Unraveling the atomic structure evolution of titanium nitride upon oxidation

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Article

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Abstract

Oxidation-induced structural failure is a major issue in high-strength non-oxide ceramics, yet the atomic-level structural changes underlying phase transformation have remained elusive. Here, we present a study that employs state-of-the-art aberration-corrected environmental transmission electron microscopy to unravel the atomic-scale structural evolution of titanium nitride during dynamic oxidation. Our findings reveal two distinct reaction pathways, each characterized by the migration of titanium atoms through the formation of chains of titanium vacancies and staggered titanium vacancies. We demonstrate that these pathways are significantly influenced by both crystal orientation and surface curvature. Our rigorous First-principles calculations elucidate the underlying mechanism, revealing that titanium atoms have the highest kinetics for moving out along the \( \{200\} \) family, while their movement is modulated by surface strain involved in curvature changes. This insight is further substantiated by macroscopic oxidation experiments, affirming that the precision control of material orientation indeed enhances antioxidative performance. Our research holds immense scientific and technological significance, advancing our understanding of materials' antioxidation performance and ultimately bolstering durability and extending lifespan.

Introduction

Oxidation is a fundamental chemical process that can significantly impact the performance, durability, and reliability of both structural and functional materials utilized in technological applications such as engineering, telecommunications, energy storage, and conversion\(^1\)\textsuperscript{–}\textsuperscript{5}. The safe operation of engineering applications depends on how structural stability that could be maintained by restraining small cracks forming inside the material\(^6\). Oxidation failure is generally finished by phase transformation, accompanying with large internal stress and cracks generation induced by the volume change\(^7\). What's more, oxidation embrittlement effect generated by reaction- and diffusion-controlled regimes, also called stress corrosion cracking, will be assisted creep and stress rupture at high temperatures, which are significantly threat to the application safety\(^8\).

Titanium nitride (TiN) is a ceramic material with exceptional physical and chemical properties, e.g. high melting points (ca. 3000°C), hardness, wear resistance, and chemical inertia\(^9\), resulting in their wide technical applications at high temperatures, especially in hostile environments\(^10\)\textsuperscript{–}\textsuperscript{16}. However, it is also susceptible to thermal oxidation corrosion that severely limits their applicability\(^17\)\textsuperscript{–}\textsuperscript{19}. Early studies on TiN oxidation process and phase transformation suggest a series of titanium oxides might be formed\(^20\), including anatase TiO\(_2\)\textsuperscript{18}, rutile TiO\(_2\)\textsuperscript{21}, Ti\(_3\)O\(_5\)\textsuperscript{22}, and intermediate phase of TiO\(_x\)N\(_y\)\textsuperscript{23}, etc. The oxidation of TiN appears to be complex because of the apparent disparity of the results, which mainly comes from the existence of variety of oxides with a stable structure. The phases of new-formed oxides are varying with temperature and pressure inasmuch as they have an effect upon the reaction kinetics. While up to now, all intermediate Ti-O\(_x\) or Ti-O-N structures, especially the atomic structures are rarely been reported, and related oxidation dynamic are largely unknown. In-depth understanding the underlying mechanisms and
dynamic of oxidation corrosion is crucial for TiN materials to improve their safety in long-term service and broaden their application horizons.

Owing to recent advances, \textit{in situ} transmission electron microscopy (TEM) has revolutionized the study of material dynamic reaction process, including either physical or chemical reactions, by allowing to directly visualizing structural evolution at real time\textsuperscript{24−30}. For example, the effect of water vapor on oxidation of nickel-chromium alloy were clearly revealed in the dynamic oxidation reaction process by the \textit{in situ} aberration-corrected environmental transmission electron microscopy (AC-ETEM), suggesting water-vapor-enhanced oxidation is associated with proton-dissolution-promoted formation, migration, and clustering of both cation and anion vacancies.\textsuperscript{29} In our study, real-time atom motions during the phase transformation from TiN to anatase TiO\textsubscript{2} is directly disclosed by using \textit{in situ} AC-ETEM. Evidence is provided for the presence of multiple simultaneous oxidation pathways during the oxidation process of TiN, revealing the highest active side of TiN \{200\} plane for Ti atom diffusion and the influence mechanism of morphological curvature on the oxidation pathways.

