Impact of oxygen adsorption on the electronic properties of titanium nickel surfaces

Vukosi Chauke[1*], *David* Tshwane[2], *Phuti* Ngoepe[1], *and Hasani* Chauke[1]

[1]Materials Modelling Centre, University of Limpopo, South Africa

[2]Next Generation Enterprises and Institutions Cluster, CSIR, South Africa

Abstract. This study investigates the impact of oxygen adsorption on the electronic properties of the titanium nickel (TiNi) (110) surface using density functional theory (DFT). Surface energy calculations for the (100), (110), and (111) surfaces identify (110) as most stable (0.115 J m^{-2} across terminations). On this surface, adsorption at Ti-top, Ni-top, and bridge sites was assessed; the bridge site is most favourable (E_{ads} = −5.111 eV), suggesting strong chemisorption and inducing surface relaxations. Oxygen adsorption introduces localized states near the Fermi level and reduces the DOS at E_F. Total and projected DOS highlight Ti 3d, Ni 3d, and O 2p contributions, consistent with partial charge transfer to oxygen and increased surface stability. The work function rises for all sites, with the largest shift for the bridge configuration. These findings elucidate how oxygen alters TiNi surface reactivity and electronic behaviour, providing guidance for improving TiNi performance in oxidizing environments relevant to biomedical, aerospace, and catalytic applications.

1 Introduction

Titanium nickel (TiNi), a binary intermetallic compound, is highly valued for its shape memory effect, superelasticity, and superior corrosion resistance. These properties make it suitable for a wide range of applications, particularly in biomedical implants, aerospace components, and catalytic systems [1,2]. However, the surface behaviour of TiNi plays a critical role in determining its long-term reliability, especially when exposed to oxygen-rich environments.

Oxygen adsorption is known to alter the surface electronic structure, mechanical properties, and chemical reactivity of Ti-based materials [3]. For TiNi alloys specifically, surface oxidation can affect properties such as surface energy, conductivity, and work function factors essential for their operational stability and compatibility in practical applications [4]. Surface modifications induced by oxygen may introduce impurity states near the Fermi level, influence charge redistribution, and lead to surface reconstruction, ultimately impacting the alloy's performance in service conditions [5].

Although several studies have investigated oxygen interaction with titanium and nickel individually, detailed insights into the adsorption behaviour on specific crystallographic

* Corresponding author: vukosichauke721@gmail.com

orientations of TiNi, particularly the (110) surface, are still limited [6-9]. In this work, we employ density functional theory (DFT) to examine oxygen adsorption on the TiNi (110) surface, exploring adsorption site preferences, surface energy trends, electronic structure changes, and work function variations. The findings provide essential insights into the oxidation behaviour of TiNi, which can guide future surface engineering strategies for enhanced performance in biomedical, aerospace, and catalytic environments.

2 Methodology

All density functional theory (DFT) calculations involved in the present study were carried out using the CASTEP code [6, 7]. The Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) was applied to describe the exchange-correlation energy and potential [8], and the ultra-soft pseudopotential was selected to deal with the electrons–ionic cores interactions [9]. The Monkhorst-Pack scheme was used to generate the k-point grids [10]. A k-point mesh of 4 × 4 × 4 and a cut-off energy of 450 eV were adopted to optimize the bulk structure of TiNi, while a k-point mesh of 4 × 4 × 1 with the same cut-off energy was used for the initial crystal cell [10]. The calculated lattice parameters were a = b = c = 3.011 Å, α = β = γ = 90° for the bulk TiNi, which are in good agreement with reported experimental and theoretical studies [3, 11], proving the reliability of the calculated methods.

After structural optimization, TiNi surface was cleaved from the optimized bulk structure. A five-layer symmetrical slab model with a vacuum thickness of 30 Å was constructed to prevent interaction between periodic images. The surface energies of the TiNi surface were calculated using the following expression [12]:

$$\gamma = \frac{(E_{slab} - NE_{bulk})}{2A} \quad (1)$$

Following the surface energy calculation, different oxygen adsorption was modelled on the TiNi (110) surface. Geometry optimization and total energy calculations were performed to determine the adsorption energy, calculated as follows [13]:

$$E_{ads} = \left[E_{system} - (E_{adsorbent} + E_{adsorbate})\right] \quad (2)$$

Finally, the work function (Φ) of both clean and water-adsorbed surfaces was calculated to evaluate the influence of adsorption on the electronic structure. The work function was computed using the equation [14]:

$$\Phi = E_{\text{vacuum}} - E_F \quad (3)$$

To investigate the effect oxygen, different coverages from low to high were simulated. The most stable configurations were identified by comparing the adsorption energies and examining the corresponding work function shifts.

