The ferrite/oxide interface and helium management in nano-structured ferritic alloys from the first principles

Litong Yang^{1,2}, Yong Jiang^{1,2,3*}, Yuan Wu⁴, G. Robert Odette^{4*}, Zhangjian Zhou⁵, Zheng Lu⁶

¹ School of Materials Science and Engineering, and ² Key Lab of Nonferrous Materials of Ministry of Education, Central South University, Changsha, 410083, China

³ National Key Lab for Powder Metallurgy, Central South University, Changsha 410083, China

⁴ Materials Department, University of California, Santa Barbara, 93106, USA

⁵ School of Materials Science and Engineering, University of Science and Technology, Beijing, 100083, China

⁶ School of Materials and Metallurgy, Northeastern University, Shenyang, 110819, China

Abstract

Nano-size Y-Ti-oxides are largely responsible for the extraordinary mechanical properties and irradiation tolerance of nano-structured ferritic alloys (NFAs). Here we report a theoretical study to assess the characters and possible roles of the ferrite/oxide interface in managing neutron transmutation product helium in NFAs. Using one observed *cube-on-cube* orientation relationship, various candidate structures of the ferrite/Y₂Ti₂O₇ interfaces were constructed and the associated energies were carefully evaluated. The interface phase diagram is obtained by expressing the energy as a function of temperature and internal oxygen activity (expressed in terms of oxygen partial pressure). The oxide interfaces are predicted to be Y/Ti-rich at thermodynamic equilibrium for the wide temperature range of interest. Vacancy formation energies are lower and helium segregates to the interfaces, in preference to the iron matrix and grain boundaries. Combined with our previous results on bulk-phase Y₂Ti₂O₇, the profound implications of nano-oxides to helium management in NFAs are discussed.

Keywords

Nano-structured ferritic alloys; Y₂Ti₂O₇; interface; helium; density functional theory

* Corresponding authors.

E-mail address: yjiang@csu.edu.cn (Y. Jiang); odette@engineering.ucsb.edu (G. Robert Odette)

1. Introduction

Nano-structured ferritic alloys (NFAs) are characterized by fine grains and an ultra-high density of Y/Ti-enriched nano-oxides [1-5], representing a new class of potentially transformational structural materials, especially for advanced fission and fusion energy applications [6-10]. The nano-oxides, which precipitate from the matrix during hot consolidation, are remarkably stable both at high temperatures and after large neutron irradiation doses. They can effectively impede dislocation climb and glide, and they enhance vacancy-SIA (self-interstitial atom) recombination; thus, they are responsible for the high tensile, creep, and fatigue strength, as well as the irradiation tolerance of NFAs [6, 11-21]. Most notably, the high density of nano-oxides results in a greatly reduced size of helium bubbles in the ferrite matrix and lower amount of helium reaching grain boundaries. Consequently, many manifestations of damaging irradiation effects, such as void swelling and helium embrittlement, are greatly mitigated in NFAs [6, 11, 12]. However, a comprehensive understanding of the mechanism responsible for the multi-functional role of nano-oxides is not yet in hand.

Various studies have suggested that the nano-oxides might range from coherent solute-enriched clusters or Guinier-Preston-type zones, to near-stoichiometric complex oxides, that are primarily the pyrochlore $\text{Y}_2\text{Ti}_2\text{O}_7$ and to a lesser extent orthorhombic Y_2TiO_5 (and/or even less some other possible oxides in crystalline and even amorphous phases) [16, 22-31]. In our previous work [32, 33], we have shown from first principles that helium in NFAs partitions and is *deeply* trapped in both $\text{Y}_2\text{Ti}_2\text{O}_7$ and Y_2TiO_5 oxides. The Boltzmann partitioning factors at 773K were estimated to be in the order of $\sim 10^{10}$ and 10^8 for bulk Y_2TiO_5 and $\text{Y}_2\text{Ti}_2\text{O}_7$, respectively. Thus even small volume fractions of nano-oxides can effectively sequester hundreds to thousands appm of helium generated in fusion neutron environments, depending on their number density. Specifically, dispersing helium atoms into a large number of small oxides limits the helium bubble size in matrix and the corresponding damage

potential.

While the previous results shed useful insights on helium management by the nano-oxides in NFAs, one may still ask if the interfaces of the oxides could be equally - if not more - critical by directly forming oxide-associated bubbles. In either case, it is important to determine the energies of helium in all potential residence sites. Besides helium issues, the oxide interfaces play a dominant role in many other aspects of NFA processing and service functionality, ranging from interactions with dislocations and boundaries to oxide nucleation, growth, and coarsening kinetics. Therefore, understanding the ferrite/oxide interface structures, energies, and their interaction with various microstructural and defect features, such as helium, is one of the key requirements for optimizing NFAs and achieving a correspondingly comprehensive understanding of helium fate and consequences.