\textbf{Results}

\textbf{The first oxidation pathway of TiN}

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images of TiN upon oxidation at atomic scale, illustrating the complete phase transformation from cubic TiN to tetragonal anatase TiO\textsubscript{2}. Figure 1 displays time-resolved structural evolution of an individual TiN during thermal oxidation process, successfully achieved by the setup built on AC-ETEM platform (Supplementary Fig. 1). That allows direct observation of the dynamic oxidation reaction process at high temperature (range of RT – 900°C) in oxygen. In order to obtain reliable results, a static time of approximately 5–10 minutes is necessary to maintain image stability, due to obvious image shift and vibrating caused by the thermal expansion of the SiN film as changing the temperature and pressure. The starting time of the first stable image was set as \(t_0\). As shown in Fig. 1a, initial TiN phase nearly has no change during the static period, the orientation of such particle can be labeled as zone axis of [001] with two sets of crystal planes of (200) and (020), respectively, being perpendicular to each other. The inset in the lower right corner presents the corresponding fast Fourier transform (FFT) image of Fig. 1a. Figure 1g and 1h illustrates the schematic image of atomic structure of both TiN and anatase TiO\textsubscript{2} phases, in where displays the atomic configuration and atomic radii, as well as the numbers of Ti observed along the [001] axis.

Under oxidation conditions of 450°C and 50 Pa oxygen pressure, after 15 minutes, 5–7 vacancies of titanium atoms (Fig. 1b) are identified along the (200) direction at the near surface region of the particle. Intriguingly, we discovered that titanium vacancies created a periodic array of defects with one row of titanium atom absence every three (200) crystal planes. In other words, there are two regular (200) planes between every two planes with vacancies, just as shown in the second step in Fig. 2e. With oxidation
progressing, an increasing number of titanium vacancies (Fig. 1c) appeared along both the (200) and (020) directions, following the same periodicity. That implies more titanium-nitrogen bonds have been broken to subsequently form titanium-oxygen or titanium-oxygen-nitrogen bonds. The work by Janina et al\textsuperscript{31} also demonstrated that certain titanium atoms in TiN have a tendency to bond with oxygen during the initial oxidation process. This results in titanium departure from TiN crystal lattice sites with leaving vacancies at those sites. Theoretical calculation results confirm that the presence of titanium vacancies arranged in chains facilitate to reducing the internal energy and enhancing the structure stability of the oxide system, though this phenomenon has not been experimentally validated to date\textsuperscript{31}. Thus, the presence of periodic atom row absence would largely contribute to the following oxidation proceeding and the initial structures characteristics of titanium-oxygen bond formation. The generation of titanium vacancies along the (200) direction during the oxidation process is not coincidental, we observed the same phenomenon in other regions (Supplementary Fig. 4) and along another zone axis of [110] as well, as shown in Fig. 1j. These above observations together prove TiN displays the highest oxidation activity along the crystal planes of \{200\} family compared to other crystal planes. To gain deeper insights, we conducted rigorous First-principles calculations to evaluate the migration barriers of titanium atoms along series of crystal planes (refer to Fig. 1h for the results). Consistently, our calculations are in constant with the notion that the influence of titanium migration along the (200) plane is comparatively minimal. These findings underscore the pivotal role played by the (200) crystal plane in the oxidation of TiN, highlighting its significance in this context.