3 Results and discussion

3.1 Surface energy

Surface energy is the excess energy present at a material's surface compared to its bulk. The energy is a critical aspect influencing surface-related phenomena like wetting, adhesion, and reactivity [15]. Surface energy is essential for assessing the stability of TiNi surface structures

and their reactivity to adsorbates such as oxygen and water. By analysing surface energy changes, we can gain insights into surface modification strategies for tailoring TiNi properties to specific applications, such as enhancing corrosion resistance or promoting biocompatibility [16]. Ultimately, the study of surface energy informs the design and optimisation of TiNi-based materials for various practical uses.

Figure 1 shows the optimised structures of TiNi (100), (110) and (111) surfaces with different terminations, and Table 1 presents the calculated surface energies. Comparing different terminations, it was found that all TiNi terminated surfaces display the least energy. It was observed that the (110) surface is the most favourable for all terminations. TiNi termination on (110) surface demonstrates higher stability with the lowest surface energy value of 0.115 J/m^2 as compared to the other terminations. While specific surface energy values for TiNi surfaces are not readily available, studies on similar materials like titanium nitride (TiN) offer some insights with TiN (100) Surface 0.424 J/m² TiN (110) Surface (0.110 J/m²) and TiN (111) Surface (0.357 J/m²) [17]. This observation suggests that the surface is the least chemically reactive among the studied orientations; this will lead to long-term durability and resistance to degradation.

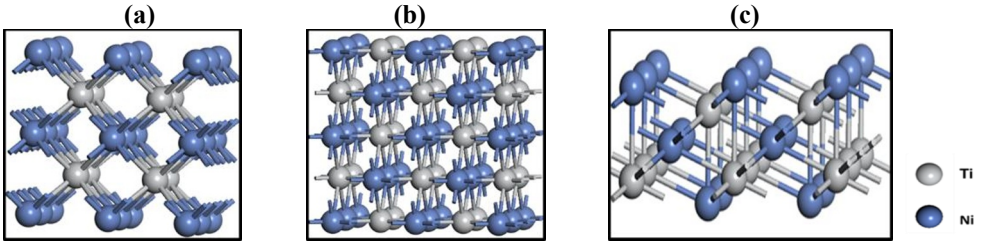

Fig. 1. Optimised structure of (a) TiNi (100) surface, (b) TiNi (110) surface and (c) TiNi (111) surface.

Table 1. Calculated surface energies for different terminations.

Surfaces	Termination	Area (Å^2)	$E_{surface}$ (J/m^2)
(100)	Ti	186.52	1.203
	Ni	186.52	1.188
	TiNi	216.59	1.021
(110)	Ti	424.72	0.126
	Ni	455.59	0.122
	TiNi	486.46	0.115
(111)	Ti	227.39	0.952
	Ni	234.78	0.732
	TiNi	284.68	0.651

3.2 Adsorption

3.2.1 Structural adsorption

Structural adsorption describes the site-specific interaction and geometrical arrangement of an adsorbate on a surface, critically influencing adsorption energy, electronic structure, and surface reactivity [18]. Figure 2 shows a top view of TiNi (110) surface structures with oxygen atoms adsorbed at a different site: the bridge site, Ti-top, and Ni-top. In the Ti-top structure, oxygen sits directly above a titanium atom, likely forming a strong bond because of Ti's high reactivity with oxygen. In contrast, the Ni-top structure places oxygen above a

nickel atom, where the interaction is generally weaker due to Ni's lower oxygen affinity. In the bridge configuration, the oxygen atom is positioned between a surface Ti and Ni atom, allowing interaction with both and typically leading to stronger binding due to higher coordination. These configurations help compare how adsorption behavior varies with site type on the TiNi surface.

