Computational Materials Science 130 (2017) 249–256

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Adhesion and diffusion at TiN/TiO_2 interfaces: A first principles study

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ARTICLE INFO

Article history:
Received 26 July 2016
Received in revised form 17 October 2016
Accepted 8 November 2016

Keywords:
Titanium nitride
Titanium oxide
Oxidation
Density functional theory
Nudged elastic band theory
Diffusion
Work of adhesion

ABSTRACT

This work uses density functional theory (DFT) calculations to analyze the energetics and stability of TiN/TiO_2 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.

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 temperatures [1–6], including cutting tools, turbines [7], 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/TiO_2 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 TiO_2 are constructed using the rutile and anatase phases of TiO_2 and the (0 0 1) and (1 1 1) 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/TiO_2 interfaces.

2. Background

TiN oxidizes to form a rutile TiO_2 scale except at the TiN/TiO_2 interface, at which a thin gray film develops consisting of oxidized

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http://dx.doi.org/10.1016/j.commatsci.2016.11.017
0927-0256/

and reduced states of titanium oxide, including Ti_2O_3, Ti_3O_5, and TiO [8]. The presence of so many different Ti oxidation states indicates that the oxide nucleates and grows at the TiN/TiO_2 interface rather than at the surface, at which stoichiometric TiO_2 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 Fig. 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/TiO_2 interface.

The type of point defects that form in TiO_2 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 forms 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 $2 \times 2 \times 1$ 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 TiO_2 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 Fig. 2.

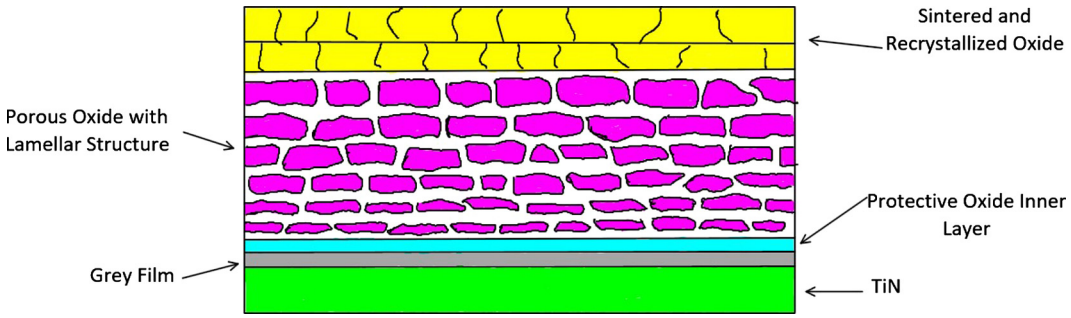

Fig. 1. Schematic of the cross section of the oxide scale structure on TiN [8].

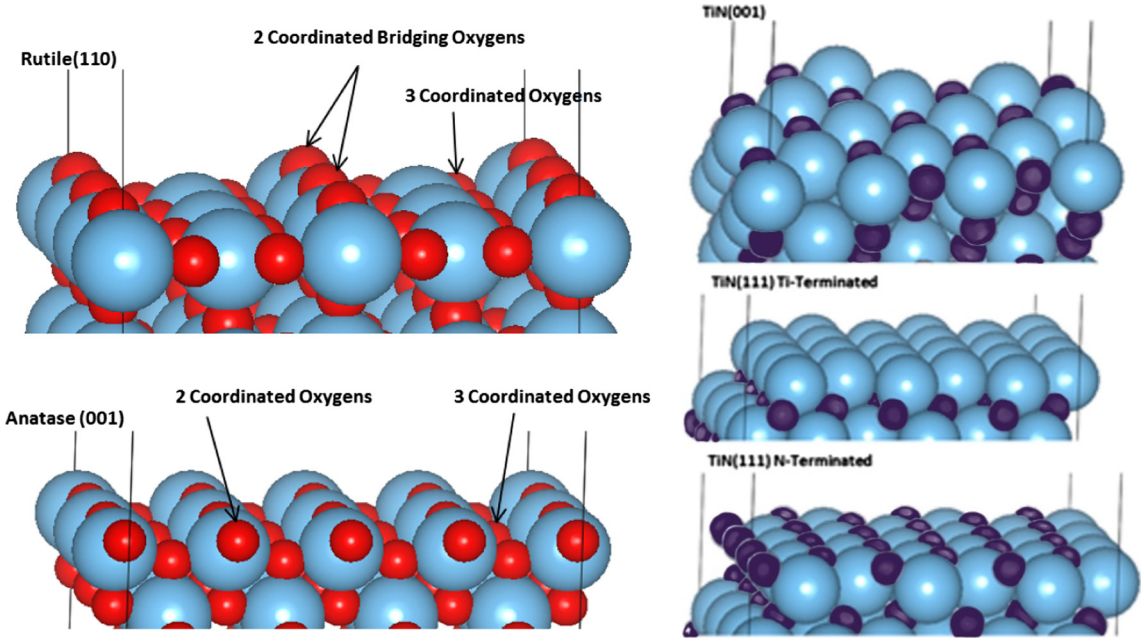

Fig. 2. Relaxed TiO_2 and TiN surfaces used to construct TiN/TiO_2 Interfaces; Titanium (Blue), Oxygen (Red), Nitrogen (Purple). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)