Following one hour of oxidation treatment, a substantial influx of oxygen atoms penetrated the TiN lattice, resulting in pronounced lattice distortion. Consequently, it becomes unfeasible to clearly visualize atomic structure changes of TiN in this specific area (Fig. 1e). Nonetheless, drawing from the atomic structures gathered during the oxidation process depicted in Supplementary Fig. 5, we made rational deductions regarding the structural evolution throughout the entire oxidation process. The region depicted in Fig. 2a corresponds to the [001] axis of TiN, where titanium vacancies emerge along the (020) crystal plane. By employing line profiles, we compared the variations in atomic contrast across four distinct regions spanning. Ten columns of titanium atoms were selected in parallel to the (200) crystal plane, with each individual column denoted by uppercase letters A-J. We used the alignment of column D atoms to obtain the relative displacement of atoms in different regions. In the region without titanium vacancies (i.e., the 4# curve in Fig. 2c), titanium atoms are arranged strictly in accordance with atom sites in the lattice structure of TiN, and the spacing between every two titanium atoms is measured as 0.21 nm. In the other three curves, we observed partially missing atomic columns (i.e., columns B, E, and H), which corresponded to the generation of titanium vacancies. Wherein one titanium vacancy emerged every three atom columns, corroborating the phenomenon observed in Fig. 1. Additionally, we noticed that after vacancy formation, neighboring titanium atoms approached the vacancies, with columns A and C moving closer to their original positions in column B, reducing the distance between columns A and C. Employing First-principles calculations, we realized that the driving force is the difference in internal energy among the intermediate oxide structures that are subsequent to the creation of titanium vacancies (Fig. 2f). The simulation results demonstrate that after the formation of titanium vacancies, oxygen
atoms tend to occupy the vacancy sites and form titanium-oxygen bonds with the titanium atoms on both sides of the vacancies, thereby reducing the distance between the two columns of atoms.

With prolonged oxidation time, the amounts of titanium vacancies gradually increase, leading to the generation of titanium vacancies on the other crystal planes of (020) between the adjacent two vacancy columns (Fig. 2b). Through image contrast comparisons in Fig. 2d, we observed that newly generated titanium vacancies were arranged with one vacancy existing in every three titanium atoms. These newly formed titanium vacancies result in the formation of a regularly arranged Z-shaped Tetris block (as shaped as formed in the third step in Fig. 2e) morphology between two long chains of titanium vacancies (The structure of this Z-shaped Tetris block can be observed more intuitively in Supplementary Fig. 8b).

Additionally, we compare the system energies of two potential intermediate structures based on the current vacancy formation pattern (Fig. 2g). The results indicate a lower system energy for the Z-shaped structure compared to the square structure, inasmuch as a Z-shaped intermediate structure prefers forming during oxidation. The presence of titanium vacancies on both sides of the vacancy chain is correlated, and this mechanism of vacancy formation leads to the formation of staggered atomic pairs, as depicted in the third step of Fig. 2e. The structure within the green dashed box in Fig. 1e is identical to that in Fig. 2b, suggesting that these two areas experience the same oxidation process. Subsequent to the formation of the Z-shaped intermediate structure, we further observed the presence of an atomic arrangement along the anatase [001] axis within the oxide (Supplementary Fig. 5c). Structurally, the uniform dispersion of atoms within the plane leads to the transition from the Z-shaped intermediate structure to the atomic arrangement along the anatase [001] axis, effectively alleviating internal stress. Hence, we propose that during the mid-to-late stages of the oxidation process, the oxide optimally adjusts atomic distances to relieve the internal stresses generated during oxidation. This adaptive mechanism leads to the development of a transitional structure resembling the fourth step depicted in Fig. 3e, ultimately resulting in the transformation into anatase. This indicates that there is a fixed correspondence between TiN and anatase, i.e., TiN [001] corresponds to anatase [001] after oxidation.

However, we observed some areas where the oxidation paths were unclear, such as the green dashed circle in Fig. 1c, where no long chains of titanium vacancies along the (200) or (020) directions formed. Similar phenomena have been observed in the oxidation process of other particles (see Supplementary Fig. 6), which may be attributed to different modes of titanium vacancy formation. Furthermore, certain areas exhibited low signal-to-noise ratios, posing challenges in determining the detailed oxidation pathways.

**The second oxidation pathway of TiN**

To enhance our comprehensive understanding of the oxidation process, we refined the reaction conditions to promote milder conditions, resulting in decelerated oxidation rates and prolonged reaction durations. This adjustment facilitated the acquisition of additional structural insights during the oxidation process. Figure 3 presents a series of HAADF-STEM images of TiN particles in the oxidation
process, taken at reducing the reaction conditions (Temperature: 400°C, and O\textsubscript{2} pressure of 20 Pa).

