Adhesion and Diffusion at TiN/TiO₂ Interfaces: A First Principles Study

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Abstract

This work uses density functional theory (DFT) calculations to analyze the energetics and stability of TiN/TiO₂ interfaces. Specifically, the work of adhesion and migration energy barriers for oxygen diffusion through the interface are calculated for multiple interface geometries and terminations. It is found that the stability of defect free interfaces is controlled by the work of adhesion because the migration energy barriers for oxygen across the interface are high in all cases. It is also found that the TiN termination significantly affects the work of adhesion.

Keywords:

Titanium Nitride, Titanium Oxide, Oxidation, Density Functional Theory, Nudged Elastic Band Theory, Diffusion, Work of Adhesion

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1. Introduction

TiN is known for its corrosion resistance, wear resistance, high hardness, and extremely high melting temperature, making it an ideal material for applications at elevated temperatures¹⁻⁶, including cutting tools, turbines⁷, and protective heat shields. Unfortunately these applications are often in oxygen-rich environments, favoring the formation of oxide scales which lack the desirable properties of the base material. Therefore, understanding the oxidation properties of TiN is of major importance.

Oxides tend to be more brittle than their base material counterparts. While in most cases oxidation is a spontaneous process that cannot be prevented, in some instances it can be controlled. Under certain conditions in the TiN/TiO₂ system, a protective oxide scale acts as a diffusion barrier and prevents further corrosive attack at ambient temperatures and oxygen partial pressures. The oxide scale formed in the case for TiN has been characterized extensively and has been found to break down, leading to catastrophic oxidation above ~800°C.⁸ Such uncontrolled oxide growth at high temperatures makes high temperature applications of TiN problematic.⁹ Efforts to increase the operating temperature will be greatly facilitated by a mechanistic understanding of oxide growth.

Electronic-structure calculations at the level of density functional theory (DFT) can be used to investigate and develop a detailed understanding of the interface structure in complex material systems at the atomic and electronic level. Such modeling can be of particular importance in the characterization of interfaces since they are buried within a material and therefore are difficult to probe experimentally. The initial stages of oxidation of TiN have been extensively investigated using DFT. These

investigations focus mostly on the kinetic evolution of the initial oxidation process, such as the most likely sites for adhesion, the diffusion of oxygen across the surface, and the effect of vacancy structures on the evolution of the oxide scale.^{10, 11} While these studies illuminate the initial kinetic evolution of the oxide scale, they do not quantify the adhesive nature of a fully developed oxide scale or the kinetics of continued oxide growth at a developed interface.

In this work, interfaces between various surfaces of TiN and TiO₂ are constructed using the rutile and anatase phases of TiO₂ and the (001) and (111) terminations of TiN. The work of adhesion is calculated for each interface in order to gauge the protective nature of the interfaces. Nudged elastic band (NEB) studies are then conducted to determine the migration barriers for oxygen diffusion across the interfaces to gauge the likelihood of continued oxide growth at established TiN/TiO₂ interfaces.

2. Background

TiN oxidizes to form a rutile TiO₂ scale except at the TiN/TiO₂ interface, at which a thin gray film develops consisting of oxidized and reduced states of titanium oxide, including Ti₂O₃, Ti₃O₅, and TiO.⁸ The presence of so many different Ti oxidation states indicates that the oxide nucleates and grows at the TiN/TiO₂ interface rather than at the surface, at which stoichiometric TiO₂ would be expected to grow. Growth of an oxide scale must then rely on the diffusion of oxygen through the oxide scale and across the interface rather than merely on diffusion of metal cations to the surface.⁹

The evolution of the oxide scale is highly dependent on temperature. Below 800°C, the oxide scale that forms is protective; at these temperatures growth of the oxide is initially rapid but eventually slows and then stops as the diffusion distances

increase. Above this temperature, however, uncontrolled growth of the oxide can be seen in TiN due to the formation of cracks in the oxide that allow more rapid diffusion of oxygen through the oxide scale.⁸ This is due to high tensile stresses in the oxide scale. An inner protective oxide layer then forms as oxygen continues to diffuse through the porous oxide layer, which eventually delaminates, causing the cycle to repeat, resulting in the structure shown in Figure 1. There are two main properties that control the protective nature of the oxide. The first is the energy of adhesion. If the scale has a low work of adhesion then the probability of delamination increases, creating paths of fast track diffusion of oxygen through the scale.⁹ The second is the energy barrier for oxygen migration across the substrate/oxide interface. In this case, if the migration energy is low, then oxidation can take place by diffusion of oxygen across the TiN/TiO₂ interface.

