

Chapter

Interstitial Oxygen Engineering in Titanium Alloys: From Fundamental Strengthening/Damping Mechanisms to Multiscale Heterostructure Design

X. G. Wang, L. Y. Sun and F. X. Yin

Abstract

This chapter reviews how interstitial oxygen regulates strengthening and damping in titanium alloys from the atomic scale to macroscopic properties. Oxygen occupies the octahedral interstices of the titanium lattice and exists as a random solid solution, locally ordered structures, oxygen-stabilized phases, and interfacial segregation, which can transform into one another with composition and processing. In strengthening, oxygen pins dislocation cores through short-range chemical interactions, regulates the competition between twinning and slip, suppresses the stress-induced martensitic transformation, stabilizes the ω phase, and promotes spinodal decomposition. Through these mechanisms, high-oxygen alloys achieve high strength without embrittlement once the oxygen distribution and deformation path are controlled. The high damping of β -Ti is attributed to the Snoek-type anelastic relaxation of solid-solution oxygen, which involves the stress-induced reorientation of the elastic dipoles formed by interstitial oxygen rather than the motion of mobile defects, so that high damping and high strength are no longer mutually exclusive. For example, Ti-36Nb-0.9O achieves $\tan \delta$ of 0.104 together with a yield strength of 1090 MPa. This concept has been extended from Ti-Nb-O to refractory high-entropy alloys, where strong lattice distortion and broad distributions of oxygen migration barriers widen the damping temperature range. The strengthening and damping responses are therefore controlled by how oxygen is distributed across these scales rather than by its content alone. Multiscale heterostructure design based on oxygen distribution provides a promising route toward titanium alloys that combine high strength, high damping, and low cost.

Keywords: titanium alloys, interstitial oxygen, solid-solution strengthening, Snoek-type damping, heterostructure design

1. Introduction

Titanium and its alloys exhibit high specific strength, good corrosion resistance and favorable biocompatibility and have been widely used in aero-engines, deep-sea equipment, chemical devices and biomedical implants [1–4]. As service demands increase, the design of titanium alloys has moved from optimizing a single property toward combining multiple functions. Structural components are expected to combine strength with toughness; orthopedic implants require a low modulus together with a long fatigue life; and precision equipment needs to provide adequate load-bearing capacity and good damping behavior at the same time. However, the inherent strength-ductility and damping-strength trade-offs in titanium alloys largely restrict their further application [5–7]. For example, $\alpha + \beta$ alloys represented by Ti–6Al–4V show a good combination of strength and ductility but limited damping capacity, whereas conventional high-damping alloys such as MnCu-based alloys possess excellent damping performance but their yield strength is generally too low to meet the requirements of structural components [8].

Among the factors that control the performance of titanium alloys, oxygen plays a particularly distinctive role in both mechanical and damping behavior [9]. As a typical interstitial solute, oxygen produces pronounced solid-solution strengthening in pure titanium and $\alpha + \beta$ titanium alloys [10]. Conventional physical metallurgy, however, holds that excessive oxygen (typically > 0.3 wt.%) leads to a marked loss of room-temperature ductility and low-temperature brittle fracture [11–13]. This strength-ductility trade-off forces industry to tightly control the oxygen content, which raises metallurgical costs and limits the use of titanium sponge and recycled titanium powder [14].

In recent years, advances in characterization and first-principles calculations have gradually clarified the role of oxygen in titanium alloys, offering new opportunities for designing high-performance titanium alloys through oxygen engineering. Using aberration-corrected transmission electron microscopy combined with first-principles calculations, Yu et al. [15] directly observed the segregation of oxygen atoms near the cores of screw dislocations in α -Ti and revealed that oxygen pins the dislocation cores through short-range chemical interactions. Beyond randomly distributed interstitial oxygen, researchers have progressively identified a variety of oxygen configurations in different titanium-based systems, including local-range-ordered oxygen (LRO–O) [16], ordered oxygen complexes (OOCs) [17, 18], oxygen segregation at twin and grain boundaries [19], and oxygen-induced FCC titanium phases [20, 21]. These configurations act on dislocations, deformation modes and phase transformations in different ways, so the strengthening and damping responses of titanium alloys are largely determined by the oxygen configuration and its host phase.