Figure 3a illustrates atomic structure of TiN observed along the [001] axis, while Supplementary Fig. 7 provides a magnified HAADF image revealing a clearly visible grain boundary. The adjacent grains exhibit same zone axis of [001] with a grain boundary angle of 3°. Prior to the observation of this area, different regions of the sample have undergone varying degrees of oxidation, and long chains of titanium vacancies aligned along (200) have generated at the right edge of grain 2. However, the oxidation behavior at the left edge of the grain 2 and the edges of the grain 1 exhibit distinct characteristics compared to the previous observations, e.g. arrangement of titanium vacancies are consistent with those shown in the green circle in Fig. 1c. It suggests that no difference in the atomic structure evolution and phase transformation even though altered the reaction conditions to a milder status. After 55 minutes of oxidation, four distinct oxide structures were identified on the TiN, depicted in Fig. 3c, and Supplementary Fig. 8 sequentially displays the magnified HAADF images, which include the long chains of titanium vacancies and the staggered atomic pairs structure. Here named these distinct structures as the first oxidation path (Path I). The other two oxide structures are categorized as the second oxidation path (Path II) since they are absence in the Path I. Under varying reaction conditions, both oxidation pathways occurred, suggesting that temperature and oxygen pressure are not determining factors for the distinct oxidation pathways in TiN. The structure observed in the grain 1 should be the initial structure in the Path II, whereas the structure at the left edge of the grain 2 emerged later in the Path II (the supporting evidence will be discussed later).

Following the complete transformation of the sample into titanium dioxide (Fig. 3e), we subjected the oxide to heating in an oxygen environment. As a result, we observed a morphological reconstruction without any further phase transformation that consistent with previous reports\textsuperscript{32–34}. Figure 3e illustrates the presence of two atomic steps consisting of anatase (101) crystal planes on the left edge of the oxide (Supplementary Fig. 9). However, these atomic steps exhibit instability under the current environmental conditions. In Fig. 3e to 3f, the outermost atomic step progressively diminishes from bottom to top. Subsequently, in Fig. 3g, the following outermost atomic step initiates its disappearance from the top. Finally, in Fig. 3h, the outermost atomic step completely vanishes, leading to the formation of a regular oxide shape. We conducted First-principles calculations to assess the system energy of oxide configurations characterized by varying numbers of steps. The results demonstrate that a reduction in the number of steps contributes to the establishment of more stable systems (Supplementary Fig. 10).

Consequently, the oxide exhibits a tendency to adopt flat surfaces. In the following sections, we elucidate the second oxidation pathway (Path II) of TiN by meticulously tracing the atomic structural evolution of the right edge of grain 1 throughout the oxidation process.

Figure 4a presents the atomic structure of an intermediate phase in the Path II, three distinct regions that encompassed crystal planes of (200) and (020) to accurately deduce the structure evolution. These regions are selected to include both vacancy-containing and vacancy-free areas labeled with dashed blue, orange and green, respectively (Fig. 4a). In Fig. 4g, the 1# curve displays changes in atomic contrast for the repeating units along (200) after oxidation, every three atoms with relatively strong contrast are
surrounded by two atoms with weaker contrast. Each repeating unit is separated by a titanium vacancy and adjacent planes of repeating units are arranged in a staggered pattern. The related atom configuration is shown in the first step of Fig. 4j, with atoms of weaker contrast represented in lighter colors. We observed a significant reduction in atomic spacing at where containing vacancies compared to regions without vacancies. The average interplanar spacings of the (200) and (020) planes decreased from 0.21 nm to 0.19 nm after the vacancies emerged, as depicted in Fig. 4g and 4h. First-principles calculations indicated that continuous infiltration of oxygen atoms into the TiN lattice resulted in the formation of bonds with the surrounding titanium atoms. These titanium-oxygen bonds lead to a reduction in the interatomic distance, therefore, a general decrease in atomic spacing is observed in the vacancy-rich regions (Supplementary Fig. 9).

As shown in Fig. 4b-d, in Path II, as the oxidation process unfolds, the presence of titanium vacancies and a general reduction in atomic spacing lead to a gradual decrease in the angle between the (200) and (020) crystal planes. This phenomenon can be attributed to internal strains induced by structural changes or phase transformations. When the (200) crystal plane tilts to a certain degree, a portion of the atoms are subjected to compressive strains in their vicinities, causing them to deviate from their original lattice positions, as highlighted in the red box during the second step of Fig. 4j. As the (200) crystal plane continues to rotate, two atoms from the upper and lower rows approach closer, subsequently moving far away from their initial positions due to lattice compression, as indicated by the red box in the third step of Fig. 4j.

