. The positions of O atoms above the surface are also marked in the figure for reference. As we can see from Fig. 8(a), metal-N bonds are mostly ionic with slight directional distortions. That is, the charges at metal sites always transfer to nearby N nuclei, in spite of Ti, Zr or Al atoms. Al atoms provide less charge than the Ti atoms, since the number of valence electrons of Ti is larger than Al. Furthermore, one can observe that the charge concentrates also between atoms to form covalent

1 bonds.

2 When 1 Zr atom replaces 1 Ti atom in surface layer, the nearby Ti atom is promoted
3 to escape the surface layer, so that loss of charge appears in the vacancy left behind
4 (Fig. 8 (b)). The Zr atom provides more charge than the replaced Ti atom, since it has
5 more valence electrons, and breaks the covalent bond between the nearby N atoms
6 around the vacancy. The charge transfer between atoms a few positions away from the
7 Zr atom is not influenced a lot, as may be seen from a comparison with the Zr-free
8 TiAlN surface.

9 For the Ti atoms which have O atoms on top in the 3 Å distance from the surface
10 initially, charges will also concentrate between Ti and O atoms to form ionic bonds, if
11 the distance between Ti-O is less than 1.87 Å. In Fig. 8 (b), the escaped Ti atom
12 formed Ti-O bonds with the nearest 3 O atoms, so that we do not observe any ionic
13 bond between metal atoms in the surface layer and the impending O atoms.

14

15 **3.2 Simulations at 1123K**

16 **3.2.1 Structure of the surface after relaxation**

17 We further investigate the effect of Zr on the TiAlN oxidation process at the
18 temperature of 1123K. Fig. 9 shows the interaction of the TiAlN(0 0 1) surface with 4
19 O atoms. Again, the individual O atoms interact with the surface Ti atoms but not with
20 Al atom, for the same reasons as mentioned above. The Ti atoms which left the
21 TiAlN/O interface layer, are about 0.77 Å away, more than the case at 300K. The
22 interface layer also looks more disordered than at 300K. Fig. 10 (a) clearly shows that

1 the O atoms moved away from their original location. This is not surprising, because
2 the O atoms are more active at the high temperature, and it is more difficult to be
3 bound by metal atoms. There are five Ti-O bonds observed and measured. Table 1
4 shows their bond lengths, which are in range of 1.60~1.79 Å, consistent with the
5 equilibrium 1.62 Å or 1.78 of the Ti-O dimer in the vacuum or above the surface.

6 Fig. 11 shows the TiAlZrN surface after 8000fs at 1123K. Unlike the case at 300K,
7 the O atoms react exclusively with Ti, not with other metal atoms. Fig 10 (b) shows
8 that the O atoms again move away from top of Zr and Al atom. Table 1 lists the bond
9 lengths of the Ti-O, which are about 1.61-1.70 Å, much shorter than that at 300K.
10 Additionally, no Zr-O bond is observed, suggesting the Ti-O bonds are more stable
11 than at 300 K, thus no Ti vacancies were generated in the surface at 1123 K.
12 Considering from MS calculations at 0K shown in Fig. 7, we also learned that the
13 addition of Zr in TiAlN surface changes the lowest bonding energy sequence from
14 $Zr-O < Ti-O < Al-O$ in the vacuum to $Ti-O < Zr-O < Al-O$ above the TiAlZrN surface.
15 It is concluded that the addition of Zr atom promotes the interaction of Ti and O at
16 TiAlZrN surface and leading a more stable surface at 1123K. It is known
17 experimentally that the TiAlZrN has a better oxidation resistance than the TiAlN at
18 1123K or TiAlZrN at 300K. Our findings are consistent with these observations.

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20 3.2.2 Charge density difference

21 To further clarify the role of the Zr doping in the TiAlN at 1123K, the charge
22 density difference maps were calculated. Figs. 12 (a) and (b) show the results for

1 TiAlN and TiAlZrN surface at 1123K, respectively. It follows, that the metal-N bonds
2 are mostly ionic with slight directional distortions, as the charges from the metal
3 atoms always transfer to the nearby N atoms, similarly to the case at 300K. On the
4 other hand, one can find that the amount of transferred charge from metal atoms to N
5 atoms is smaller. The covalent bonding between the nearby N atoms is stronger, as
6 more charge is gathered between them. Electrons will be more excited at the higher
7 temperature thus leading to a more frequent hopping between metal and N atoms, so
8 that besides higher charge transfer from metal atoms to N atoms, there is also more
9 charge transfer from N to metal atoms. Overall this leads to the charge transfer from
10 metal atoms to N atoms being less at 1123K than at 300K.

11

12 **4 Conclusions**

13 The TiAlN and TiAlZrN (1 Zr atom replaces 1 Ti atom) surfaces covered with 4 O
14 atoms at 300K and 1123K were simulated by *ab initio* molecular dynamics. From the
15 atomic displacements and bond formed after the relaxation, together with the analysis
16 of charge density difference maps, we find that at 300K, the addition of Zr promotes
17 Ti atom to escape from the surface, thus benefitting the formation of a vacancy and
18 TiO₂. From MS calculations at 0K, we find that the addition of Zr in TiAlN surface
19 changes the lowest bonding energy sequence from Zr-O < Ti-O < Al-O in the vacuum
20 to Ti-O < Zr-O < Al-O above the TiAlZrN surface. From MD simulations at 1123K,
21 we find that no Ti vacancies were generated in the surface. Moreover, less charge is
22 transferred from metal to N atoms, together with the bond lengths between Ti and O

1 atoms are shorter. These finds suggest that the addition of Zr atom promotes the
2 interaction between Ti and O at TiAlZrN surface and leading a more stable surface at
3 1123K. Our findings explain the experimental observations that the TiAlZrN has a
4 better oxidation resistance than the TiAlN at 1123K and than TiAlZrN at 300K.