In terms of mechanical strengthening, the key challenge lies in improving the strength while avoiding embrittlement. By distributing oxygen nonuniformly within the α lamellae and fully partitioning iron into the β phase, Song et al. [22] prepared a Ti–0.34O–3.25Fe alloy with 1194 ± 8 MPa tensile strength and $21.9 \pm 2.2\%$ elongation. Yang et al. [23] increased the oxygen content to ≥ 0.4 wt.% to activate $\langle c + a \rangle$ pyramidal slip in the α phase and tailored the α – β slip-transfer interfaces, enabling Ti–0.45O–4Fe to attain $\geq 14\%$ uniform elongation and $\geq 27\%$ total elongation at yield strength ≥ 980 MPa. Such nonequilibrium oxygen distributions benefit from the ultrahigh cooling rates and repeated interlayer thermal

cycling of additive manufacturing (AM) [20, 22]. These results demonstrate that high-oxygen raw materials, conventionally regarded as detrimental impurities, can overcome the strength-ductility trade-off under appropriate compositional design and processing.

The damping capacity of β -Ti alloys is attributed mainly to Snoek-type anelastic relaxation induced by interstitial oxygen atoms, offering a route to low-frequency vibration damping. Yin et al. [9] first reported Snoek-type high damping in β -Ti-Nb-O in 2006. Subsequently, Yu and Yin [24, 25] applied a statistical-mechanical analysis to the broadened Snoek relaxation peak in ternary body-centered cubic (BCC) alloys; Yin et al. [26] studied the anelastic-relaxation anisotropy in highly textured Ti-Nb-O and quantified the relationship between orientation parameters and relaxation strength; and Lu et al. [27] systematically examined how alloying elements such as, Al, Sn, Cr, Mn, and Fe modulate the Snoek relaxation based on the d-orbital energy level (Md). This design strategy has recently been extended to multicomponent systems [18]. These results show that the same design strategy remains effective in more complex alloy systems.

To date, oxygen-doped titanium alloys have been studied extensively from the perspectives of AM, strength-ductility design and biomedical application. However, the strengthening and damping effects of oxygen, together with their synergy, remain poorly understood. Most studies have examined strength or damping separately, and few have linked the two through the same oxygen configurations. This review chapter focuses on oxygen-doped titanium alloys and proceeds from the atomic scale to macroscopic properties. Section 2 discusses the site occupancy, structural forms and interfacial segregation of oxygen. Sections 3 and 4 review the oxygen-mediated strengthening and Snoek-type damping mechanisms, respectively. Section 5 summarizes multiscale heterostructure design strategies and outlines future directions.

2. Site occupancy and structural forms of interstitial oxygen in titanium alloys

Oxygen dissolves in titanium as interstitial atoms and shows a preference for the octahedral interstitial sites. Yu et al. [15] directly confirmed that oxygen occupies the octahedral interstitial sites of the HCP structure by high-angle annular dark-field scanning transmission electron microscopy, as shown in **Figure 1a**. According to the Ti-O binary phase diagram, the oxygen solubility in α -Ti is as high as about 33 at.% (about 14 wt.%) [28, 29], whereas the solubility in β -Ti is much lower [20]. This difference makes oxygen partition into the α phase preferentially in $\alpha + \beta$ alloys, thereby influencing phase partitioning and microstructural evolution.

The lattice distortion induced by oxygen at the octahedral interstices is anisotropic, and differs between the two phases. In α -Ti, Kang et al. [30] found that the c/a ratio of α -Ti increases as the oxygen content increases from 0.082 wt.% to 0.268 wt.%. Wang et al. [31] further showed that the c/a ratio increases from 1.567 to 1.616 with increasing oxygen content, which alters the relative ease of prismatic, pyramidal and basal slip. In β -Ti, oxygen occupies the octahedral interstices of the BCC lattice, producing tetragonal distortions and oriented elastic dipoles [24]. These dipoles form the structural basis of the Snoek-type anelastic relaxation discussed in Section 4. This anisotropic distortion has been further confirmed at the