The angle between the (020) and (200) crystal planes can reach a minimum of 69°, and when a certain number of titanium atoms have completed their migration, the angle between them stops decreasing and gradually starts to increase. This is evident in Fig. 4d, where the angle between the two crystal planes in that region returns to 76° when the titanium atoms selected in the second and third steps of Fig. 4j complete their migration. Over time, the atomic structure with staggered atomic pairs undergoes a relaxation process and evolves into those belonging to anatase TiO$_2$ of [001] axis (Supplementary Fig. 10), in coincidence with the rotation returning to 90° (as depicted in Fig. 4e and 4f). It is worth mentioning that in Fig. 4i, the atomic spacing does not change in structural relaxation process; rather, it just leads to changes in the relative positions of the atoms. From this, it is evident that the correspondence between TiN and TiO$_2$ observed in the Path I that also applies to the Path II, meaning that an epitaxy relationship between TiN [001] and anatase [001].

**The influence of curvature on the oxidation pathway**

In summary, we observed two main oxidation pathways during the transformation process from TiN to anatase TiO$_2$. Intermediate oxidation structures for both oxidation pathways have been observed in the oxide under various reaction conditions, including different temperatures and oxygen pressures. Hence, it can be concluded that temperature and oxygen pressure do not dictate the TiN reaction pathway. According to the analysis above, we find out that the surface curvature plays a significant role in determining the pathways via influencing structure evolution during oxidation process. With relatively flat
edges, just like the area where the red sphere is located at Fig. 5c, the oxidation proceeding mainly
depends on the Path I. For example, this surface edges of particles in Fig. 1, as opposed to the flatness
observed in the left edge of grain 2 in Fig. 3. Conversely, the Path II is more prevalent in regions with
curved edges, just like the area where the blue sphere is located at Fig. 5c. Motivated by these
experimental findings, we delve into a detailed analysis through first-principle calculations to uncover the
intricate influence of curvature on oxidation pathways

Figure 5a demonstrates that when the curvature radius of the grain exceeds 4.5 nm, the oxidation
pathway tends to follow the Path I. Conversely, as curvature radii are smaller than 4.5 nm, the Path II
becomes more favorable (The curvature radius at this location is defined based on the radius of the
circumscribed circle in the respective region, as shown in Supplementary Fig. 11). The curvature of the
materials would generate both axial and tangential stresses, which significantly influences both the
oxidation rate and the morphology of the oxide layer. These tensile stresses are found along the
axial direction and compressive stresses are along the tangential direction. As the curvature radius
decreases, the material experiences an increasing compressive stress, which's magnitude is directly
proportional to the strain with a constant composition.22 Due to the limitations of simulation dimensions
and the periodic boundary conditions, it is not feasible to simulate an entire spherical structure. Therefore,
we employ lateral strain tension to mimic the curvature of the material. Figure 5b displays a relatively
limited response to applied strain along Path I, while a noticeable reduction in system energy was
observed with the application of positive strains exceeding 2% along Path II. As a result, the greater
tendency to follow the Path II is regulated by the smaller surface curvature radii of TiN nanoparticles,
because of elevated stress status upon oxidation.

The effect of (200) crystal plan on the oxidation resistance
of TiN

Building on the insights gained from the atomic-level oxidation processes, we now shift our focus to the
influence of the (200) crystal plane on the oxidation of bulk TiN. In both pathways, oxidation
predominantly initiates along the (200) crystal plane. Accordingly, two distinct titanium nitride materials
were engineered: one with a distinct orientation along the (200) crystal plane, and the other with an
absence of discernible orientation. This tailored design seeks to elucidate the impact of the (200) crystal
plane on the oxidation dynamics of titanium nitride. As observed in Supplementary Fig. 13, under
identical thermal treatment conditions, the TiN material with a (200) preferred orientation demonstrates
increased susceptibility to oxidation. Post heat treatment, detectable diffraction peaks indicative of
titanium oxide were evident in the former, while the latter, with a random orientation, exhibited an absence
of such distinctive peaks. Upon elevating the heat treatment temperature to 600 °C and maintaining it for
40 minutes, detectable diffraction peaks indicative of titanium oxide emerge in the randomly oriented TiN
samples. Significantly, at this juncture, the intensity of the titanium oxide diffraction peaks in the (200)
preferred orientation sample triples that of its randomly oriented counterpart. This emphasizes the
potential for enhancing the antioxidative performance of TiN through careful control of its orientation.
Discussion