Figure 1: Schematic of the cross section of the oxide scale structure on TiN⁸

The type of point defects that form in TiO₂ depends strongly on the oxygen partial pressure, temperature, and the presence of impurities. In concentrations close to stoichiometric, oxygen tends to form coupled charged vacancies and titanium tends to form interstitials.¹² TiN tends to form Schottky defects or a coupled vacancy pairs.¹³

3. Methods

The DFT calculations were performed using the Vienna ab initio Simulation Package (VASP)¹⁴⁻¹⁷ with the projector augmented-wave (PAW) method with the generalized-gradient approximation (GGA). The Perdew-Burke-Ernzerhof density functional (PBE)¹⁸ was used to describe the exchange-correlation energy. The kinetic energy cutoff was 400 eV and a 2x2x1 k-point mesh was used for the final interfacial structures, with only the $k_z=0$ point used in the direction perpendicular to the interface. Unless otherwise specified, all structures were relaxed with energy and force relaxation criteria of 10^{-4} eV and 0.01 eV/Å.

The interfaces were constructed using the rutile and anatase structures for TiO₂ and the rocksalt structure for TiN. For the oxide, energetically-favorable, geometrically flat surfaces were used: (110) rutile and the (001) anatase, shown in detail in Figure 2. Experimentally, the (110) rutile surface has been shown to be the most stable surface.¹² For the anatase phase the (101) surface is experimentally the most stable, low-energy surface. However, this surface has a terraced structure. The (110) and (001) anatase surfaces represent geometrically favorably flat surfaces. The (110) surface is a high energy surface; thus the (001) surface was determined to be a more suitable surface to investigate first.

The (001) surface has the second lowest surface energy for the anatase phase. The stability of the (110) rutile and (001) anatase surfaces can be understood as a result of autocompensation, which predicts that the most stable surfaces are those where the dangling bonds of the anions are compensated by the dangling bonds of the cations¹⁹ The oxides were paired with the (001) TiN surface, the low energy surface which can also be explained by autocompensation, and the (111) terminated TiN

surface which is the low stress surface. While the (111) terminated TiN surface has the lowest stress, it is also the highest energy surface due to its polarity.²⁰ The dipole correction in VASP was used for calculations involving the (111) TiN surfaces to increase the speed of convergence of the calculation. The (001) and Ti- terminated and N-terminated TiN (111) surfaces are also shown in detail in Figure 2.

Figure 2: Relaxed TiO_2 and TiN surfaces used to construct TiN/ TiO_2 Interfaces; Titanium (Blue), Oxygen (Red), Nitrogen (Purple)

Because experimentally the oxide is thin overlayer to the nitride, in-plane strain was imposed on the oxide only, with the in-plane lattice parameter of the TiN fixed to its bulk value. The strain was calculated for multiple combinations of the TiN and TiO_2 surfaces previously presented, as shown in Table 1. Two interfaces were chosen which minimized the strain in each direction parallel to the interfaces, while having computationally convenient small dimensions. Table 1 shows the calculations used to determine the dimensions of the interface parallel to the interface where the bolded

cases, represent the dimensions that were selected. Strain calculations for two other possible interfaces, $\text{TiO}_2\text{rutile}(110)/\text{TiN}(111)$ and $\text{TiO}_2\text{anatase}(001)/\text{TiN}(001)$, were analyzed, but full interfaces were not built due to the large strains that would be imposed on the oxide layer.

Table 1: Determination of dimension of substrate and oxide layer for minimal stress. The bold text represents the dimensions used to build each interface, using one unit cell thickness perpendicular to the interface. For the bottom two structures no dimensions were selected because all computationally accessible simulation cells had unrealistically high stresses.