In the present work, we focus on the $\text{Y}_2\text{Ti}_2\text{O}_7$ interfaces with the matrix. The pyrochlore $\text{Y}_2\text{Ti}_2\text{O}_7$ is generally observed to be the primary nano-oxide precipitate phase in NFAs [13]. Different orientation relationships (ORs) of ferrite/ $\text{Y}_2\text{Ti}_2\text{O}_7$ have been observed. Ribis et al. reported a *cube-on-cube* OR for thermally-coarsened $\text{Y}_2\text{Ti}_2\text{O}_7$ as $\{100\}\langle 100\rangle_{\text{ferrite}}//\{100\}\langle 100\rangle_{\text{Y}_2\text{Ti}_2\text{O}_7}$ [34]. Using state-of-the-art aberration-corrected TEM, Ciston et al [35] observed two other types of ORs for small $\text{Y}_2\text{Ti}_2\text{O}_7$ nano-oxides, i.e. the *Baker-Nutting* OR of $\{100\}\langle 100\rangle_{\text{ferrite}}//\{100\}\langle 110\rangle_{\text{Y}_2\text{Ti}_2\text{O}_7}$ and a *cube-on-edge* OR of $\{100\}\langle 100\rangle_{\text{ferrite}}//\{110\}\langle 100\rangle_{\text{Y}_2\text{Ti}_2\text{O}_7}$. More recently, Dawson et al. reported that the *cube-on-cube* OR is more prevalent than the *Baker-Nutting* OR [36]. It is also worth noting that we recently developed a mesoscopic ferrite/ $\text{Y}_2\text{Ti}_2\text{O}_7$ interface by directly electron-beam depositing Fe onto different facets of single-crystal $\text{Y}_2\text{Ti}_2\text{O}_7$. High-resolution TEM, X-ray diffraction, and electron backscattering diffraction (EBSD) characterization showed two ORs of $\{110\}\langle 100\rangle_{\text{ferrite}}//\{111\}\langle 110\rangle_{\text{Y}_2\text{Ti}_2\text{O}_7}$ and $\{100\}\langle 100\rangle_{\text{ferrite}}//\{111\}\langle 110\rangle_{\text{Y}_2\text{Ti}_2\text{O}_7}$ for $\text{Y}_2\text{Ti}_2\text{O}_7$ {111}[37], the *Pitsch* OR of

$\{110\}<111>_{\text{ferrite}}//\{100\}<110>_{\text{Y}_2\text{Ti}_2\text{O}_7}$ for $\text{Y}_2\text{Ti}_2\text{O}_7$ $\{100\}$, and the *cube-on-edge* OR of $\{100\}<100>_{\text{ferrite}}//\{110\}<100>_{\text{Y}_2\text{Ti}_2\text{O}_7}$ for $\text{Y}_2\text{Ti}_2\text{O}_7$ $\{110\}$ surfaces.

By reviewing all these experimental characterization results, we decided to focus on the more prevalent *cube-on-cube* OR of the ferrite/ $\text{Y}_2\text{Ti}_2\text{O}_7$ interfaces, i.e. $\{100\}<100>_{\text{ferrite}}//\{100\}<100>_{\text{Y}_2\text{Ti}_2\text{O}_7}$ [34,36]. We first calculated the interface configurations and the associated energies with all possible stoichiometric and coordination types, as a function of temperature (T) and oxygen partial pressure (p_{O_2}). The interface phase diagram was constructed to determine the most energy-favorable interface structures and termination chemistries for a wide temperature range of interest. Further calculations were performed to compare various helium trapping sites at both perfect and vacancy-containing interfaces. The results were then carefully compared with those previously obtained for bulk $\text{Y}_2\text{Ti}_2\text{O}_7$ and in the ferrite matrix, to assess the nano-oxide interface role in trapping helium and forming associated helium bubbles. This provides a foundation for proposing a modified mechanism for helium transport and fate in NFAs.

2. Calculation methods

All structural relaxations and energetic calculations were performed using the density functional theory (DFT) code - VASP (Vienna Ab-initio Simulation Package) [38], with the plane-wave basis sets. The electron-core interaction was described by the Blöchl projector augmented wave method (PAW) within the frozen-core approximation [39] as implemented in VASP. The plane-wave basis sets were generated with valence configurations of He-1s², Fe-3d⁶4s², Y-4s²4p⁶4d¹5s², Ti-3s²3p⁶3d²4s², and O-2s²2p⁴. Validation of the exchange-correlation (XC) functional was performed by fitting the energy-volume relation for bcc Fe and pyrochlore $\text{Y}_2\text{Ti}_2\text{O}_7$ to the universal equation of state [40]. The tested XC-functionals included local-density approximation (LDA) [41], and the generalized gradient

approximation (GGA) with the Perdew-Wang-91 functional (PW91) [42] and the Perdew-Burke-Ernzerhof (PBE) functional [43]. The PAW-PW91 functionals were finally chosen for all subsequent calculations, since they yielded the best prediction of bulk bcc Fe ($a=2.8303\text{\AA}$, bulk modulus $B=174\text{GPa}$) and pyrochlore $\text{Y}_2\text{Ti}_2\text{O}_7$ ($a=10.1835\text{\AA}$, $B=183\text{GPa}$), compared to experiments and other calculations [44-52].

To model the interfaces, we used a ferrite/oxide/ferrite sandwich supercell with a vacuum thickness of at least $12\text{\AA}$ and with a $2\times 2\times 1$ Monkhorst-Pack k -mesh. The electronic relaxation algorithm employed the residual minimization scheme - direct inversion in the iterative subspace (RMM-DIIS). All ground-state configurations were optimized using a high energy-cutoff of 500 eV for the plane-wave basis sets. For all the interface structures considered, the calculations allowed for full relaxation by varying atomic configurations in space to minimize the Hellman-Feynman forces (using a combined blocked Davidson + RMM-DIIS algorithm) until the total forces on each ion were converged to within $0.02\text{ eV/\AA}$.

3. Results and discussion

3.1 Interface structures

It is not practical to have an arbitrarily large unit cell with misfit dislocations included naturally, so we chose to strain the $\text{Fe}(100)$ and the $\text{Y}_2\text{Ti}_2\text{O}_7(100)$ surfaces into commensuration in a manner consistent with the Ribis' cube-on-cube OR. The resulting interface structure of $\text{Fe}(100)(2\sqrt{2}\times 2\sqrt{2})/\text{Y}_2\text{Ti}_2\text{O}_7(100)(\sqrt{2}/2\times \sqrt{2}/2)$ is shown in Fig. 1. In this sandwich supercell of $\text{Fe}/\text{Y}_2\text{Ti}_2\text{O}_7/\text{Fe}$, each Fe block contains five atomic layers with a total of forty Fe atoms and the oxide block consists of a conventional unit cell of $\text{Y}_2\text{Ti}_2\text{O}_7$. This supercell has the lowest strains to commensuration: the Fe lattice is compressed by 5.1% and the $\text{Y}_2\text{Ti}_2\text{O}_7$ lattice is stretched by 5.4% along