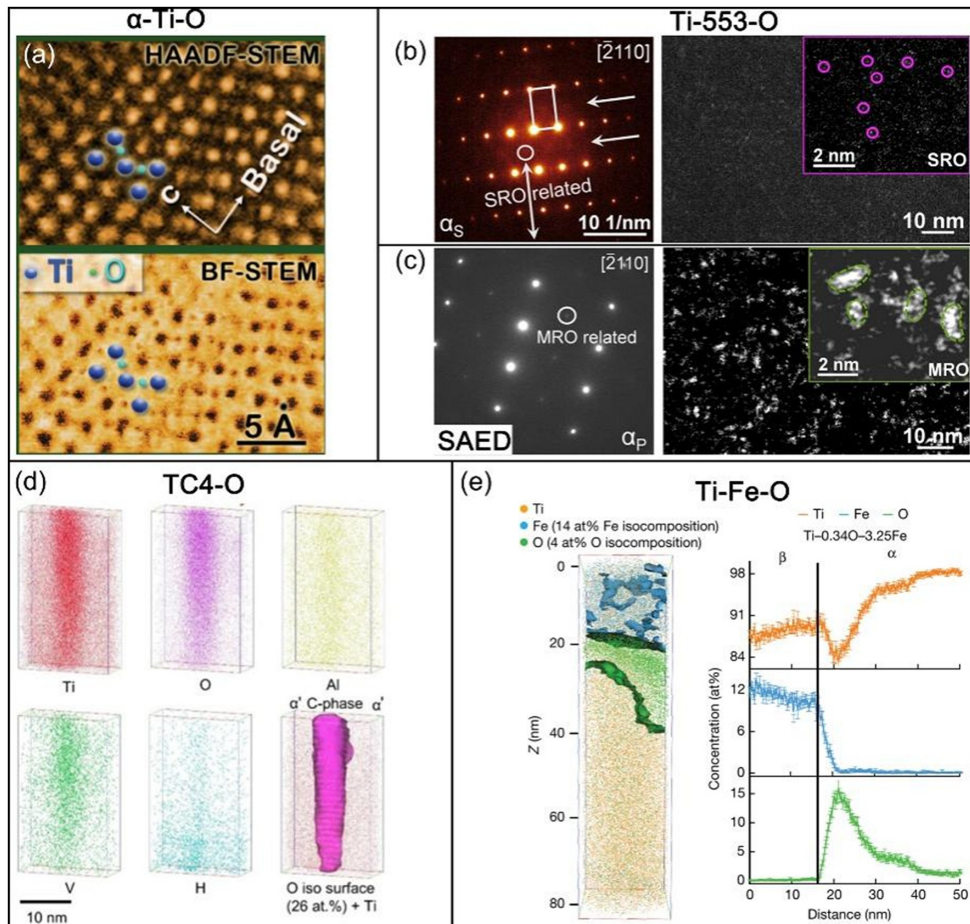


Figure 1.

The configuration of oxygen in titanium alloys. (a) Oxygen at octahedral interstitial sites of α -Ti [15]. (b) Short-range and (c) medium-range ordered oxygen in Ti-5Al-5Mo-5V-3Cr-O [16]. (d) Oxygen-stabilized FCC phase in additively manufactured Ti-6Al-4V-O [20]. (e) Oxygen and iron partitioning across the α/β interface in Ti-0.34O-3.25Fe [22].

atomic scale. Using first-principles calculations, Li et al. [32] determined the local distortions and elastic-dipole characteristics of C, N, and O in BCC transition metals, and Wang et al. [33] directly observed columns of oxygen atoms at the octahedral interstices along the $[11\bar{2}0]$ direction in Ti-0.4O using iDPC-STEM.

Oxygen does not exist only as a random interstitial solid solution in titanium alloys. In metastable β matrices, oxygen can form nanoscale ordered structures through interactions with neighboring atoms. In the Ti-5Al-5Mo-5V-3Cr alloy containing 0.36 wt.% oxygen, Mao et al. [16] used selected-area electron diffraction and STEM to identify LRO-O structures intermediate between oxides and random interstitials (Figure 1b, c). The fine secondary α phase contained short-range ordered oxygen (SRO-O) about 0.7 nm in size (Figure 1b), while the coarse primary α phase contained medium-range ordered oxygen (MRO-O) about 1.6 nm in size (Figure 1c). In both phases, the oxygen atoms occupied the octahedral or tetrahedral interstices of the HCP lattice [16]. In BCC high- and medium-entropy alloys rich in

elements with a strong affinity for oxygen, such as, Ti and Zr, oxygen tends to form OOCs. Lei et al. showed that in the TaNbHfZrTi refractory high-entropy alloy doped with 2.0 at.% oxygen, the OOCs improve strength and ductility simultaneously [18]. Jiao et al. [34] later found that reducing the phase stability and enhancing the (Ti, Zr) chemical short-range order promote OOC formation in Ti–Zr–Nb medium-entropy alloys. In both length scale and degree of order, these ordered oxygen structures are intermediate between random solid-solution oxygen and stable oxides.

Under the nonequilibrium conditions of AM, oxygen can also take part in forming new stable phases. In Ti–6Al–4 V produced by laser powder bed fusion (L-PBF), Wang et al. [20] found an oxygen-supersaturated FCC titanium phase whose oxygen content reached about 30 at.%, while the surrounding α' matrix contained only about 2.8 at.% (**Figure 1d**). First-principles calculations showed that oxygen has a lower formation energy at the octahedral interstices of FCC-Ti and that the high cooling rate of L-PBF, the local deformation induced by the martensitic transformation, and the local enrichment of oxygen by diffusion together promote the in-situ transformation from HCP to FCC [20]. The ultra-fast cooling does not change the site preference of oxygen. It suppresses diffusion and prevents oxygen from homogenizing, and in the resulting oxygen-rich regions, the lower formation energy of oxygen in the FCC lattice drives the HCP-to-FCC transformation and stabilizes the FCC phase [35]. In metastable β -Ti, oxygen also affects the precipitation of the ω phase [36, 37]. These phase transformations and their strengthening effects are discussed in Section 3.