Interface	Direction	Properties				
		Oxide X TiN Dimensions	Oxide In-Plane Dimensions (Å)	TiN In-Plane Dimensions (Å)	% Strain	# atoms
Rutile(110)/TiN(001)	x	2x1	5.946	4.240	28.69%	44
		3x2	8.919	8.481	4.92%	70
		4x3	11.892	12.721	-6.97%	96
	y	1x2	6.438	8.481	-31.73%	34
		2x3	12.876	12.721	1.21%	60
		3x4	19.314	16.961	12.18%	86
Anatase(001)/TiN(111)	x	2x1	7.331	5.192	29.18%	72
		3x2	10.996	10.384	5.57%	132
		4x3	14.662	15.575	-6.23%	192
	y	5x4	18.327	20.767	-13.31%	252
		2x1	7.938	6.003	24.37%	72
		3x2	11.907	12.007	-0.84%	132
Rutile(110)/TiN(111)	x	4x3	15.876	18.010	-13.44%	192
		2x1	5.946	5.192	12.68%	60
		3x2	8.919	10.384	-16.42%	104
	y	4x3	11.892	15.575	-30.97%	148
		1x1	6.438	6.003	6.75%	44
		1x2	6.438	12.007	-86.50%	72
		2x3	12.876	18.010	-39.87%	116
		3x4	19.314	24.013	-24.33%	160
Anatase(001)/TiN(001)	x	1x1	3.665	4.240	-15.68%	30
		2x1	7.331	4.240	42.16%	52
		3x2	10.996	8.481	22.88%	82
		4x3	14.662	12.721	13.24%	112
	y	1x1	7.938	4.240	46.58%	30
		1x2	7.938	8.481	-6.83%	38
		2x3	15.876	12.721	19.87%	68
		3x4	23.814	16.961	28.78%	98

Two termination geometries were used for the rutile (110) surface: the stoichiometric surface and the high temperature non-stoichiometric reconstruction in which the 2-coordinated bridging oxygens were removed.¹² The bridging oxygen atoms in the (110) termination make the surface extremely stable and energetically unreactive; we thus expect that the reconstruction will result in a stronger work of adhesion. Moreover, the bridging oxygens in the unreconstructed surface might also create a geometrical barrier to adhesion as they stick out of the surface. Both the Ti-terminated and the N-terminated surfaces were investigated for the TiN (111) surface. In all, four interfacial geometries were investigated.

An appropriate thickness of each phase was determined by calculating the surface energy of increasingly thicker slabs with zero in plane stress until the surface energy converged to within $\pm 0.005 \text{ eV/\AA}^2$, as shown in Figure 3. For each surface a vacuum of 20 $\text{\AA}$ was added. The stoichiometric surface energies (γ_s) were calculated in the usual manner, as shown in Equation 1. For the non-stoichiometric surfaces (1x2 (110) rutile reconstruction/(111) TiN) the chemical potential of the missing atoms (μ) times the number of atoms removed from the surface (m) was also subtracted out, as shown in Equation 2. The chemical potentials for oxygen and nitrogen was calculated using their molecular forms; the chemical potential of titanium was calculated from bulk titanium. Each interface was relaxed for a maximum of ten geometric steps; the relaxed surfaces used to construct the four interfaces are shown in Figure 4.

$$\gamma_s = \frac{(E_{\text{surface}} - n * E_{\text{Bulk}})}{2A} \quad \text{Eq. (1)}$$

$$\gamma_s = \frac{E_{\text{surface}} - n * E_{\text{Bulk}} - m * \mu}{2A} \quad \text{Eq. (2)}$$

Figure 3: The surface energy vs. slab thickness for the surface structures used to construct the TiN/TiO₂ Interfaces.

Figure 4: TiO₂ and TiN thin slabs used to construct the interfaces the TiN/TiO₂ Interfaces; Ti (Blue), Oxygen (Red), Nitrogen (Purple).

4. Interfacial Structures

Geometrical relaxations were obtained for three of the four interfacial structures presented in Figure 4; the final relaxed structures can be seen in Figure 5. The interfacial energy (γ_I) and work of adhesion (W) were calculated for all of the relaxed structures. The Interfacial energy is defined in a similar manner to surface energy and is

given in Equation 3. The work of adhesion was defined as the Interfacial energy minus the surface energies of each slab used to create the interface as given in Equation 4.

$$\gamma_I = \frac{(E_{Interface} - n_{TiN} * E_{TiN} - n_{Oxide} * E_{Oxide})}{2A} \quad \text{Eq. 3}$$

$$W = \gamma_{S_TiN} + \gamma_{S_Oxide} - \gamma_I \quad \text{Eq. 4}$$

After many attempts, it was found that the stresses were so high in the stoichiometric rutile(110)/TiN(001) structure that the DFT calculations could not be made to converge; as previously hypothesized, the 2-coordinated bridging oxygens were found to be the cause of the high stresses and the instability. As the geometric relaxation progressed the bridging oxygens, repulsed by the TiN surface, attempted to move into the plane of Ti, causing a large buildup of stresses in the direction parallel to the interface which became catastrophic during the relaxation; this case was not considered further. The non-stoichiometric, 1x2 reconstructed surface had considerably lower stresses than the stoichiometric counterpart, which can be seen in Table 2, due to the absence of bridging oxygens and it exhibits the second highest work of adhesion, as seen in Table 3.