In this study, we combined ETEM experiments with first-principle calculations to investigate the atomic structure evolution of TiN in dynamic the oxidation process. The oxidation reaction originates from the generation of periodic array of titanium vacancies along TiN crystal plane of (200), due to their lowest migration barriers for titanium atoms. Two distinct oxidation pathways are firstly distinguished based on the atom structures of intermediate phases stably appeared in the oxidation process. And notably, Our first-principles calculations emphasized that is the primary factor of surface curvature determining the selection of the oxidation pathway in TiN. Additionally, an intriguing reconstruction of anatase TiO$_2$ has been clearly identified that underscores the tendency of anatase to adopt morphologies with regular and flat edges. Based on a thorough understanding of the atomic structure evolution during the oxidation process of titanium nitride, successfully enhancing its oxidation resistance was achieved by adjusting the content of the (200) crystal plane in titanium nitride materials. In conclusion, our study bridges the gap between experimental observation and theoretical understanding, shedding new light on the intricate oxidation dynamics of TiN. What's more, comprehensively offer valuable insights for structure-property relations including both engineering and functional applications.

Methods

TEM Sample Preparation

TiN nanoparticles (TiN, 20 nm, 99.0%, Macklin) were dispersed in ethanol solution, and the well-dispersed solution was dropped onto a Micro Electromechanical System (MEMS, MEMS Chips for NanoEx-i/v) chip. The chip was then heated using an infrared lamp to evaporate the ethanol inside the chip. After complete evaporation of ethanol in the observation window of the chip, the chip was clamped onto a heating holder (NanoEx-i/v MEMS Holder).

In situ TEM characterization of TiN

The oxidation experiments were conducted using spherical aberration corrected ETEM (Themiz G3 ETEM 80–300 kV, Thermo Fisher Scientific, USA) equipped with an aberration corrector. The ETEM enabled observation of in situ oxidation with a partial pressure up to 2 kPa and at a temperature of up to 1,000°C. The setup used in this study is illustrated in Supplementary Fig. 1. TiN nanoparticles were dispersed onto a MEMS chip and connected to an external power source (Supplementary Fig. 1b). A resistive wire near the observation window on the chip was used to heat the sample region. The dynamic oxidation was operated at 300 kV in HAADF-STEM mode with a measured resolution of better than 0.8 Å. The probe convergence angle for HAADF-STEM mode was set at 25.1 mrad, while the collection angle ranges from 47 mrad to 200 mrad. Before oxidation, the sample were annealed at 150°C in high vacuum < $1 \times 10^{-5}$ Pa, resulting in a clean surface. Pure oxygen (~ 99.99%) was introduced into the TEM column to oxidize the nanoparticles at a given temperature and pressure. As shown in Supplementary Fig. 2, BC/O and PP/O were used to detect the gas pressure inside the system and before entering the electron microscope.
chamber, respectively. In this experiment, the gas pressure inside the electron microscope chamber was adjusted to 20 or 50 Pascal (Pa) (as shown in Supplementary Fig. 3). The introduction of O₂ into the microscope was also confirmed by connecting a mass spectrometer to the exhaust port of the microscope. The detected species with molecular masses of 14 and 28 at the initial stage of O₂ introduction were identified as N₂, which served as a protective gas in the gas path. The concentration of N₂ gradually decreased with the introduction of oxygen.

**Density Functional Theoretical Calculation**

The DFT calculations were performed using the first-principles electronic-structure code Quantum Espresso. The Perdew-Burke-Ernzerhof (PBE) exchange-correlation approximation was used to calculate the total energy. A plane-wave energy cutoff of 450 eV and the estimated error is less than 10⁻⁶ eV with a Monkhorst-Pack k-mesh of 2 × 2 × 2 uniformly distributed in the Brillouin zone.