$\langle 100 \rangle_{\text{Fe}} // \langle 100 \rangle_{\text{Y}_2\text{Ti}_2\text{O}_7}$), leading to a perfect matching of $4d\{110\}_{\text{Fe}}$ with $4d\{440\}_{\text{Y}_2\text{Ti}_2\text{O}_7}$. The associated commensuration strain is slightly larger than, yet as close as possible to, that deduced from Ribis' observations (where every $8d\{110\}_{\text{Fe}}$ matches $9d\{440\}_{\text{Y}_2\text{Ti}_2\text{O}_7}$ perfectly [34]). The strain effect shall be regarded as highly localized, only within a few atomic layers from the interface plane (as modeled in Fig. 1), since misfit dislocations can effectively relax the strains - more in deeper layers.

Given the OR and the interfacial strains, the stability of an interface structure is dictated by interfacial stoichiometry and interfacial coordination [53, 54]. According to our previous study [55], a polar free surface of $\text{Y}_2\text{Ti}_2\text{O}_7$ may have various possible chemical terminations, or stoichiometry, depending on the oxygen activity (expressed in term of oxygen partial pressure). Similarly, depending on the internal local oxygen activity, one of three typical stoichiometry types is selected on the oxide side of the ferrite/ $\text{Y}_2\text{Ti}_2\text{O}_7$ interface, namely the stoichiometric (labeled as *stoi*), the non-stoichiometric Y/Ti-rich (*ns-2Y2Ti*), and the non-stoichiometric O-rich type (*ns-5O*). For each stoichiometry type, we further considered at least two different coordination types (shown in Fig. 1), by translating the metal relative to $\text{Y}_2\text{Ti}_2\text{O}_7$, i.e. placing the Fe atoms right above the Y and Ti atoms ("*top-coordinated*"), or at the bridge sites of the Y and Ti atoms ("*bridge-coordinated*"). The latter configuration may also be seen as the O-top coordination. The interface coordination type and stoichiometry dictate the local chemical environment at interface, which in turn dictates the interface structure and properties, such as formation energy, relative stability, adhesion strength, and segregation effects. Note, these effects have been studied for other metal/oxide systems including $\text{Ni}/\text{Al}_2\text{O}_3$ and $\text{Cu}/\text{Al}_2\text{O}_3$ [53, 54, 56-58]. Calculations of the resulting interface ensembles suggested that the bridge-coordinated interfaces, either Y/Ti-rich or stoichiometric, always have lower formation energies than their top-coordinated counterparts. The top-coordinated, O-rich interface is particularly unstable: it transforms immediately into a bridge-coordinated configuration during the full relaxation of the structure. Thus all the

following calculations and discussion are restricted to the bridge-coordinated interfaces that, again, can be either Y/Ti-rich, stoichiometric, or O-rich.

Fig. 1 The sandwich supercell for the $\text{Fe}(100)(2\sqrt{2} \times 2\sqrt{2})/\text{Y}_2\text{Ti}_2\text{O}_7(100)(\sqrt{2}/2 \times \sqrt{2}/2)$ interface and the two representative coordination types: (a) Y/Ti-top and (b) Y/Ti-bridge. For clarity, we only show the interfacial atoms of Fe, Y, and Ti in top-views.

3.2 Oxygen chemical activity and interface phase diagram

NFAs are typically processed by mechanically alloying Fe-based pre-alloyed powders (Fe, Ti, Cr) with Y_2O_3 oxide powders by high-energy ball milling. The Y_2O_3 constituents are mechanically forced into solution (dissolved) by ball milling, and then precipitate with Ti from the matrix during the subsequent hot consolidation [1, 15, 59]. We chose to represent the equilibrated chemical reaction as

To determine the appropriate interface structure under a given thermodynamic equilibrium condition, we employed a defect thermodynamic model for interface energy (γ_I) in accordance with Eq. (1), as

$$\begin{aligned} \gamma_I &= \frac{1}{2A} (G_0 - N_{\text{Fe}}\mu_{\text{Fe}} - N_{\text{Y}_2\text{O}_3}\mu_{\text{Y}_2\text{O}_3} - N_{\text{Ti}}\mu_{\text{Ti}} - N_{\text{O}_2}\mu_{\text{O}_2}) \\ &= \frac{1}{2A} [G_0 - N_{\text{Fe}}\mu_{\text{Fe}}^0 - \frac{1}{2}N_{\text{Ti}}\mu_{\text{Y}_2\text{Ti}_2\text{O}_7}^0 + (\frac{1}{2}N_{\text{Ti}} - N_{\text{Y}_2\text{O}_3})\mu_{\text{Y}_2\text{O}_3}^0 + \frac{1}{2}(2N_{\text{Ti}} + 3N_{\text{Y}_2\text{O}_3} - N_{\text{O}})(\mu_{\text{O}_2}^0 + kT \ln p_{\text{O}_2})] \end{aligned} \quad (2)$$

Here G_0 is the Gibbs free energy of the interface ensemble, while N_i and μ_i are, respectively, the number and chemical potential of each species i ($i=\text{Fe, O, Y, Ti, Y}_2\text{Ti}_2\text{O}_7$, or Y_2O_3). The superscript “0” refers to the pure bulk state of each species, and A is the cross-sectional area of the interface. p_{O_2} refers to the oxygen partial pressure that reflects the local oxygen activity near the interface, and T is the temperature. Note, if we assume that a fixed Y:Ti ratio holds in all these interface ensembles, i.e.