Figure5: Fully relaxed TiN/TiO₂ Interfaces

The most stable interface constructed was the anatase(001)/TiN (111) Ti-terminated interface, which exhibited the lowest stresses, as shown in Table 2. The stresses found in each structure were compared to the bulk moduli of all of the oxides and nitrides for a relative comparison of stability for all of the cases. This structure also had the highest work of adhesion, as seen in Table 3. At the interface, the two-coordinated oxygen atoms, which in bulk are in the same plane as the Ti, were pulled towards the Ti-terminated TiN (111) surface.

Table 2: Stresses in fully relaxed Interfaces

Interface	Bulk Modulus (GPa)	Stress (GPa)		
		A	B	C
Rutile(110) 1x2 Reconstruction	218-220 ^{21, 22}	0.0738	-0.357	-0.0598
TiN(001)	320 ²³			
Anatase(001)	59-178 ²⁴	-0.0541	0.0479	0.0205
TiN(111) Ti-Terminated	320 ²³			
Anatase(001)	59-178 ²⁴	0.136	0.136	0.519
TiN(111) N-Terminated	320 ²³			

Table 3: Energetics of fully relaxed Interfaces. The stoichiometric rutile/TiN(001) did not converge.

Interface	Energy (J/m ²)			
	TiN Surface Energy	TiO ₂ Surface Energy	Interfacial Energy	Work of Adhesion
Stoichiometric Rutile(110) TiN(001)	0.531	0.127	X	X
Rutile(110) 1x2 Reconstruction TiN(001)	0.531	1.36	1.46	0.43
Anatase(001) TiN(111) Ti-Terminated	4.88	0.950	4.12	1.71
Anatase(001) TiN(111) N-Terminated	4.34	0.950	4.88	0.044

This behavior was not seen in the N-terminated (111) interface. While the 2-coordinated oxygen is weakly bonded, as will be seen in subsequent sections, the oxygens did not relax into the interface unless positioned directly opposite a nitrogen. The charge density for the N-terminated and the Ti-terminated interfaces are shown side by side in Figure 6, where it can be seen that two isolated oxygens bonded across the interface in the N-terminated structure. By contrast, every 2-coordinated oxygen in the Ti-terminated interface relaxed into the interface, creating strong bonding across the

interface. Another N-terminated interface was built in which all of the oxygens were placed within the interface; here the oxygens not directly opposite a nitrogen relaxed back into the oxide. This resulted in the highest stresses of all of the stable interfaces and a very low work of adhesion.

Figure 6: Charge density maps for the interfaces between anatase and the N-terminated and Ti-terminated (111) TiN, illustrating the degree of bonding across the interface. The yellow shells represent the electron clouds. The Blue spheres were along the boundary condition and are the electron clouds that have been bisected along that boundary.

As discussed in the Introduction, the trend in the works of adhesion can be expected to be one indicator of which interface is the most likely to be protective at elevated temperatures. The anatase (001)/TiN(111) Ti-terminated interface exhibits the highest work of adhesion of the interfaces studied, while the anatase(001)/TiN(111) N-terminated interface exhibits the lowest work of adhesion. From a materials processing perspective, this is problematic because the termination may be difficult to control as oxidation progresses, especially if diffusion of oxygen across the interface leads to continued growth of the oxide.

5. Oxygen Diffusion Through the Interface

The second primary property that controls the protective nature of a bulk oxide is the energy barrier for the diffusion of oxygen across the interface. If there is a low energy path across the interface, even if the interface is stable, uncontrolled growth of

the oxide is likely, especially at high temperatures where the diffusion of oxygen is faster. To determine the energy barriers for oxygen diffusion across the interfaces, a Nudged Elastic Band (NEB)²⁵ study was conducted by taking a single oxygen in each interface structure and moving it through the first layer of the TiN. For each interface, the path that had the largest open area for oxygen diffusion was chosen for investigation. For the TiN(001) interface, this path was through the cubic hole into the tetrahedral site, as shown in Figure 7. For the TiN(111) interfaces, this path was through the octahedral hole into the octahedral site between Ti and N layers, as shown in Figure

Figure 7: Schematic of the oxygen diffusion path to be investigated for the TiN(001) Interfaces where the large blue atoms are Ti, the small purple atoms are nitrogen and the red atom is oxygen.