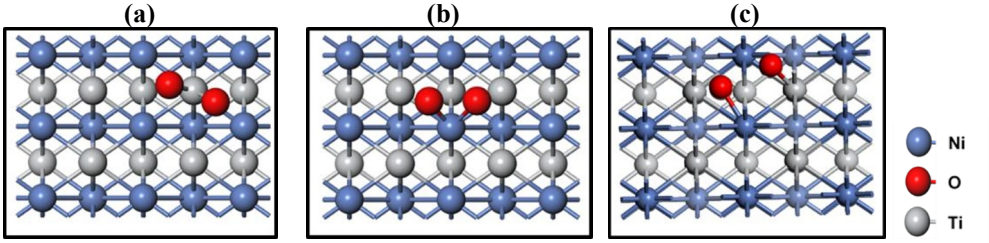

Fig. 2. Optimised atomistic structures of oxygen molecule adsorption on TiNi (110) surface: (a) Titanium site adsorption, (b) nickel site adsorption, and (c) bridge site adsorption.

3.2.2 Adsorption energy

Adsorption energy is the fundamental characteristic of the adsorbate (oxygen molecule) interaction with an adsorbent (TiNi surface) [19]. Figure 3 presents the adsorption energy relation for adsorbed oxygen molecules on the TiNi (110) surface. It was observed that all the adsorption sites possess negative adsorption energy on the TiNi (110) surface indicating a spontaneous reaction and energetically favourable. The adsorption energies were found to be thermodynamically favourable.

The bridge site possesses the most stable adsorption energy of -5.111 eV, which is in agreement with the reported -5.321 eV [20]. To provide a more comprehensive discussion, it is important to consider the adsorption energies on other sites as well Values for oxygen adsorption on the Ti (top) site typically range from -4.7 eV to -5.0 eV [16, 21], which is in close agreement with our calculated value of -4.328 eV. On the Ni (top) site, previous studies report adsorption energies around -4.5 eV to -4.8 eV [22, 23], which are lower than our calculated value of -5.049 eV. This indicates that oxygen may preferentially adsorb on the bridge and Ni (top) sites, but the bridge site remains the most favourable due to its slightly lower energy compared to the Ni (top) site.

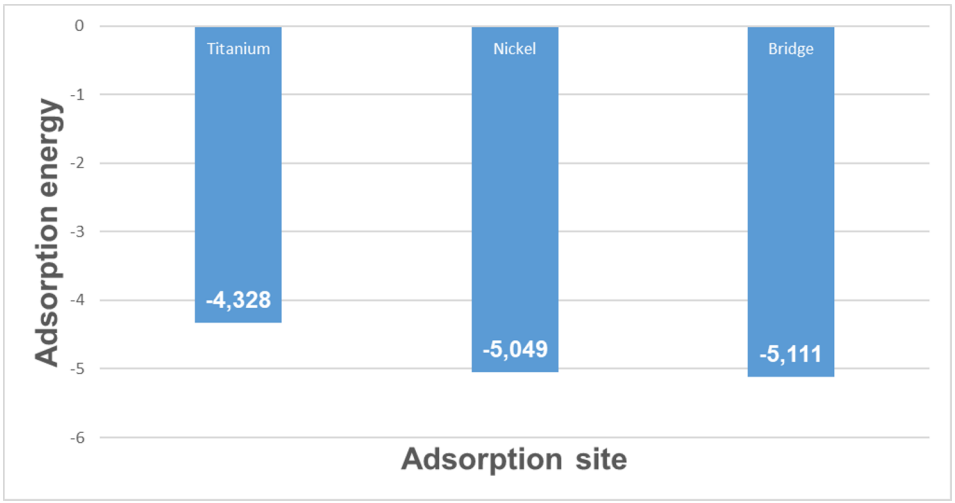

Fig. 3. Adsorption energy of oxygen adsorbed via different sites (top and bridge) of TiNi (110) surface.