In addition to solid solution and ordered structures within the matrix, oxygen also segregates at various interfaces. Prithiv et al. [19] found that oxygen segregated strongly at both low- and high-angle grain boundaries in Ti–5Al–5Mo–5V–3Cr–0.5Fe by atom probe tomography, where the boundary oxygen concentration reached 1.6–1.7 at.%, about three times that of the matrix, and increased the chemical driving force for α -phase nucleation at the boundaries. In AM Ti–0.34O–3.25Fe, oxygen enriches the α phase while iron enriches the β phase across the interface (**Figure 1e**) [22]. Oxygen behavior at twin boundaries depends on the twin type. Chong et al. [38] reported that oxygen preferentially segregates to $\{10\bar{1}2\}$, $\{10\bar{1}1\}$, and $\{11\bar{2}1\}$ twin boundaries, but not to $\{11\bar{2}2\}$ and $\{11\bar{2}4\}$ boundaries. On the $\{332\} <113>$ deformation twin boundaries in metastable β -Ti, Chong et al. [39] observed oxygen segregation by atom probe tomography, with a peak of about 1.79 at.%, higher than the matrix value of 0.92 at.%. The degree of interfacial oxygen enrichment also depends on grain size. In Ti–0.3O, Chong et al. found that the peak oxygen concentration at the boundaries of the coarse grains (68 μm) reached 2.0 at.%, about twice the intragranular value of 1.1 at.%. When the grains were refined to the ultrafine regime (about 2.0 μm), the oxygen segregation was diluted to a level close to that within the grains, which suppressed oxygen embrittlement at low temperature [40]. Interfacial oxygen distribution can therefore be tailored by grain size design rather than being an intrinsic property of the material.

Overall, oxygen can exist in titanium alloys in several forms, including random solid solution atoms, local ordered structures, OOCs, oxygen-stabilized phases, and interfacial segregation [41]. These forms can transform into one another as the oxygen content, alloy composition and processing conditions change. The strengthening and damping mechanisms discussed in the following two sections all rely on controlling these forms of oxygen.

3. Strengthening mechanisms of oxygen in titanium alloys

The strong strengthening of α -Ti by oxygen lies in its interaction with dislocations, which has not been clearly understood for a long time. Classical theory assumes that screw dislocations produce only shear stress fields and interact weakly with interstitial atoms that cause isotropic expansion, leading to the expectation that oxygen strengthening would be limited. Yu et al. [15] revised this view by combining transmission electron microscopy with first-principles calculations. They observed that oxygen was concentrated near the cores of screw dislocations in α -Ti, and that as a screw dislocation glides on the prismatic plane, the octahedral interstice occupied by oxygen along its path contracts sharply, forcing the oxygen to hop to a lower-energy neighboring interstice. This process must overcome a relatively high energy barrier of 0.42–0.95 eV. The pronounced strengthening by trace oxygen results from the strong short-range chemical repulsion at the dislocation core, rather than from the conventional elastic interaction.

At the macroscopic scale, this solid solution strengthening effect of oxygen can be quantified. Sun et al. let pure titanium powder absorb oxygen up to 0.64 wt.% during powder metallurgy and, after subtracting the contribution of grain refinement, obtained a yield strength increase of about 769.8 MPa/wt.%, while the material retained an elongation of 26%. This was attributed to the c/a ratio remaining within the beneficial range of 1.588–1.590 [10]. A similar effect is found in β -type biomedical alloys, where adding suitable amounts of Fe and O to Ti–Nb–Ta–Zr increases the yield strength while keeping a low elastic modulus [42]. A high oxygen content, therefore, does not necessarily sacrifice ductility. The key lies in how oxygen alters the deformation mechanism of the alloy. The following paragraphs discuss the various strengthening routes that oxygen achieves by regulating deformation mechanisms and by stabilizing metastable phases.