5

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14

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1 Table 1. The measured bond lengths ($\text{\AA}$) from the present *ab initio* MD simulations.
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Temperature	Bond	TiAlN	TiAlZrN
300K	Ti-O	1.59	1.57
	Ti-O	1.75	1.83
	Ti-O	1.79	1.83
	Ti-O	1.80	1.85
	Ti-O		1.91
	Ti-O		1.96
	Zr-O		2.07
1123K	Ti-O	1.60	1.61
	Ti-O	1.65	1.65
	Ti-O	1.66	1.70
	Ti-O	1.79	1.71
	Ti-O	2.08	

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Table 2. Equilibrium bond lengths and bonding energies (with respect to **the lowest bonding energy of Al-O** as a reference state) of 3 metal-oxygen dimers in the vacuum and **O above Al, Ti and Zr atoms in the constructed TiAlZrN surface as a function of the distance between the O and the metal atoms**

Dimer		Ti-O	Zr-O	Al-O
In the vacuum	Bond length ($\text{\AA}$)	1.62	1.75	1.64
	Bonding energy (eV)	-2.84	-3.40	0
Above TiAlZrN surface	Bond length ($\text{\AA}$)	1.78	1.96	1.79
	Bonding energy (eV)	-1.29	-0.73	0

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2 Fig. 1 $\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}(001)$ -O interactions as a function of coverage. MD snapshots (side
3 views) at 300K are shown at (a) 0.22 monolayers and (b) 0.33 monolayers O coverage.

4 The atomic species are represented with different colors: Ti (blue), Al (chocolate), N
5 (grey), O (red).

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2 Fig. 2 (a) Side view and (b) top view of the TiAlZrN model used in our simulations. O

3 atoms were initially placed 3 Å from the surface. The total vacuum space is 15 Å.

4 The atomic species are represented by different colors: Ti (blue), Al (chocolate), N

5 (grey), O (red), Zr (green).

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2 Fig. 3 The structure of the TiAlN(001) surface **after the 8000 fs MD simulations** at

3 300K: (a) side view and (b) top view of TiAlN. The atomic species are represented by

4 different colors: Ti (blue), Al (chocolate), N (grey), O (red).

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(a)

(b)

Fig. 4 Displacement vector of O atoms at 300K after 8000 fs. (a) TiAlN, where O atoms leave the position on top of the Al atoms and only bind with Ti atoms. (b) TiAlZrN, where O atoms leave the original location and gathered to the escaped Ti atom. The atomic species are represented by different colors: Ti (pink), Al (blue), N (green), O (white).

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2 Fig. 5 Bond energy of Al-O bond, Ti-O and Zr-O bond in the vacuum as a function of
3 bond length, **using the lowest bonding energy of Al-O as a reference state.**
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2 Fig. 6 The structure of TiAlZrN surface **after the 8000 fs simulation** at 300K: (a) side
 3 view and (b) top view of TiAlZrN. **One Ti atom near a Zr atom escapes from the**
 4 **TiAlZrN surface, generating a Ti vacancy in the surface, and the escaped Ti atom**
 5 **bonds with the nearest O atoms to form TiO₂.** The atomic species are represented by
 6 different colors: Ti (blue), Al (chocolate), N (grey), O (red), Zr (green).

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3 Fig. 7 Bond length and bond energies for O above the TiAlZrN surface, using the
 4 lowest bonding energy of Al-O as a reference state. It is found that the addition of Zr
 5 in TiAlN surface changes the lowest bonding energy sequence from Zr-O < Ti-O <
 6 Al-O in the vacuum (Fig. 5) to Ti-O < Zr-O < Al-O above the TiAlZrN surface.

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Fig. 8 Charge density difference maps for the simulations at 300K for (a) TiAlN and (b) TiAlZrN.

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2 Fig. 9 The structure of the TiAlN surface **after the 8000 fs MD simulations** at 1123K:

3 (a) front view and (b) top view. The atomic species are represented by different colors:

4 Ti (blue), Al (chocolate), N (grey), O (red).

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5 Fig. 10 Displacement vectors of O atoms at 1123K after 8000 fs. (a) TiAlN and (b)

6 TiAlZrN, where O leaves the position on top of the Al atom and only interact with the

7 Ti atoms. The atomic species are represented by different colors: Ti (pink), Al (blue),

8 N (green), O (white).

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2 Fig. 11 The structure of the TiAlZrN surface after the 8000 fs MD simulations at
 3 1123K: (a) front view and (b) top view. The O atoms move away from top of Zr and
 4 Al atom and only interact with the Ti atoms. The atomic species are represented by
 5 different colors: Ti (blue), Al (chocolate), N (grey), O (red), Zr (green).

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(a)

(b)

Fig. 12 Charge density difference maps for the simulations at 1123K for (a) TiAlN and (b) TiAlZrN.