3.3 Density of states

To gain deeper insights into the electronic structures of alloys, we turn our attention to a crucial property, the density of states (DOS). This concept, along with its counterpart, the partial density of states (PDOS), provides valuable information about electron behaviour within materials [24]. Figure 4 shows the plots of total density of states (TDOS) and PDOS of $TiNi/O_2$, the x-axis represents the energy levels, and the y-axis represents the density of states. The calculated TDOS shows metallic behaviour, predominantly dominated by Ti 3d, Ni 3d, and O 2p states. Lower energy peaks are mainly occupied by Ni d-states, whereas the higher energy peaks are predominantly from the Ti d-states, which suggests high reactivity with the adsorbent. The calculated DOS reveals the presence of a pseudo gap around the Fermi level, characterized by a depletion of electronic states near EF. This pseudo gap formation can be attributed to the hybridization between Ti 3d, Ni 3d, and O 2p orbitals, which creates bonding and antibonding states separated by an energy gap. The decrease in the density of states near the Fermi level as compared to the clean TDOS of TiNi (110) surface [25] suggests a partial charge transfer from the surface atoms to the adsorbate.

This observation also quantifies the increase in stability of the material. Based on these observations, we conclude that oxygen molecules chemisorb onto the TiNi (110) surface, forming covalent bonds and enhancing the stability of the surface.

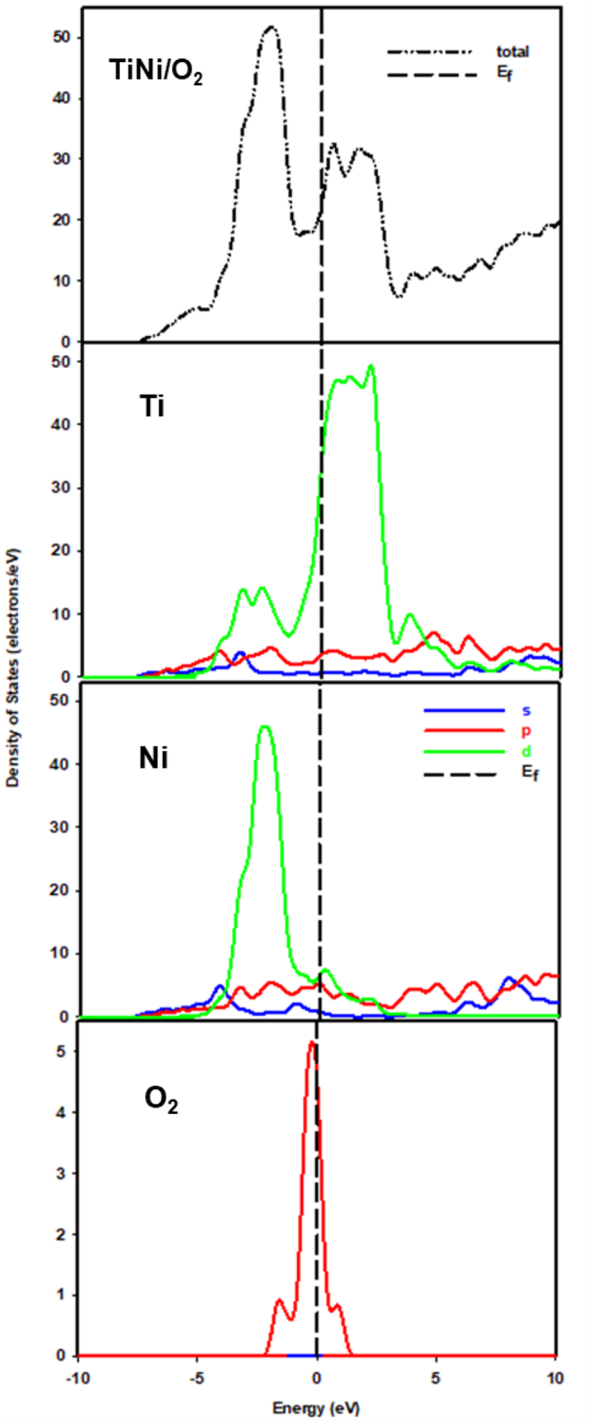

Fig. 4. Total and partial density of states of TiNi/O2. The Fermi energy is taken as the energy zero.