$N_Y=N_{Ti}$, or $N_{Y_2O_3} = \frac{1}{2}N_{Ti}$ [55], we can rewrite Eq. (2) as

$$\gamma_1 = \frac{1}{2A} [G_0 - N_{Fe}\mu_{Fe}^0 - \frac{1}{2}N_{Ti}\mu_{Y_2Ti_2O_7}^0 + \frac{1}{2}(2N_{Ti} + 3N_{Y_2O_3} - N_O)(\mu_{O_2}^0 + kT \ln p_{O_2})] \quad (3)$$

We further assume that temperature effects on the Gibbs free energy of the interface ensemble (G_0) can be largely cancelled out with those of the two component bulks (μ_{Fe}^0 and $\mu_{Y_2Ti_2O_7}^0$) in Eq. 3. Thus we need only consider the temperature effect on the free energies of O_2 ($\mu_{O_2}^0$) using JANAF table values [60] for O_2 molecules. An isothermal section of the interface phase diagram can be thus obtained, by plotting the calculated γ_1 against p_{O_2} at any given temperature.

Fig. 2 shows the calculated isothermal section of the interface phase diagram at $T=1100$ K, with a direct comparison between with and without the temperature correction on $\mu_{O_2}^0$. In either case, the GGA overbinding of O_2 has been taken into account by following the instruction in Ref. [61]. Clearly, the non-stoichiometric interface energy is not a constant value, but varies with the ambient T and p_{O_2} , as suggested in Eq. (3). With the temperature correction on $\mu_{O_2}^0$, the predicted interface energies shifted notably to higher p_{O_2} values. At this temperature, the Y/Ti-rich (*ns-2Y2Ti*) interface dominates for p_{O_2} below $\sim e^{-28}$ while the O-rich (*ns-5O*) dominates for p_{O_2} above $\sim e^{-26}$. The critical p_{O_2} values for nonstoichiometric-to-stoichiometric transitions are marked as points *a* and *b*. Apparently, with increasing p_{O_2} , the most energetically favorable interface structure would change from the Y/Ti-rich to stoichiometric and then to the O-rich, following the same trend as seen for the $Y_2Ti_2O_7(100)$ free surface [55]. But in contrast to the free surface results, the non-stoichiometric interfaces (both Y/Ti- and O-rich) dominate here in a much wider range of p_{O_2} , leaving an *extremely* narrow range of p_{O_2} ($-28 < \ln p_{O_2} < -26$) for preferentially forming a stoichiometric interface.

Fig. 2 shows clearly how the interface structure evolves with temperature and the matrix p_{O_2} . Thus one question immediately follows: which interface phase is expected in NFAs, at the given temperature, for example for $T=1100$ K. Experimentally determining the matrix p_{O_2} is very difficult.

Fe itself does not internally oxidize in NFAs, but from a purely thermodynamic viewpoint, the upper limits of the matrix p_{O_2} are, in principle, controlled by equilibrium with an Fe-oxide (i.e. FeO, Fe₂O₃, or Fe₃O₄).

The critical oxygen partial pressure for FeO can be approximated as

$$\ln p_{O_2} = \frac{2\Delta G_{FeO}^0(T)}{RT}, \quad (4)$$

where $\Delta G^0(T)$ is the Gibbs standard formation energy of FeO at the temperature T , in accordance with the reaction $Fe + \frac{1}{2}O_2 \rightarrow FeO$. Here p_{O_2} is the matrix oxygen partial pressure reflecting the local oxygen activity at the interfaces. R is the ideal gas constant, 8.314 J/(mol·K). Similarly,

$$\ln p_{O_2} = \frac{2}{3} \frac{\Delta G_{Fe_2O_3}^0(T)}{RT}, \quad (5)$$

$$\ln p_{O_2} = \frac{1}{2} \frac{\Delta G_{Fe_3O_4}^0(T)}{RT}, \quad (6)$$

for Fe₂O₃ and Fe₃O₄, respectively. Using $\Delta G_{FeO}^0 = -200.67$, $\Delta G_{Fe_2O_3}^0 = -537.171$, and $\Delta G_{Fe_3O_4}^0 = -762.463$ kJ/mol for $T = 1100$ K as tabulated in the JANAF Tables [60], the oxidation of FeO, Fe₂O₃, or Fe₃O₄ requires a threshold p_{O_2} of $\sim e^{-44}$, e^{-42} , or e^{-39} , respectively. That is, the internal p_{O_2} must be below $\sim e^{-44}$ for $T = 1100$ K in order to form only the Y/Ti-oxides in NFAs. By mapping this upper limit of p_{O_2} onto the isothermal interface phase diagram (highlighted as the blue region in Fig. 2), we determine that the cube-on-cube ferrite/Y₂Ti₂O₇ interface at $T=1100$ K is thermodynamically Y/Ti-rich, typically with a non-stoichiometric 2Y2Ti (*ns-2Y2Ti*) termination. The corresponding interface energy is thus predicted to be no more than 0.8 J/m², falling into the reasonable value ranges of coherent (0.005~0.2 J/m²) and semi-coherent (0.2~0.8 J/m²) interfaces [62]. The *ns-2Y2Ti*-terminated Y₂Ti₂O₇ interface corresponds to a chemical composition of Y_{2.5}Ti_{2.5}O₇ that is favorably comparable to an EELS result of nano-oxide precipitates in NFAs as Y_{2.2}Ti_{2.3}O₇ [22].

Fig. 2 The calculated isothermal section of the Fe(100)/Y₂Ti₂O₇(100) interface phase diagram at $T = 1100\text{K}$. Comparison is made between with and without the temperature correction on oxygen chemical potentials. In either case, the interface is predicted to be Y/Ti-rich in NFAs, typically with a non-stoichiometric 2Y2Ti (*ns-2Y2Ti*) termination.

