



High temperature oxidation resistance in titanium–niobium alloys



B.E. Tegner^a, L. Zhu^{a,b}, C. Siemers^c, K. Saksl^d, G.J. Ackland^{a,*}

^a School of Physics, SUPA and CSEC, The University of Edinburgh, Edinburgh EH9 3JZ, UK

^b School of Materials Science and Engineering, Beihang University, Beijing 100191, China

^c Technische Universität Braunschweig, Institut für Werkstoffe, Langer Kamp 8, 38106 Braunschweig, Germany

^d Slovak Academy of Sciences, Institute of Materials Research, Watsonova 47, 04353 Kosice, Slovak Republic

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ABSTRACT

Titanium alloys are ideally suited for use as lightweight structural materials, but their use at high temperature is severely restricted by oxidation. Niobium is known to confer oxidation-resistance, and here we disprove the normal explanation, that Nb⁵⁺ ions trap oxygen vacancies. Using density functional theory calculation, scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) we show that Nb is insoluble in TiO₂. In fact, the Ti–Nb surface has three-layer structure: the oxide itself, an additional Nb-depleted zone below the oxide and a deeper sublayer of enhanced Nb. Microfocussed X-ray diffraction also demonstrates recrystallization in the Nb-depleted zone. We interpret this using a dynamical model: slow Nb-diffusion leads to the build up of a Nb-rich sublayer, which in turn blocks oxygen diffusion. Nb effects contrast with vanadium, where faster diffusion prevents the build up of equivalent structures.

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1. Introduction

Titanium alloys have a combination of low weight and high strength which makes them attractive for a wide range of applications [1–3]. Much of the cost of titanium stems from the difficulty in reducing the oxide to the metal [4,5], but once purified, titanium is resistant to reoxidation on account of a thin TiO₂ layer which forms spontaneously when a clean surface is exposed to air. However, at temperatures above 600 °C, this oxidation resistance is dramatically lost. This effect prohibits the application of titanium alloys in high temperature environments, e.g. in gas turbines, for which they are otherwise very well suited.

Considerable empirical efforts have been made to improve the oxidation resistance at high-temperature of both Ti and TiAl, and the most effective of these are alloying with silicon or niobium [6–10]. Silicon causes the formation of a thin SiO₂-layer at the metal-oxide interface forming a diffusion barrier for oxygen. Niobium is most stable as a pentavalent ion, and it has previously been believed that the effect is due to Nb⁵⁺ ions in the TiO₂ surface layer; it was proposed that Nb⁵⁺ ions induce compensating Ti³⁺ ions which in turn trap the oxygen vacancies whose motion provides the mechanism for oxide growth [6,8]. Other postulated causes involve Nb₂O₅, cosegregation with Al or N, and formation

of mixed oxides [7]. It is curious that Vanadium does not inhibit oxide growth, although one might expect that V⁵⁺ ions should play a similar role to Nb⁵⁺. Furthermore, in recent calculation we have shown that a system of TiO₂ coexisting with Ti is not thermodynamically stable [11], and that the rate-limiting step in oxide growth is the production of oxygen vacancies at the metal-oxide interface [12,13], not the diffusion in the oxide. A single-layer barrier leads to linear growth, not the \sqrt{t} dependence expected for a diffusion process [14].

To examine these issues we have performed a combination of experimental and theoretical studies on binary Ti–Nb and Ti–V alloys. The purpose of this is to uncover whether Nb is solely responsible for oxidation resistance, to study the mechanism by which it operates, and to explain why vanadium is different.

2. Methods

2.1. DFT simulation details

We have carried out electronic structure calculations using density functional theory using the VASP [15], code with up to 360 atoms.

The projector augmented wave (PAW) method [16], was employed to describe the electron-core interaction, with the 3p semicore electrons of all 3d elements being treated as valence [17]. Exchange–correlation effects were described using the spin-corrected parameterization of Perdew and Wang (PW91) [18]. These choices were compared with various alternatives [19] (Appendix), which also helps to quantify the accuracy of the theory. Ground-state atomic structures were obtained by moving atoms to reduce the Hellmann–Feynman forces, to less than

* Corresponding author.

E-mail address: gjackland@ed.ac.uk (G.J. Ackland).

0.05 eV/Å. Diffusion barriers were calculated using the nudged elastic band method, and are in agreement with previous work where it exists [20,21]. The cutoff energy is set as 300 eV, and Gamma k-point sampling is used.

The driving force for Nb-segregation is the difference in chemical potential between oxide and the metal. This calculated using an interface structure that contains both oxide and metal [13] ($9 \times 9 \times 55 \text{ \AA}$; 360 atoms). Specifically, it is the difference in total energy between two calculations: one with Nb substituted for a Ti atom in the metal, and one with Nb substituted for a Ti in the oxide. These two simulations have precisely the same number of each atomic species, so the atomic chemical potential is set automatically. The presence of the metal in the supercell calculations gives rise to a Fermi surface which automatically sets the chemical potential for the electrons, avoiding the complications regarding the charge state of the ions encountered for defects in ionic material.