3.4 Work function

The work function is the minimum amount of energy that is necessary to move an electron from a solid to a position that is beyond the surface of the solid [26]. This function is a reflection of how difficult it is for electrons to escape from solids. Table 2 shows that the work function changes to 3.821 eV when oxygen is absorbed compared to a clean surface (3.741 eV) [25]. As the oxygen-adsorbed atom changes, so does the size of the resulting work function. We can see that when oxygen binds to the bridge site, the value increases. This suggests that the oxygen molecule adsorption impedes the electron escape from TiNi

When evaluating corrosion resistance, it is well established that the electrochemical potential (φ) is closely linked to the work function (Φ), which reflects electron stability [27]. Their relationship is represented by the contact potential difference between the metal and the solution interface, which remains constant for the same metal in a specific solution. Therefore, a linear correlation exists between electrochemical potential and work function, with an increase in the work function indicating a positive shift in corrosion potential. Based on this principle, it can be inferred that oxygen adsorption could improve the corrosion resistance of TiNi alloy. This is not only because the titanium oxide protective film, as commonly noted in the literature [28], shields the metal from corrosive environments, but also due to the increased difficulty for electrons to escape from the metal caused by oxygen adsorption.

Table 2. The work function of clean TiNi surface and $TiNi/O_2$

	Work function (eV)	**Theoretical (eV) [25]**
TiNi (110)	3.745	3.764
$TiNi/O_2$	3.821	3.885

4 Conclusion

This study has demonstrated that oxygen adsorption significantly alters the electronic properties of the TiNi (110) surface. Among the low-index surfaces investigated, the (110) orientation exhibited the lowest surface energy and confirming it as the most stable configuration. Adsorption energy calculations showed that the bridge site was the most energetically favourable for oxygen adsorption, with a highly negative value of -5.111 eV, indicating strong chemisorption. Oxygen adsorption induced notable surface relaxation and altered the surface's electronic behaviour. Analysis of the TDOS and PDOS revealed the dominant contributions from Ti 3d, Ni 3d, and O 2p orbitals, with the system maintaining metallic characteristics. The decrease in the DOS near the Fermi level after oxygen adsorption, compared to the clean surface, indicates partial charge transfer from the surface atoms to the adsorbate and an associated increase in surface stability. Furthermore, a rise in the work function across all adsorption sites, most prominently at the bridge site, confirms the electronic influence of oxygen interaction. Collectively, these findings highlight the strong coupling between oxygen and the TiNi surface, with significant implications for enhancing the alloy's performance in oxidative environments such as biomedical implants, aerospace components, and heterogeneous catalysts.

This research was carried out at the University of Limpopo's Materials Modelling Centre (MMC). We acknowledge Centre for High-Performance Computing (CHPC) based in Cape Town for their computing resources.
This research received no external funding. All work was supported by the authors' institution.
Data availability: All data reported in this work is available upon request to the corresponding author.

References

1. Y. Chen, C. Ortiz Rios, B. McLain, J. W. Newkirk, and F. Liou, TiNi-Based Bi-Metallic Shape-Memory Alloy by Laser-Directed Energy Deposition. Mater. **15**, 3945 (2022).
2. Y. Tong, B. Yu, Y. Li, and H. Hou, Recent Development of TiNi-Based Shape Memory Alloys with High Cycle Stability and High Transformation Temperature. Adv. Eng. Mater. **22**, 1900496 (2020).
3. X. Wang, D. Xie, M. Hou, M. Guan, and Y. Leng, Effects of oxygen adsorption on the corrosion behaviour of the Ti (0001) surface: a DFT investigation. Phys. Chem. Chem. Phys. **26**, 24370–24383 (2024).
4. D. Wang, Z. Zhang, Y. Liu, and Y. Yang, Revealing the role of dithiocarbamate ester group in hydroxamic acid flotation of cassiterite with in-situ AFM, DFT and XPS. Appl. Surf. Sci. **604**, 154521 (2024).
5. C. Li and S. Tosoni, Halide adsorption on close-packed metal electrodes. Surf. Sci. **733**, 122164 (2024).
6. J. Chen, J. Li, X. Wang, *et al.*, Advanced capabilities for materials modelling with Quantum ESPRESSO. Mater. Lett. **285**, 129088 (2021).
7. J. Liu, Y. Wang, Y. Li, *et al.*, First-principles calculations on the stacking fault energy, surface energy and dislocation properties of $NbCr_2$ and $HfCr_2$, Comput. Mater. Sci. **140**, 334–340 (2017).
8. J. Yang, S. Meng, L. Xu, and E. Wang, Water adsorption on hydroxylated silica surfaces studied using the density functional theory. Chin. Phys. B **14**, 25–32 (2005).
9. X. Liu, H. Wang, and J. Zhang, Hydrogen Diffusion into Pd (100) Subsurface: Role of Co-adsorbed Bicomponent Species on Surface. Appl. Surf. Sci. **533**, 147448 (2020).
10. S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. I. J. Probert, K. Refson, and M. C. Payne. First-principles methods using CASTEP. Z. Kristallogr. Cryst. Mater. **220**, 67–570 (2005).
11. J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized Gradient Approximation Made Simple. Phys. Rev. Lett. **77**, 3865–3868 (1996).
12. D. Vanderbilt, Soft self-consistent pseudopotentials in a generalized eigenvalue formalism. Phys. Rev. B **41**, 7892–7895 (1990).
13. H. J. Monkhorst and J. D. Pack, Special points for Brillouin-zone integrations. Phys. Rev. B **13**, 5188–5192 (1976).
14. C. Yan, Q. Zeng, W. He, J. Zhu, First-principles investigation on the adsorption and dissociation of O_2 and H_2O molecules on the Ni-rich TiNi alloy surface, Appl. Surf. Sci. **534**, 147570 (2020).
15. D. Ionita, M. Caposi, I. Demetrescu, S. Ciuca, I. A. Gherghescu, Investigation of corrosion behaviour of NiTi shape memory alloy in physiological solutions, Mater. Corros. **66**, 472–478 (2015).
16. J. C. Boettger, Nonconvergence of calculated surface energies with increasing slab thickness. Phys. Rev. B **49**, 16798–16800 (1994).
17. P. Giannozzi, O. Andreussi, T. Brumme, O. M. Buongiorno Nardelli, N. Marzari, et al., Advanced capabilities for materials modelling with Quantum ESPRESSO, J. Phys.: Condens. Matter **32**, 395902 (2020).
18. H. B. Michaelson, The work function of the elements and its periodicity. J. Appl. Phys. **48**, 4729–4733 (1977).