However, for purposes of generality it is useful to treat the equilibrium thermodynamics baseline considering all possible solute oxidation reactions. Note, the transition pressure values (points *a* and *b*) in Fig. 2 that determine the relative stabilities of the interface phases vary sensitively with temperature. Tracking these transitions at various temperatures enables the construction of the full equilibrium interface phase diagram in Fig. 3. The phase boundaries, which are constructed with these transition points, are labeled as solid curves *a* and *b* in Fig. 3. In addition, using the CALPHAD results [63, 64] and JANAF data [60], seven dotted and dot-dashed curves are calculated in accordance with various possible reaction thermodynamics, namely Curve (1): $\text{Y} + \text{O}_2 \rightarrow \text{Y}_2\text{O}_3$, Curve (2): $\text{Y} + \text{Ti} + \text{O}_2 \rightarrow \text{Y}_2\text{Ti}_2\text{O}_7$, Curve (3): $\text{Ti} + \text{O}_2 \rightarrow \text{TiO}$, Curve (4): $\text{Y}_2\text{O}_3 + \text{Ti} + \text{O}_2 \rightarrow \text{Y}_2\text{Ti}_2\text{O}_7$, Curve (5): $\text{Ti} + \text{O}_2 \rightarrow \text{Ti}_2\text{O}_3$, Curve (6): $\text{Cr} + \text{O}_2 \rightarrow \text{Cr}_2\text{O}_3$, and Curve (7): $\text{Fe} + \text{O}_2 \rightarrow \text{Fe}_x\text{O}_y$. Note that Curve (7) is plotted based on the formation of FeO only, which determines the lowest p_{O_2} limit for forming Fe_xO_y (including FeO, Fe₂O₃, and Fe₃O₄) in NFAs. The formation of Fe₂O₃ and Fe₃O₄ always requires a higher p_{O_2} than FeO (as seen in Fig. 2), and thus, for better clarity, is not explicitly shown in Fig. 3. For conditions above Curve (1), due to the extremely low values of p_{O_2} , no solute oxidation can be expectable in NFAs, even at high temperatures; while for conditions below Curve (7), thermodynamically the iron matrix itself will be oxidized. The five dot-dashed curves (i.e. Curve (1), (3), (5), (6), and (7)), together with the two solid curves (*a* and *b*), divide the phase diagram into eight phase preference zones, namely (I) Fe(Cr/Y/Ti/O), (II) Y₂O₃+Fe(Cr/Y/Ti/O), (III) Y₂Ti₂O₇

(Y/Ti-rich)+Y₂O₃+TiO+Fe(Cr/Ti/O), (IV) Y₂Ti₂O₇(Y/Ti-rich)+Y₂O₃+TiO/TiO₂+Fe(Cr/O), (V) Y₂Ti₂O₇(Y/Ti-rich)+Y₂O₃+TiO/TiO₂+Cr₂O₃+Fe(O), (VI) Y₂Ti₂O₇(Y/Ti-rich)+Y₂O₃+TiO/TiO₂+Cr₂O₃+Fe_xO_y, (VII) Y₂Ti₂O₇(stoi)+Y₂O₃+TiO/TiO₂+Cr₂O₃+Fe_xO_y, and (VIII) Y₂Ti₂O₇(O-rich)+Y₂O₃+TiO/TiO₂+Cr₂O₃+Fe_xO_y. The potential to form multiple oxide phases, associated with a wide range of possible p_{O_2} values, along with the *extremely* narrow Zone (VII), rationalizes the frequent failure to observe fully stoichiometric nano-oxide Y₂Ti₂O₇ using various experimental techniques, as reviewed in Ref. [1].

Fig. 3 Calculated phase diagram for in-situ Y₂Ti₂O₇ in NFAs. Zone I: single phase Fe(Cr/Y/Ti/O) with dissolved Y, Ti, Cr, and O, Zone II: double phase region of Y₂O₃+Fe(Cr/Y/Ti/O), Zone III: multi-phase region of Y₂Ti₂O₇(Y/Ti-rich)+Y₂O₃+TiO+Fe(Cr/Ti/O), Zone IV: multi-phase region of Y₂Ti₂O₇(Y/Ti-rich)+Y₂O₃+TiO/TiO₂+Fe(Cr/O), Zone V: Y₂Ti₂O₇(Y/Ti-rich)+Y₂O₃+TiO/TiO₂+Cr₂O₃+Fe(O), Zone VI: Y₂Ti₂O₇(Y/Ti-rich)+Y₂O₃+TiO/TiO₂+Cr₂O₃+Fe_xO_y, Zone VII: Y₂Ti₂O₇(stoi)+Y₂O₃+TiO/TiO₂+Cr₂O₃+Fe_xO_y, Zone VIII: Y₂Ti₂O₇(O-rich)+Y₂O₃+TiO/TiO₂+Cr₂O₃+Fe_xO_y.

Further, it should be noted that the actual matrix p_{O_2} may be far in excess of thermodynamic equilibrium values for Y₂Ti₂O₇ precipitation. Significant internal oxidation of Fe, or even Cr, has not been observed in the actual NFAs, and appears to be kinetically prohibited. Here we consider neither non-equilibrium p_{O_2} , nor kinetics, but rather adopt a limiting and fixed thermodynamic viewpoint as the foundation for assessing the Y/Ti-rich (*ns-2Y2Ti*) interface structure and the interface interactions with helium and point defects.

3.3 Helium trapping at nano-oxide interfaces

The major significance of bulk-phase oxides to helium trapping and tolerance in NFAs has been shown in our previous studies ($\text{Y}_2\text{Ti}_2\text{O}_7$ [32] and Y_2TiO_5 [33]). However, for a full understanding of helium ultimate fates in NFAs, the possible roles of nano-oxide interfaces must be also examined. We have suggested that, from the first-principles calculations, the $\text{Y}_2\text{Ti}_2\text{O}_7$ interfaces with the *cube-on-cube* OR are thermodynamically Y/Ti-rich (see Fig. 2 and 3). In this section, we assess the capability of such oxide interfaces to trap helium. Both perfect and the defective (vacancy and helium-containing) ferrite/ $\text{Y}_2\text{Ti}_2\text{O}_7$ interfaces are carefully examined.

