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Oxygen-induced lattice distortion in β-Ti_3Nb and its suppression effect on β to α'' transformation

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Abstract

We report a first-principles density functional theory study on the interaction of interstitial O atoms in body-centered cubic β-Ti_3Nb alloy, the lattice distortion induced by O and its effect on the β to α'' transformation. Our calculations demonstrate strong repulsion between O atoms in general, but also reveal a weak attraction at an O–O separation of around 5.63 Å ($\sqrt{3}a$), which corresponds to a Ti_6Nb_2O structure. At low concentration ($Ti_{96}Nb_{32}O$), O induces a local α''-like structure in β-Ti_3Nb lattice, albeit to the extent of the nearest- and next-nearest neighbors, and exerts either a remarkable (6–8 meV atom^{-1}) or a negligible (0–1 meV atom^{-1}) energy barrier to the β to α'' transformation, dependent on the orientation of its elastic dipole with respect to the external stress. At high concentration (Ti_6Nb_2O), interstitial O atoms give rise to the shuffling of neighboring $\{110\}$ planes along the $\langle 1\bar{1}0\rangle$ direction and generate a semi-α'' structure, which is believed to be the nanodomain structure observed in experiment by Miyazaki and co-workers. In both cases, O brings up suppression effect on the β to α'' transformation.

Keywords: Ab initio calculations; Martensitic transformation; Shape memory alloys; Nanodomains; Interstitials

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1. Introduction

Since the beginning of the new century, we have witnessed β-Ti–Nb-based alloys being applied in many fields due to their high strength, low density and good corrosion resistance. The addition of oxygen could turn some β-Ti–Nb-based alloys such as Ti–Nb–Ta–Zr–O into fascinating gum metals [1,2] that bear desirable properties, including high strength, high yield strain, high ductility and low elastic modulus. Those with both an extraordinarily low Young's modulus and superelasticity are particularly suitable for application as biomedical implants [3]. Superelasticity displayed in β-Ti–Nb alloys comes from a first-order and reversible phase transformation from body-centered cubic (bcc) β to orthorhombic martensitic phase α''. It is now well established that O additions can not only suppress the formation of α'' phase by increasing the critical stress, but also reduce the transformation strain in these alloys [4–7]. How O plays its role, however, remains elusive.

Miyazaki et al. [8,9] have carefully studied the effect of O using transmission electron microscopy (TEM) and X-ray diffraction (XRD) measurements, together with a model analysis employing soft-spin version of the random field Ising model [10], which takes into account the non-nearest-neighbor interactions. Their TEM images provide evidence that O initiates transverse displacement between neighboring $\{110\}$ planes along the $\langle 1\bar{1}0\rangle$ direction, which

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is exactly the scenario of the shuffling mode of the β to α'' martensitic transformation. It was therefore proposed that O induces local α'' nanodomains. The α'' nanodomains distribute homogeneously and randomly in β matrix with varying orientations of elastic dipoles. The randomly oriented elastic dipoles behave as local barriers to suppress the long-range β to α'' martensitic transformation in Ti–Nb alloys.

This explanation of the role played by O appears to be quite sound. Nevertheless, since there is only a qualitative agreement between measurements and Ising model analysis [9], we were prompted to have a closer look at the transformation scenario suggested by Miyazaki et al. We found that there are several pieces of cloud making the formation of nanodomains blurred in atomic scale. (i) The α'' nanodomains were found to be homogeneously and randomly distributed in the matrix, but they were also found to be well separated. An immediate question is: what is the distribution of O? If it is uniformly distributed, then why do α'' nanodomains appear in some places but not in others? If O is concentrated in some sporadic places where nanodomains form, what is the critical content of O for the automatic local β to α'' transformation to occur? (ii) The nanodomains were suggested to have an atomic structure close to the α'' phase, but how close is it? (iii) Outside of the nanodomains in the matrix, probably at low O concentration, what is the lattice distortion like around an interstitial O? Is there any contribution to the total suppression effect of O on the long-range β to α'' transformation from these parts?