19. R. W. Carpick, Introduction to Contact Mechanics, (CRC Press, Boca Raton, FL, 2012).
20. W. Liu, S. Liu, and L. Wang, Surface Modification of Biomedical Titanium Alloy: Micromorphology, Microstructure Evolution and Biomedical Applications. Coatings, **9**, 249 (2019).
21. A. Dehghanghadikolaei, H. Ibrahim, A. Amerinatanzi, M. Hashemi, N. S. Moghaddam, M. Elahinia, Improving corrosion resistance of additively manufactured nickel–titanium biomedical devices by micro-arc oxidation process, J. Mater. Sci. **54**, 7333–7355 (2019).
22. I. Sit, M. A. Young, J. D. Kubicki, and V. H. Grassian, Distinguishing different surface interactions for nucleotides adsorbed onto hematite and goethite particle surfaces through ATR-FTIR spectroscopy and DFT calculations. Phys. Chem. Chem. Phys. **25**, 20557–20566 (2023).
23. M. N. Ghazisaeidi, F. Ghal-Naghi, and B. G. Yacobi, Enhanced photocatalytic hydrogen production by the formation of TiNT–BN bonds. Appl. Surf. Sci. **623**, 157005 (2023).
24. C. Yan, Q. Zeng, W. He, and J. Zhu, First-principles investigation on the adsorption and dissociation of O_2 and H_2O molecules on the Ni-rich TiNi alloy surface. Appl. Surf. Sci. **534**, 147570 (2020).
25. F. Wu, H. Chen, Z. Yang, J. Qiao, and Y. Hou, Investigation on the electronic structures, elastic and thermodynamic properties of TiNi, Ti_2Ni and $TiNi_3$ intermetallic compound. Mater. Today Commun. **34**, 105273 (2023).
26. T. Roman, F. Gossenberger, and J. G. Forster-Tonigold, Halide adsorption on close-packed metal electrodes. Phys. Chem. Chem. Phys. **16**, 13630–13634 (2014).
27. P. Giannozzi, O. Andreussi, T. Brumme, O. M. Buongiorno Nardelli, and N. Marzari, J, Quantum ESPRESSO toward the exascale. Chem. Phys. **152**, 154105 (2020).
28. V. Chauke, D. M. Tshwane, P. E. Ngoepe and H. R. Chauke, Probing the stability of nickel titanium (100) and (110) surfaces: A DFT study, in Proceedings of South Africa Institute of Physics, SAIP, 3-7 July 2023, Richards Bay, South Africa (2023).