In α -Ti, oxygen first inhibits deformation twinning [30, 43]. Kang et al. found that the deformation twins became finer and fewer with increasing oxygen content and were largely suppressed at high oxygen levels (**Figure 2a–c**). This occurred because the higher c/a ratio raised the shear strain required for twinning, while the interstitial oxygen atoms impeded the atomic shuffling required for twinning [30]. Comparing pure Ti and Ti–0.3O under compression at 300 K and 77 K, oxygen reduced the deformation-twin fraction, which dropped from 20–32% in pure Ti to 0 at 300 K and only 23% at 77 K in Ti–0.3O (**Figure 2a–c**) [43]. Twinning is an important way for HCP metals to accommodate strain along the c axis, and once it is inhibited, this role must be accommodated by $\langle c + a \rangle$ pyramidal slip. Wang et al. [31] recorded a similar progressive change in slip mode in oxygen-gradient pure titanium, from prismatic $\langle a \rangle$ slip to pyramidal $\langle c + a \rangle$ slip and then to basal slip (**Figure 3a**). However, $\langle c + a \rangle$ slip is difficult to activate, and its full activation is critical to maintaining ductility in high-oxygen titanium alloys. The activation conditions depend on temperature, strain rate, and alloy composition. Chong et al. [38] found that oxygen changed the dislocation glide from wavy to planar through an interstitial drag mechanism and noted that this process is sensitive to temperature and strain rate (**Figure 3b**). Wang et al. [33] showed, by experiments at a high strain rate of about $4,000 \text{ s}^{-1}$ that prismatic $\langle a \rangle$ slip became dominant in Ti–0.4O while pyramidal slip remained largely inactive because prismatic slip has the strongest strain-rate sensitivity and is the most readily activated at high strain rates.

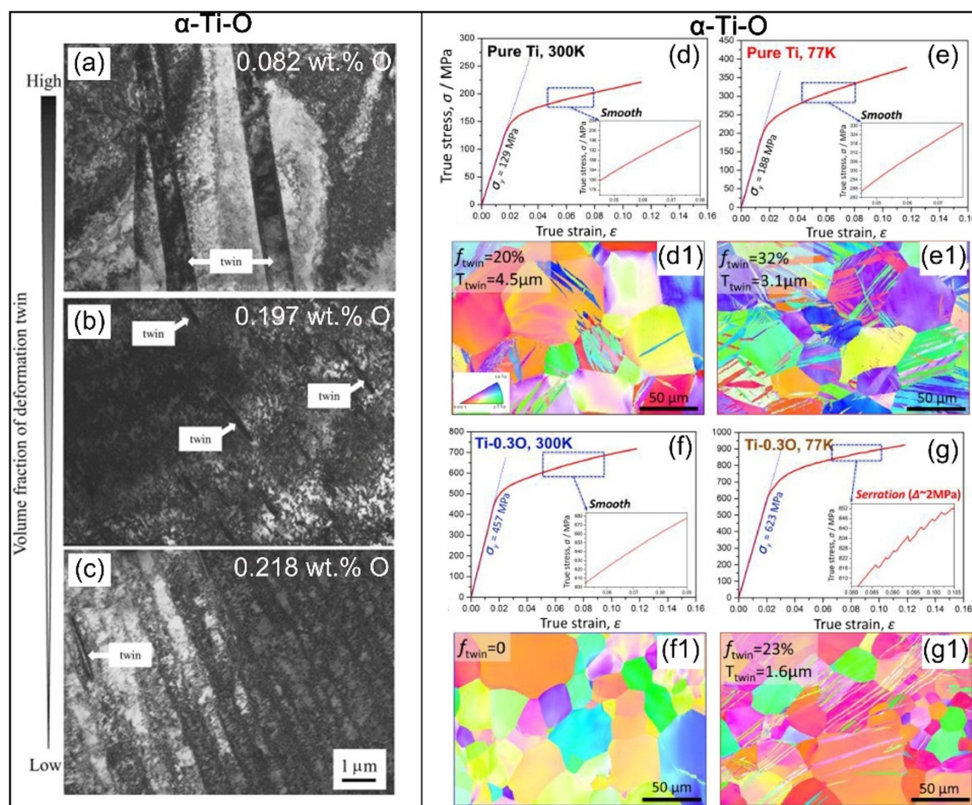


Figure 2. Oxygen suppresses deformation twinning in α -Ti. (a–c) TEM images showing the deformation-twin fraction decreasing and twins refining as the oxygen content increases from 0.082 to 0.218 wt. % [30]. (d–g) Compressive true stress-strain curves of pure Ti and Ti–0.3O at 300 K and 77 K. (d1–g1) Corresponding EBSD-IPF maps after 10% plastic strain [42].