The convergence errors of these calculations is negligible, but uncertainty of around 10% arises from the exchange–correlation functional and the choice of pseudopotential (See Appendix for details). This does not affect the central results of this paper which depend only on the fact that it is always energetically favourable to transfer Nb, V or O from the oxide into the metal.

2.2. Sample preparation

We produced seven different alloys: Commercially pure-Ti grade 2 and Ti with 0.1%, 0.5%, 1% and 2% Nb and with 1% and 2% V (formulae use weight-%). We used ASTM-B348 Ti with 99.9% pure Nb and V. Alloys were produced by cold-hearth plasma-arc melting, doubly flushed with argon and evacuated to 5×10^{-5} mbar (3 times remelting), followed by casting into a water-cooled copper mould and stress-relief annealed at 700 °C for 1 h in argon. To remove possible surface layers, moulded bars were straight-turned to a final diameter of 12 mm and ground (ASTM P800) to produce a smooth finished surface for the oxidation tests. Nb and V are strong stabilizers of the cubic β -titanium phase [6,22], therefore, the amount of niobium and vanadium had to be limited to 2% to exclude the formation of a two-phase alloy. For sample production, the bars were sectioned into slices of 10 mm length by low-speed disc cutting and again ground with P800 grinding paper. Samples were weighed by precision scales (accuracy: 0.1 mg) and measured by a micrometre gauge (accuracy 0.01 mm).

2.3. Oxidation

Oxidation was carried out in a standard air furnace at 800 °C \pm 5 °C for 24, 48, 72, 96, 144 and 288 h. Three samples of each alloy have been used for each condition. The samples were positioned in Al_2O_3 containers so that contamination of the specimens, e.g. by chemical reactions, could be neglected. In addition, it was ensured that even if parts of the oxide layer peeled off during oxidation all fragments were collected with the sample to measure the weight gain.

After weighing, all the oxidised cylinders were embedded into Epomed amorphous, glass fibre reinforced polymer by warm embedding at 180 °C, 200 bar, for 10 min followed by water cooling, which produced excellent gap filling. About 1 mm of the face was removed by grinding to remove the oxide layer and possible preexisting alpha-case. Afterwards, the sample cross sections were ground (with papers P240, P400, P600, P800, P1200, P2500), polished (9 μm , 6 μm , 3 μm , 1 μm , OPS+ H_2O_2) and etched with Kroll's solution.

The microstructure and the characteristics of the oxide layer have been investigated in a ZEISS Axiolmager M2m optical microscope and a Hitachi TM 3000 scanning electron microscope equipped with a Bruker Quantax 70 energy dispersive X-ray detection system. Element mapping on carbon-coated samples has been performed to locate Nb and V.

2.4. Microfocussed XRD

One sample of Ti 2Nb alloy, oxidised for 96 h, was used in a micro-focused hard X-ray experiment at beamline P07 at PETRA III. The beam energy was 84.40 keV, resulting in a wavelength of 0.01462 nm. The sample had its polymer removed and was ground to 5 mm thickness. It was oriented as shown in Fig. 5 so that the focused beam passed only through alloy or oxide.

80 diffraction patterns were taken from this sample, starting at the oxide layer towards the centre of the specimen. The area of exposure was 3 $\mu\text{m} \times$ 30 μm . Each pattern overlapped with the previous by approx. 2 μm . The patterns were recorded using a Perkin Elmer 1621 detector, using ten shot averaging [23]. As a result, about 35 patterns from the oxide layer, 10 patterns from the oxide–metal–interface region and 35 patterns of the base material could be analysed. The related phases have been identified using the fit2D and CMPR software [24].

3. Theory and calculation

To assist interpretation of our calculated and experimental results, we introduce a diffusion model to follow the dynamical growth of the surface structures.

Diffusion in the system is governed by three factors, the diffusion constant (determined by atomic migration barriers and attempt frequencies), the driving force (chemical potential) and the initial conditions. The diffusion constant for oxygen varies by many orders of magnitude between oxide and metal, and has a delta-function barrier at the interface. This is defined by the oxygen content itself and has been considered in detail in a previous paper [13].

Here we take the low concentration limit for Nb and O diffusion in the Ti bulk, with a fixed chemical potential for O at the $x = 0$ boundary, which represents the oxide interface. We assume that the migration barrier for oxygen reduced linearly with lattice spacing, so the atomic mobility varies exponentially with concentration of oxygen: the DFT calculations show that oxygen has by far the strongest effect on lattice parameter increase. The effect of this term is that in regions of high oxygen concentration, diffusion goes faster. So once a region is oxidised, the oxidation proceeds ever faster until at saturation TiO_2 is formed. This non-linear effect gives a mathematical description of the sharp interface between fully oxidised and unoxidised material.