Bearing these questions in mind, we have carried out a first-principles density functional theory investigation on the interaction of interstitial O atoms in bcc β-Ti_3Nb, the lattice distortion induced by O and its effect on the β to α'' transformation. We find the interaction between two O atoms in a $Ti_{96}Nb_{32}$ supercell to be rather complicated, but in general is strongly repulsive. At small distances, there could be a weak attraction at an O–O separation of around $\sqrt{3}a$ (5.63 Å), which corresponds to a Ti_6Nb_2O structure. At low concentration ($Ti_{96}Nb_{32}O$), O is found to induce a local α''-like structure in β-Ti_3Nb lattice, but only to the extent of several atomic shells. Depending on the orientation of its elastic dipole with respect to the external stress, a low content of O exerts either a high (6–8 meV atom^{-1}) or a negligible energy barrier to the β to α'' transformation. At high concentration (Ti_6Nb_2O), the O atoms initiate transverse displacements of neighboring $\{110\}$ planes along the $\langle 1\bar{1}0\rangle$ direction. The resulting structure is close to, but not exactly, α'', and should be better viewed as a semi-α'' structure. We propose that at either high (11 at.%) or low concentration, interstitial O can play an important role in suppressing the β to α'' transformation.

2. Methodology

Two challenges encountered by a fully first-principles description of the Ti–Nb–O system are the randomness of the O distribution and the strain-induced long-range character of the O–O interaction. Here we are particularly interested in the alloys studied by Miyazaki et al. which have an O content as high as 1.0 at.%. This means that to model this system realistically one needs a supercell containing about 100 atoms, which for the bcc β phase can be represented well by a 128-atom ($4 \times 4 \times 4$) supercell. Miyazaki et al. [9] discussed in depth the effect of randomness in the orientation of O-induced α''-like nanodomains on the β to α'' transformation, but we noticed that in their XRD images the nanodomains are very sharp, strongly indicating a well-ordered structure. We therefore believe the alignment of O inside these nanodomains is not random, presumably as a consequence of strain-induced ordering [11,12]. However, outside of the nanodomains the interstitial O could be randomly distributed in the β matrix. A careful search of the stable O–O configurations is therefore indispensible, as we can expect the O–O interaction to vary irregularly with their separation.

The Ti–Nb–O alloy composition with the highest O content in Ref. [9] is Ti–26Nb–1.00O (in at.%). Thus, Ti_3Nb–O was taken to simulate the experiment in this computational work. According to the work by Lazar et al. [13], there are 16 symmetry-equivalent configurations for β-Ti_3Nb in a 16-atom bcc supercell. Among these configurations, G1 (Fig. 1(a) is the most stable, whereas $L6_0$ (Fig. 1(b)) is slightly higher in energy (14 meV atom^{-1}) yet has a chemical decoration corresponding to the α'' phase. This means that β-Ti_3Nb in the $L6_0$ structure could transform to α'' without exchanging Ti and Nb sites. Therefore, we chose the G1 configuration to study the O-induced distortion and O–O interaction in β-Ti_3Nb and the $L6_0$ structure to calculate the energy barrier in the β to α'' transformation. α''-Ti_3Nb (Fig. 1(c)) has a *pmm*2 space group and the atomic positions are Ti $(0,0,0)$, Ti $(0.5,0.5,0)$, Ti $(0,0.6,0.5)$ and Nb $(0,0.1,0.5)$ in a four-atom unit cell. Our benchmark calculations give a lattice constant of 6.50 Å ($=2a$, a being the lattice constant of the conventional bcc unit cell) for β-Ti_3Nb, and lattice constants a, b and c of 3.30, 4.75 and 4.40 Å for α''-Ti_3Nb, consistent with previous DFT results [13,14].

A 128-atom β-Ti_3Nb (G1) supercell ($2 \times 2 \times 2$ of the unit cell shown in Fig. 1(a)) was adopted to study the O-induced local distortion and O–O interactions. In addition, a 64-atom β-Ti_3Nb ($L6_0$) supercell was used to calculate the β to α'' phase transformation in Ti_3Nb. In panel (a) of Fig. 2, we display the 128-atom β-Ti_3Nb (G1) supercell and mark the position of the first O (in yellow) and all the unequivalent positions of the second O (red symbols), all of which are in most stable octahedral interstitial sites. The 64-atom β-Ti_3Nb ($L6_0$) supercell shown in panel (b) is formed by stacking four atomic $(011)_\beta$ layers, each containing 16 atoms, along the c axis. The 64-atom α''-Ti_3Nb supercell shown in panel (c) is formed by stacking four atomic $(010)_{\alpha''}$ layers along the c axis. Not only the most stable octahedral interstitial site, but other possible sites for the sole O to reside which have been considered in