**Declarations**

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**Author contributions**

Q. Li, P. Wang, T. Wang and A, Nie conceived the ideas and supervised the project. R. Hao, W. Miao, W. Xu, Q. Li, Z. Wang, Q. Xiao performed the STEM and TEM experiments. R. Hao, W. Miao, Q. Li and A, Nie analysed the data. P. Wang and Y. Lin conducted simulations. R. Hao, Q. Li, J. Wu and H. Wang led the writing of the paper and the presentations in the figures. All authors contributed to the discussion of the results and commented on the manuscript. R. Hao and W. Miao contributed equally to this work.

**Data availability**

All data supporting the findings of this study are available within the paper and its supplementary information files. Source data are provided with this paper.

**Competing interests**

The authors declare no competing interests.

**References**


**Figures**

[a] TiN [001] 450°C O₂ 50 Pa  t₀


[5] TiN [001] 450°C O₂ 50 Pa  t₀ + 60 min


[9] Anatase [001]

[k] Energy difference (eV) vs. Layer number

Energy difference (eV) (100) (110) (111)
Figure 1

Time-resolved HAADF-STEM images reveal the oxidation process of TiN in O\textsubscript{2} with $p = 50$ Pa and $T = 450$ °C. **a-f,** The oxidation process of TiN begins with the initial phase along the [001] axis of TiN (**a**) and ultimately forms the oxidized product along the [001] axis of anatase (**f**). **g-h,** Schematic diagram of atom configuration of TiN (**g**) and anatase TiO\textsubscript{2} (**h**) phases, observed along the [001] axis, where blue spheres represent titanium atoms, while yellow and red spheres stand for nitrogen and oxygen atoms, respectively. **i-j** HAADF images of TiN along the [110] axis before and after partial oxidation. **k,** First-principles calculations regarding migration barriers on different crystal planes. The scale bar is 5 nm. The real-time structure evolutions of TiN in oxidation were recorded in Supplementary Movie 1.
Figure 2

The detailed intermediate oxide structures of TiN during the oxidation process. **a**, Row of nitrogen vacancies titanium vacancies are formed along the (020) crystal plane. **b**, Titanium vacancies are formed along the (020) crystal plane. **c-d**, Line profiles to display the image contrast comparison corresponding labeled curves in the (a) and (b), respectively. **e**, Schematic diagram illustrating the structural evolution from TiN to anatase, blue spheres represent titanium atoms, and dashed red spheres represent titanium
vacancies. **f**, The model is used to depict the crystal structure changes after introduction of titanium vacancies. **g**, The internal energy evolution of two potential intermediate structures during the oxidation process.

**Figure 3**

**Time-resolved HAADF-STEM images reveal the oxidation of TiN in O$_2$ with $p = 20$ Pa and $T = 400$ °C. **a-h**, The oxidation process of TiN begins with the initial phase along the [001] axis of TiN (**a**) and ultimately forms the oxidized product along the [001] axis of anatase (**h**). The region indicated in (**a**) contains a grain boundary, and its magnified image is shown in Supplementary Fig. 10. The scale bar is 2 nm. The real-time structure evolutions of TiN in oxidation were recorded in Supplementary Movie 2.
Figure 4

The detailed atomic structure evolution of TiN in the second oxidation pathway. a-f, Time-resolved HAADF-STEM images reveal the oxidation process of TiN, (e), (f) represent the structures at different time intervals for the left edge of grain 2, as shown within the dashed box in Fig. 3e. The scale bar is 1 nm. g-i, Line profiles about the atom column from the five boxed regions in (a), (e), (f), respectively. j, The structural evolutions from TiN to anatase, with blue spheres representing titanium atoms, and the atoms boxed with dashed red represent titanium atoms departure from their original lattice positions.
Figure 5

The first-principle calculation about the two oxidation pathways. a, A statistical analysis of the distribution of curvature radii in the regions where two different oxidation pathways occurred. b, The relationship between the internal energy difference in the oxidation proceeding and equivalent lateral strain tension (i.e. different surface curvatures) along different oxidation pathways of TiN. c, Illustrations of different oxidation pathways occurring at two distinct curvatures.

Supplementary Files

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