Diffusion gives a net flux of element i of

$$J_i = D_i c_i / \mu_i \nabla \cdot \mu_i$$

where the excess chemical potentials are

$$\mu_{\text{O}} = c_{\text{O}}(1 + Vc_{\text{Nb}}); \quad \mu_{\text{Nb}} = c_{\text{Nb}}(1 + Vc_{\text{O}})$$

and diffusion constants

$$D_{\text{O}} = D_1 \exp(1 + a_{\text{OO}}c_{\text{O}}); \quad D_{\text{Nb}} = D_2 \exp(1 + a_{\text{NbO}}c_{\text{O}})$$

where V is the mean repulsive energy per atom between O and Nb. The a_{ij} represent the effect on the mobility of j due to the other species i . This is primarily due to the increased lattice parameter, and since the effect of Nb is small, we approximate $a_{\text{NbO}} = a_{\text{NbNb}} = 0$.

In principle this model could be parameterized with DFT data (Table 1) for barriers and attempt frequencies. In practice, oxygen

Table 1

Summary of DFT calculations. The chemical “formula” indicates the number of atoms in the supercell, e.g. Ti_{63} means a 64 atom cell with one atom removed to create a vacancy. Oxygen is always located in the octahedral site, Nb and V are substitutional. The 64 atom supercell is a $4 \times 2 \times 2$ repeat of the 4-atom tetragonal hcp unit cell, while the 54 atom cell is a $3 \times 3 \times 3$ repeat of the monoclinic 2-atom cell supercell total energies are in eV compared to free atoms and volumes in $\text{\AA}^3/\text{atom}$. Binding energies denoted by μ are used as reference energy for those denoted by ΔE . “NN” denotes nearest neighbour site, “far” denotes maximum oxygen–solite distance allowed by the supercell.

System	Supercell energy	Volume	Binding energy
Ti	−7.763	17.50	$\mu_{\text{Ti}} = -7.763$
Ti_{53}	−409.52	$\Delta V_{\text{vac}} = +11.4$	$\Delta E_{\text{vac}} = +1.92$
Ti_{63}	−487.15	$\Delta V_{\text{vac}} = +11.2$	$\Delta E_{\text{vac}} = +1.92$
Ti_{54}O	−430.051	$\Delta V_{\text{O}} = +7.1$	$\mu_{\text{O}} = -10.82$
Ti_{53}Nb	−421.182	$\Delta V_{\text{Nb}} = +1.35$	$\mu_{\text{Nb}} = -9.71$
Ti_{63}Nb	−498.662	$\Delta V_{\text{Nb}} = +1.4$	$\mu_{\text{Nb}} = -9.69$
Ti_{53}NbO (NN)	−431.766	$\Delta V_{\text{Nb+O}} = +9.0$	$\Delta E = +0.24$
Ti_{53}NbO (far)	−432.002	$\Delta V_{\text{Nb+O}} = +8.4$	$\Delta E = +0.0$
Ti_{62}Nb (NN)	−488.96		$\Delta E = +0.09$
Ti_{62}Nb (far)	−488.871		$\Delta E = +0.0$
Ti_{53}V	−420.069	$\Delta V_{\text{V}} = -2.47$	$\mu_{\text{V}} = -8.59$
Ti_{63}V	−498.662	$\Delta V_{\text{V}} = -2.63$	$\mu_{\text{V}} = -8.53$
Ti_{53}VO (NN)	−430.726	$\Delta V_{\text{V+O}} = +3.42$	$\Delta E = +0.15 \text{ eV}$
Ti_{53}VO (far)	−430.832	$\Delta V_{\text{V+O}} = +3.28$	$\Delta E = +0.04 \text{ eV}$
Ti_{62}V (NN)	−490.034		$\Delta E = +0.09$
Ti_{62}V (far)	−490.90		$\Delta E = +0.0$
$\text{Ti}_{12}\text{O}_{18}$ (corundum)	−272.14	317.0	Defines μ
$\text{Ti}_{11}\text{O}_{18}+\text{Nb}$	−272.16	$\Delta V_{\text{Nb}} = +0.02$	$\Delta E = 1.833$
$\text{Ti}_{11}\text{O}_{18}+\text{V}$	−271.57	$\Delta V_{\text{V}} = -0.57$	$\Delta E = 1.523$
$(\text{TiO}_2)_{84} \text{Ti}_{107}\text{Nb}$	−3103.273		
$(\text{TiO}_2)_{83}\text{NbO}_2 \text{Ti}_{108}$	−3101.851		$\Delta E = 1.42$
$(\text{TiO}_2)_{84} \text{Ti}_{107}\text{V}$	−3103.273		
$(\text{TiO}_2)_{83}\text{VO}_2 \text{Ti}_{108}$	−3101.851		$\Delta E = 1.73$

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