In the case of a clean, defect-free Y/Ti-rich termination, various interfacial interstitial sites for helium were considered. Full structural relaxation calculations showed that five configurations are potentially stable for helium trapping, including two open interstitial sites (He^i_{A} and He^i_{B}), one Ti-tetrahedron site on the interface (He^i_{T}), and two octahedral interstitial sites in sub-layers (He^s_{A} and He^s_{B}). Fig. 4 plots the five feasible interfacial helium structures after full relaxation. For the vacancy-containing Y/Ti-rich interface, energetic calculations were performed for various possible vacancy sites, created by removing one Fe, Y, Ti, or O atom from the interface. The results suggested that the iron vacancy requires the least energy expense, and is much lower than any other types of vacancy at the interface. Thus we need only consider the iron vacancy and label it as V^i in Fig. 5(a). Up to three helium atoms were then introduced to the interstitial and vacancy sites. Fig. 5 plots the total of seven interfacial helium-vacancy clusters that result, including zero to three helium atoms sharing one interfacial vacancy [labeled as V^i , He^i_{V} , $(2\text{He})^i_{\text{V}}$, and $(3\text{He})^i_{\text{V}}$, respectively] and zero to two helium atoms occupying the interfacial vacancy accompanied by an interfacial helium (He^i_{T}) [labeled as $\text{He}^i_{\text{T}}+\text{V}^i$, $\text{He}^i_{\text{V}}+\text{He}^i_{\text{T}}$, and $(2\text{He})^i_{\text{V}}+\text{He}^i_{\text{T}}$, respectively] .

The relative stabilities of these helium-trapped interface structures can be evaluated using the corresponding formation energy, E_f , defined as

$$E_f = E_d - E_0 - m \cdot \mu_{\text{He}} + n \cdot \mu_{\text{Fe}}, \quad (7)$$

where E_d is the total energy of a defective interface, E_0 is the total energy of the clean, defect-free interface, μ_{He} is the chemical potential of helium as an isolated atom, and μ_{Fe} is the chemical potential of iron in its pure state. m is the number of helium atoms in the defective interface, and n is the number of iron vacancies if applicable.

Fig. 4 Possible interstitial sites for helium on the Y/Ti-rich interface: (a) He^i_{A} , (b) He^i_{B} , (c) He^i_{T} , (d) He^s_{A} , and (e) He^s_{B} . Corresponding top views of interfacial layers are shown at the bottom.

Fig. 5 Possible configurations of helium-vacancy clusters on the Y/Ti-rich interface: (a) V^i , (b) $\text{He}^i_{\text{T}} + \text{V}^i$, (c) He^i_{V} , (d) $\text{He}^i_{\text{V}} + \text{He}^i_{\text{T}}$, (e) $(2\text{He})^i_{\text{V}}$, (f) $(2\text{He})^i_{\text{V}} + \text{He}^i_{\text{T}}$, and (g) $(3\text{He})^i_{\text{V}}$. Corresponding top views of interfacial layers are shown at the bottom.

Table 1 summarizes the calculated formation energies of these interface structures based on Eq. 7. By referring to our previous study on helium trapping in bulk $\text{Y}_2\text{Ti}_2\text{O}_7$ versus in iron [32], it is clear that the helium energy is effectively the same at interstitial sites both on the interface and inside the oxide interior. That is, the lowest formation energy of interstitial helium on the interface ($\text{He}^i_{\text{T}}=0.95$ eV) is nearly identical to that in bulk $\text{Y}_2\text{Ti}_2\text{O}_7$ ($\text{He}^{\text{I}}_{\text{octa}}=0.94$ eV), and well within the calculational uncertainties. Both are significantly lower than that of substitutional helium occupying a vacancy in the iron matrix ($\text{He}_{\text{V}}=2.28$ eV). The formation energy of an interface vacancy ($\text{V}^i=0.62$ eV) is also much lower than that in matrix iron ($\text{V}_{\text{Fe}}=2.14$ eV). We also note that the formation energies of interstitial He^s_{A} and He^s_{B} (1.43 and 1.29 eV) at sub-interface layers are higher than that in bulk $\text{Y}_2\text{Ti}_2\text{O}_7$ ($\text{He}^{\text{I}}_{\text{octa}}=0.94$ eV). This difference, to some extent, is related to interfacial coherent strains.

Table 1 Calculated formation energies of various helium-trapped interface structures

Note that the formation energies for interfacial helium-vacancy clusters, i.e. $\text{He}_T^i + \text{V}^i$, He_V^i , $\text{He}_V^i + \text{He}_T^i$, $(2\text{He})_V^i$, $(2\text{He})_V^i + \text{He}_T^i$ and $(3\text{He})_V^i$ in Table 1, include the vacancy formation energy (according to Eq. 7). The total number of thermal vacancies is constant, as they are replenished by generation at sites like dislocation jogs. In this framework, substitutional helium can be simply seen as an alloy constituent element. In other words, the vacancy loses its identity and energy upon conversion to a lattice site occupied by helium. Thus we are able to compare all of the above formation energies with reference to the interface vacancy energy (V^i) in Fig. 6. It is shown in Fig. 6 that the proper thermodynamic He_V^i is now 0.74 eV, only slightly lower than those of $\text{He}_T^i + \text{V}^i$ (0.80 eV) on the interface and $\text{He}_{\text{octa}}^I$ (0.94 eV [32]) in the oxide interior. All these values are significantly lower than that of helium at matrix iron vacancies ($\text{He}_V = 2.28$ eV [32]). Thus helium will partition from the ferrite matrix not only to the bulk oxides but also (possibly preferentially) to their interfaces. Concentrations of interface and bulk vacancies in excess of their equilibrium values are generated by severe deformation during ball milling, as well as under irradiation. We will not consider this further in the thermodynamic framework that we adopt here, but simply regard the vacancies as fully available. It is suggested in Fig. 6 that as the helium concentration increases, it tends to consume single individual interface vacancies and interstitials to the extent possible before forming multiple helium-vacancy clusters on the interface [such as $(2\text{He})_V^i$, $(2\text{He})_V^i + \text{He}_T^i$, and $(3\text{He})_V^i$], and/or in the oxide interior [such as $2(\text{He}_{\text{octa}}^I)$, $2\text{-He}_{\text{octa}}^I$, $(2\text{He})_{\text{octa}}^I$, $3(\text{He}_{\text{octa}}^I)$, $3\text{-He}_{\text{octa}}^I$, and $(3\text{He})_{\text{octa}}^I$].