Since the activation of $\langle c + a \rangle$ slip determines the ductility of high-oxygen titanium alloys, promoting its activation becomes the key. Increasing the oxygen content of the α phase is an effective route. When the α -phase oxygen content exceeds 0.4 wt.%, $\langle c + a \rangle$ pyramidal slip is markedly activated and accommodates strain along the c axis. On this basis, Yang et al. [23] designed Ti–0.45O–4Fe and Ti–0.5O–5Fe. After L-PBF and annealing, oxygen partitioned almost entirely into the α phase, while Fe partitioned into the β phase. Both alloys combined high strength with large ductility. Ti–0.45O–4Fe reached $\geq 14\%$ uniform elongation at yield strengths ≥ 980 MPa (**Figure 4a**), and Ti–0.5O–5Fe reached $\geq 13\%$ at yield strengths $\geq 1,075$ MPa (**Figure 4b**). In-situ EBSD revealed that $\langle c + a \rangle$ slip dominated the deformation of the α phase, with $\{11\bar{2}2\} \langle c + a \rangle$ second-order pyramidal slip accounting for 52% of the slip traces. These slip traces frequently crossed the α – β interfaces over 4 to 10 lamellae, with a geometric compatibility factor of 0.8 to 1.0, and $\langle c + a \rangle$ slip carried 57% of the slip transfer (**Figure 4c**) [23]. The coarse α lamellae thicker than 1 μ m and the coherent α – β interfaces enabled the $\langle c + a \rangle$ dislocations to cross the interfaces efficiently without stress concentration, giving the alloy a large uniform ductility at high strength [23].

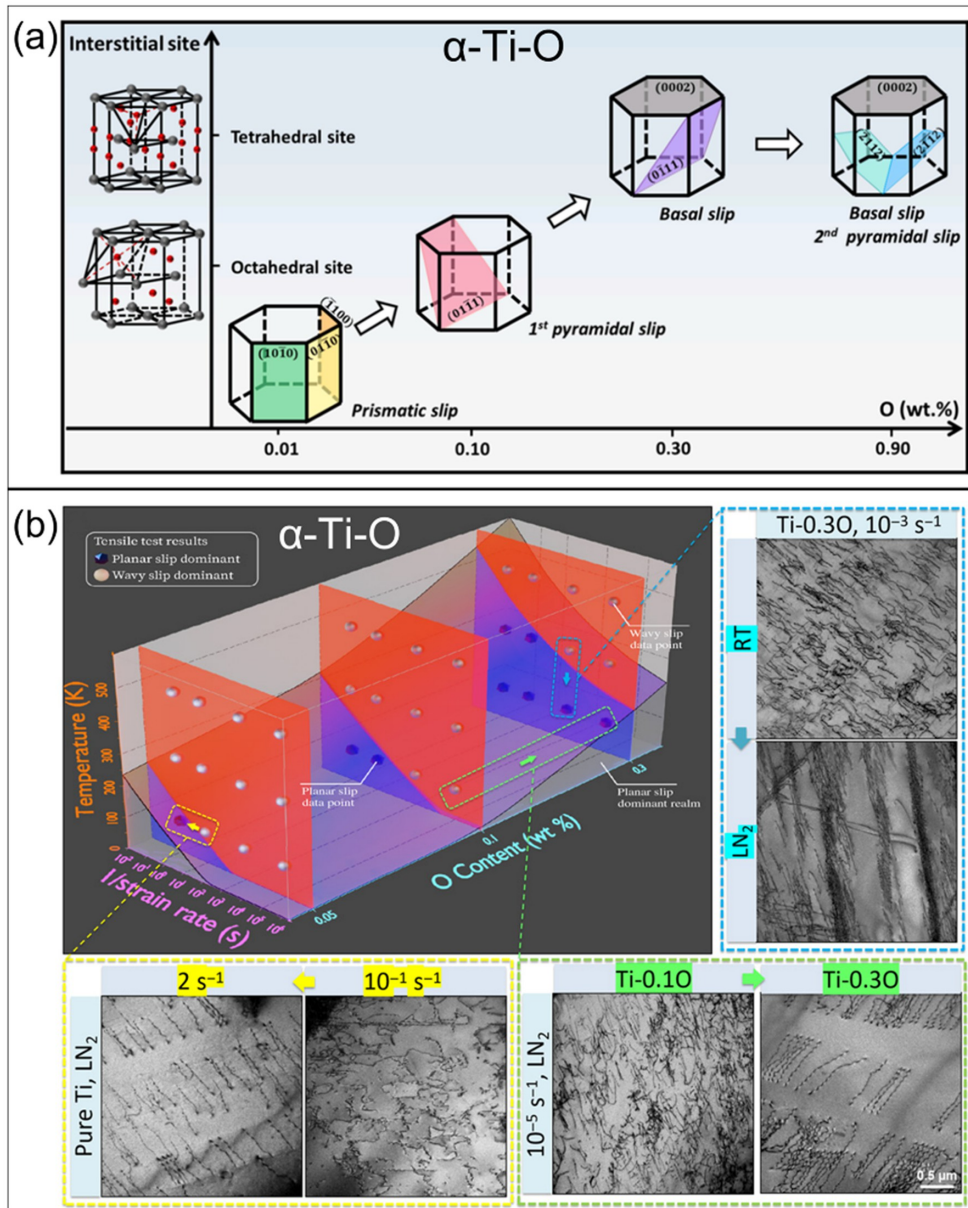


Figure 3.