Figure 8: Schematic of the oxygen diffusion path to be investigated for the TiN(111) Interfaces where the large blue atoms are Ti, the small purple atoms are nitrogen and the red atom is oxygen.

To test the convergence of the NEB calculations, the evolution of the energy with the number of geometrical relaxation steps was determined for a representative transition image for each interface. As seen in Figure 9, the energy rapidly converges. As an appropriate compromise between accuracy and computational efficiency, in all further calculations five geometrical optimization steps was used. The differences in energy between the fifth and tenth steps (0.25 eV for the TiN(111)/anatase(001) interface and 0.19 eV for the TiN(001)/rutile(110) interface) were taken as estimates of the error in the migration energies. As we shall see these estimated errors are much less than the overall energy barriers.

Figure 9: Energy of specific NEB configurations as a function of the number of geometrical relaxation steps.

The energy barriers for all three interfaces are given in Figure 10. The first thing to note is that in all cases, it is highly energetically unfavorable for the oxygen to be incorporated in the nitride layer. This indicates a strong propensity against oxidation in these defect free cases. The non-stoichiometric rutile/TiN(001) interface has only 3-coordinated oxygens at the interface. The energy barrier for the migration of a 3-coordinated oxygen through the first TiN layer is 7.47 eV with an approximate error of ± 0.19 eV. There is an initial energy barrier for the oxygen to move out of the rutile surface of 4.08 eV, with the transition state having the oxygen within the interface. In the case of both anatase interfaces, there are both 3-coordinated oxygens and a 2-coordinated oxygen. The migration barriers for both oxygens was also determined. The maximum barrier for the Ti-terminated interface was 8.63 ± 0.25 eV as compared to the nitrogen-terminated interface which had an energy barrier of 5.21 ± 0.25 eV.

Figure 10: Energy barrier for oxygen migration across three interfaces.

In all of the cases the error is much smaller than the overall barrier and in most cases, smaller than the energy difference from one image to the next. These results are consistent with the work of adhesion results. In particular, the interface with the largest work of adhesion, the anatase(001)/TiN(111) Ti-terminated interface, also has the largest energy barrier for the migration of oxygen across the interface. The interface with the lowest energy barrier is the N-terminated interface which also has the lowest work of adhesion. The strong bonding across the interface that results in a high work of adhesion also resists the diffusion of oxygen across the interface. These results are summarized in Table 4.

Table 4: Summary of the works of adhesion and maximum migration energy barriers for oxygen across the interface for all stable interfaces.

Interface	Work of Adhesion (J/m²)	Migration Energy Barrier (eV/atom)
Rutile(110) 1x2 Reconstruction	0.433	7.47± 0.19
TiN(001)		
Anatase(001)	1.71	8.63 ± 0.25
TiN(111) Ti-Terminated		
Anatase(001)	0.044	5.21 ± 0.25
TiN(111) N-Terminated		

6. Conclusions

Two properties are important in the development of a protective oxide scale in any given system. First, the interface needs to exhibit a high work of energy to avoid spallation. Second, the interface itself needs to act as a barrier to further oxidation by exhibiting high migration barriers for the movement of oxygen across the interface. In the case of TiN/TiO₂ interfaces, it was found that the energy barriers for all of the defect-free interfaces investigated were sufficiently high enough to constrain oxide growth, which means that the first property, the work of adhesion, should be the controlling property for the formation of a protective oxide scale. It was found that the interfacial system that exhibited the best qualities for the formation of a protective oxide scale was the TiN(111) Ti-terminated surface having the highest work of adhesion to anatase. However, termination is of extreme importance in this case. The N-terminated surface exhibited the lowest adhesion; interface delamination is likely for such, by which fast paths for diffusion and growth of the oxide are created. If the termination can be controlled at the interface during the initial stages of oxidation, then the TiN(111) Ti-terminated/anatase(001) exhibits the best properties for the formation of a protective oxide scale. The TiN(001)/non-stoichiometric rutile(110) has the second highest work of adhesion and could offer a viable alternative to the TiN(111) as the interfacial structure would be easier to control.

All of these cases, however, represent pristine interfaces which lack any significant density of defects such as vacancies, surface texture, or grain boundaries. Diffusion paths that include the migration of an oxygen into a nitrogen or titanium

vacancy, or the exchange of a nitrogen for an oxygen should be considered for future investigations.

As previously stated, cracks form within the oxide at elevated temperatures, forming fast path diffusion paths. Migration barriers for oxygen movement in defect structures can be expected to be much lower and could be the source of continued oxidation at elevated temperatures resulting in stresses that overcome the work of adhesion.

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