Fig. 6 Formation energies of helium-vacancy clusters on the interface compared to those in iron and in

the oxide bulk as reported in Ref. [32].

The detailed balance between the various locations governs the site-dependent helium concentrations. This in turn depends on the size of the nano-oxide. As seen in Table 1, the energy per average helium atom is ~ 1.4 eV/He-atom for small helium clusters [e.g., $(2\text{He})^i_v$ or $(3\text{He})^i_v$] sharing an interface vacancy, and is comparable to the value of ~ 1.5 eV/He-atom for $(2\text{He})^i_{\text{octa}}$ or $(3\text{He})^i_{\text{octa}}$ sharing an interstitial site in the oxide interior [32]. The corresponding Boltzmann factors between bulk and interface sites are small, i.e. the fractional concentrations would all be roughly similar. These small helium clusters may act as nucleation sites for larger equilibrium helium fluid-gas bubbles with even lower energies per atom beyond a minimum size [32]. Bubbles that are initially over-pressurized quickly equilibrate by absorbing a sufficient number of vacancies. The broader implication of the helium management in NFAs will be discussed further in Sec.3.4.

3.4 Implications of the helium management and fate in NFAs

Fig. 6 and detailed balance considerations suggest that helium is preferentially associated with the nano-oxide $\text{Y}_2\text{Ti}_2\text{O}_7$, both at its interface and in the interior. This is qualitatively consistent with the experimentally observed distribution of helium bubbles in NFAs. Fig. 7 shows an overlapped bright-field transmission electron microscopy (TEM) micrograph of a dual helium-Fe ion irradiated 14YWT NFA (MA957) at 650°C at a radiation damage level of 48 displacements per atom (dpa) and 2200 appm helium. Here, the images of helium bubbles were taken in under-focus (white features indicated by blue arrows) and the nano-oxides in focus (light gray features indicated by red arrows) conditions. The overlapping of helium bubbles and nano-oxides indicates their high degree of mutual association. A likely scenario is that helium is initially deeply trapped in the oxide, but forms interface

bubbles that are sufficiently large ($>0.5\text{-}0.6\text{ nm}$) such that the corresponding chemical potential in the fluid-gas phase is lower than in the oxide [32].

Fig. 7 The high degree of helium bubble and nano-oxide association in a 14YWT NFA dual ion irradiated at 650°C to 48 displacements per atom and 2200 appm helium, with some examples highlighted by the blue and red arrows, indicating the bubbles and nano-oxides respectively.

To further clarify the helium management and fate in NFAs, we illustrate the energetics of helium partitioning and the sequence of events leading to interface bubble nucleation in Fig. 8(a) and (b), respectively. The bars for the grain boundary (GB) energies represent the range of V^{GB} and He_V^{GB} values by DFT in the literature [65-68]. These results strongly suggest that nano-oxides prevent large quantities of vacancies (process b1) and helium (process b2) from reaching GBs. Thus the bubble sizes both in the matrix and on GBs remain far smaller than the critical radius for conversion to growing voids (under irradiation) or creep cavities (under stress).

Interface bubble formation involves two sources of excess energy: the free surfaces created by the bubble, and the work of pressurizing helium from its reference state to the condition in the bubbles, as discussed in previous studies [1, 32, 69, 70]. In the simple capillary approximation framework, both terms are estimated as $\sim 2\gamma_e/r_b$, where γ_e is an effective surface energy and r_b is the radius of the bubble. The bubbles equilibrate to accommodate the trapped helium by absorbing vacancies (process b3). That is, the oxide interfaces actually act as heterogeneous sites for helium bubble nucleation. Obviously, ultrahigh densities of nano-oxides disperse helium into even smaller sizes up to very high temperatures, whereas fewer numbers of larger oxides could actually promote swelling by quickly forming interface bubbles that are large enough to convert to growing voids [1, 71].

Fig. 8 (a) Energies of forming vacancies and trapping helium at different locations in NFAs. Locations include the ferrite matrix, the bulk oxides, the oxide interfaces, and the iron grain boundaries. (b) The schematic formation of interfacial helium bubbles in NFAs. The superscript ‘*’ refers to the DFT results available in the literature.

4. Conclusions

We have performed a density functional theory based study to assess the important roles of $\text{Y}_2\text{Ti}_2\text{O}_7$ interfaces in helium management in NFAs. The full interface phase diagram was obtained to predict the lowest energy ferrite/ $\text{Y}_2\text{Ti}_2\text{O}_7$ interface structures. Vacancy and helium interactions with the cube-on-cube oxide interfaces were examined in a framework of the equilibrium thermodynamics of NFAs. The current results were compared to our previous calculations for bulk $\text{Y}_2\text{Ti}_2\text{O}_7$ as well as to published descriptions of helium interactions with GB. This leads to the following conclusions.