Oxygen-induced evolution of slip behavior in α -Ti. (a) Transition of the dominant slip mode in oxygen-gradient pure Ti, from prismatic to pyramidal and basal slip with increasing oxygen content [31]. (b) Combined effect of temperature, strain rate, and oxygen content on the wavy slip to planar slip transition in Ti-O alloys [37].

While strain in the α phase is accommodated mainly by twinning and slip, oxygen in the metastable β phase acts primarily on the SIMT and deformation twinning. The oxygen-dislocation interaction discussed above is also relevant here. Zhang et al. [44] found that this interaction redistributes the stress field of the edge dislocation core, inducing the simultaneous nucleation of multiple martensite variants along oxygen-rich dislocations and forming nanotwins and nanomartensite in

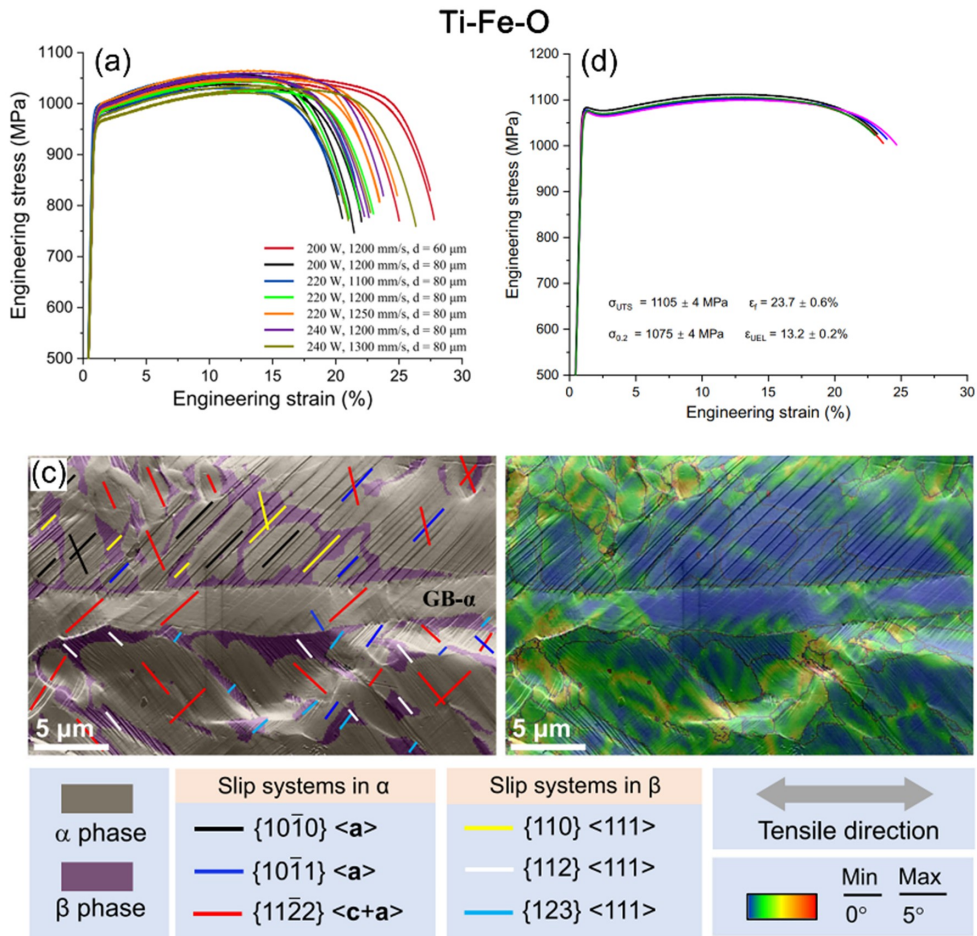
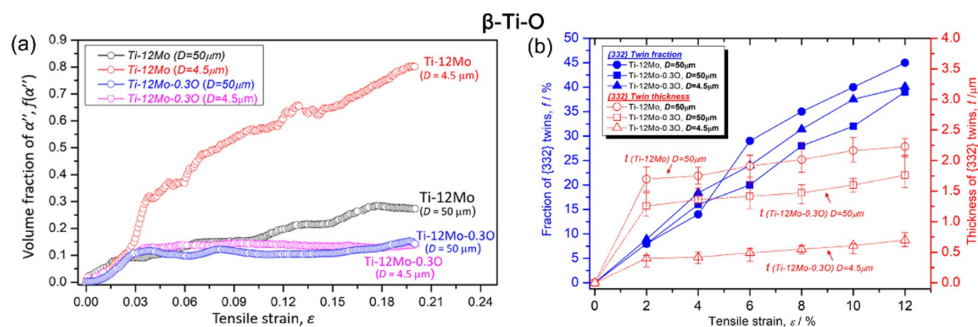