- (i) The ferrite/ $\text{Y}_2\text{Ti}_2\text{O}_7$ interface with the cube-on-cube orientation relationship of $\{100\}\langle 100\rangle_{\text{Fe}}//\{100\}\langle 100\rangle_{\text{Y}_2\text{Ti}_2\text{O}_7}$ can be Y/Ti-rich, stoichiometric, or O-rich, depending on the internal oxygen partial pressure and temperature.
- (ii) In the thermodynamic equilibrium framework, the calculated interface phase diagram predicts that the ferrite/ $\text{Y}_2\text{Ti}_2\text{O}_7$ interfaces are Y/Ti-rich, over a wide temperature range of interest. This partially rationalizes the possible non-stoichiometric nature of $\text{Y}_2\text{Ti}_2\text{O}_7$ precipitates often observed in some cases. Note, there is a wider range of possibilities for non-equilibrium results.
- (iii) Vacancy formation energies are lower at the ferrite/ $\text{Y}_2\text{Ti}_2\text{O}_7$ interface than at ferrite GBs, and the interfacial helium formation energies are close to that for helium trapping inside the bulk oxides. Thus helium can be first sequestered by the nano-oxides before it enters an even lower fluid-gas

energy state in sufficiently large interface bubbles.

- (iv) The large number of nm-sized bubbles trap most of the helium and act as sinks, or recombination (self-healing) sites, for displacement damage defects. This imbues NFAs with a remarkable degree of irradiation tolerance.

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Fig. 1 The sandwich supercell for the $\text{Fe}(100)(2\sqrt{2} \times 2\sqrt{2})/\text{Y}_2\text{Ti}_2\text{O}_7(100)(\sqrt{2}/2 \times \sqrt{2}/2)$ interface and the two representative coordination types: (a) Y/Ti-top and (b) Y/Ti-bridge. For clarity, we only show the interfacial atoms of Fe, Y, and Ti in top-views.

Fig. 2 The calculated isothermal section of the $\text{Fe}(100)/\text{Y}_2\text{Ti}_2\text{O}_7(100)$ interface phase diagram at $T = 1100\text{K}$. Comparison is made between with and without the temperature correction on oxygen chemical potentials. In either case, the interface is predicted to be Y/Ti-rich in NFAs, typically with a non-stoichiometric $2\text{Y}_2\text{Ti}$ (*ns-2Y2Ti*) termination.

Fig. 3 Calculated phase diagram for in-situ $\text{Y}_2\text{Ti}_2\text{O}_7$ in NFAs. Zone I: single phase $\text{Fe}(\text{Cr}/\text{Y}/\text{Ti}/\text{O})$ with dissolved Y, Ti, Cr, and O, Zone II: double phase region of $\text{Y}_2\text{O}_3+\text{Fe}(\text{Cr}/\text{Y}/\text{Ti}/\text{O})$, Zone III: multi-phase region of $\text{Y}_2\text{Ti}_2\text{O}_7(\text{Y}/\text{Ti-rich})+\text{Y}_2\text{O}_3+\text{TiO}+\text{Fe}(\text{Cr}/\text{Ti}/\text{O})$, Zone IV: multi-phase region of $\text{Y}_2\text{Ti}_2\text{O}_7(\text{Y}/\text{Ti-rich})+\text{Y}_2\text{O}_3+\text{TiO}/\text{TiO}_2+\text{Fe}(\text{Cr}/\text{O})$, Zone V: $\text{Y}_2\text{Ti}_2\text{O}_7(\text{Y}/\text{Ti-rich})+\text{Y}_2\text{O}_3+\text{TiO}/\text{TiO}_2+\text{Cr}_2\text{O}_3+\text{Fe}(\text{O})$, Zone VI: $\text{Y}_2\text{Ti}_2\text{O}_7(\text{Y}/\text{Ti-rich})+\text{Y}_2\text{O}_3+\text{TiO}/\text{TiO}_2+\text{Cr}_2\text{O}_3+\text{Fe}_x\text{O}_y$, Zone VII: $\text{Y}_2\text{Ti}_2\text{O}_7(\text{stoi})+\text{Y}_2\text{O}_3+\text{TiO}/\text{TiO}_2+\text{Cr}_2\text{O}_3+\text{Fe}_x\text{O}_y$, Zone VIII: $\text{Y}_2\text{Ti}_2\text{O}_7(\text{O-rich})+\text{Y}_2\text{O}_3+\text{TiO}/\text{TiO}_2+\text{Cr}_2\text{O}_3+\text{Fe}_x\text{O}_y$.

Fig. 4 Possible interstitial sites for helium on the Y/Ti-rich interface: (a) He_A^i , (b) He_B^i , (c) He_T^i , (d)

He_A^s , and (e) He_B^s . Corresponding top views of interfacial layers are shown at the bottom.

Fig. 5 Possible configurations of helium-vacancy clusters on the Y/Ti-rich interface: (a) V^i , (b) $He^i_T + V^i$, (c) He^i_V , (d) $He^i_V + He^i_T$, (e) $(2He)^i_V$, (f) $(2He)^i_V + He^i_T$, and (g) $(3He)^i_V$. Corresponding top views of interfacial layers are shown at the bottom.

Fig. 6 Formation energies of helium-vacancy clusters on the interface compared to those in iron and in the oxide bulk as reported in Ref. [32].

Fig. 7 The high degree of helium bubble and nano-oxide association in a 14YWT NFA dual ion irradiated at 650°C to 48 displacements per atom and 2200 appm helium, with some examples highlighted by the blue and red arrows, indicating the bubbles and nano-oxides respectively.

Fig. 8 (a) Energies of forming vacancies and trapping helium at different locations in NFAs. Locations include the ferrite matrix, the bulk oxides, the oxide interfaces, and the iron grain boundaries. (b) The schematic formation of interfacial helium bubbles in NFAs. The superscript ‘*’ refers to the DFT results available in the literature.

Table 1 Calculated formation energies of various helium-trapped interface structures

	He_A^i	He_B^i	He_T^i	He_A^S	He_B^S	V^i	He_T^iV^i	He_V^i	$\text{He}_V^i\text{He}_T^i$	$(2\text{He})_V^i$	$(2\text{He})_V^i\text{He}_T^i$	$(3\text{He})_V^i$
E_f (eV)	1.32	1.20	0.95	1.43	1.29	0.62	1.42	1.36	2.61	2.83	3.73	4.22