Figure 4. Oxygen-mediated $\langle c + a \rangle$ slip and slip transfer across α/β interfaces in Ti-O-Fe alloys [23]. Room-temperature tensile curves of (a) Ti-0.45O-4Fe and (b) Ti-0.50O-5Fe prepared by L-PBF after annealing at 800°C for 1 h. (c) In-situ SEM/EBSD analyses showing $\{1122\} \langle c + a \rangle$ slip dominant and slip transfer active across most α/β interfaces.

ultrahigh-strength titanium alloys. Beyond this local effect, oxygen suppresses the β - α transformation in the metastable β phase overall. First-principles calculations show strong repulsion between interstitial oxygen and substitutional Nb in the β matrix, which determines the energetically preferred oxygen sites in the β lattice [45]. Through this site preference, oxygen increases the barrier to the β - α transformation and stabilizes α martensite, as confirmed by studies of phase transformation and shape memory in Ti-Nb-O [46–49]. The SIMT and the competition among deformation modes in metastable β titanium alloys have been studied extensively as a function of β -phase stability [50–54].

In metastable β -Ti, grain refinement can anomalously cause softening instead of strengthening, and oxygen eliminates this anomaly by acting on both the SIMT and twinning. Chong et al. [39] found that refining the grains of oxygen-free Ti-12Mo did not strengthen the alloy but instead produced Lüders deformation and


Figure 5.

Oxygen suppresses stress-induced α'' martensite and refines {332} twins in Ti-12Mo. (a) Volume fraction of stress-induced α'' with tensile strain for Ti-12Mo and Ti-12Mo-0.3O at different grain sizes, showing oxygen suppressing α'' formation. (b) Fraction and thickness of {332} twins with tensile strain, showing oxygen reducing the twin thickness. Source: Adapted from the literature by Chong et al. [38].

a drop in strength, because the fine grains promoted extensive stress-induced α'' martensite, which is softer than the β matrix (**Figure 5a**). Adding 0.3 wt.% oxygen instead reduced the α'' fraction and eliminated the softening. In contrast, first-principles calculations showed that 0.3 wt.% oxygen raised the β - α'' transformation barrier from 2.0 to 4.26 meV/atom, strongly suppressing the SIMT (**Figure 5a**). At the same time, oxygen segregated at the {332} $\langle 113 \rangle$ twin boundaries, reaching 1.79 at.% compared with 0.92 at.% in the matrix, increasing the twin migration barrier, inhibiting twin thickening, and promoting new twin nucleation. The twins were thereby refined and the twin boundary density increased, giving a dynamic Hall-Petch strengthening (**Figure 5b**) [39]. Huang et al. [55] found that increasing the oxygen content from 0.04 to 0.12 wt.% caused the {112} $\langle 111 \rangle$ and {455} $\langle 522 \rangle$ twins to disappear and left only the {332} $\langle 113 \rangle$ twins. The interaction of oxygen content with {332} $\langle 113 \rangle$ twinning and the isothermal ω phase has also been examined systematically in Ti-15Mo [56].

Oxygen can also stabilize metastable phases that are usually detrimental, such as the ω phase. Chou et al. [57, 58] showed that ω stabilized by oxygen changes from embrittling to strengthening once sufficiently coarsened. The volume fraction of the ω phase increased with oxygen content (**Figure 6a, b**). When Ti-20Nb was aged at 450°C to form ω particles of 50 to 120 nm, oxygen partitioned strongly into the ω phase, reaching about 6 at.% compared with only 0.3 at.% in the β phase (**Figure 6c, d**) [58]. But the effect of oxygen on the ω phase does not increase monotonically with oxygen content. At intermediate oxygen contents, oxygen stabilizes the ω phase and delays the ω - α transformation, whereas at high oxygen contents, the α phase nucleates rapidly again [57]. Whether the ω phase strengthens or embrittles the alloy depends on the partitioning of oxygen into it, which is controlled by the aging temperature rather than by the total oxygen content alone. A similar role of interstitial elements has also drawn attention in refractory complex concentrated alloys [59].

Oxygen-induced spinodal decomposition is another strengthening route. Silverstein et al. [60] treated Ti-50Nb in an oxygen atmosphere at 800°C and introduced about 1 at.% oxygen, decomposing the uniform β phase into Ti-rich and Nb-rich regions with wavelengths of 40 to 100 nm (**Figure 6e, f**). The

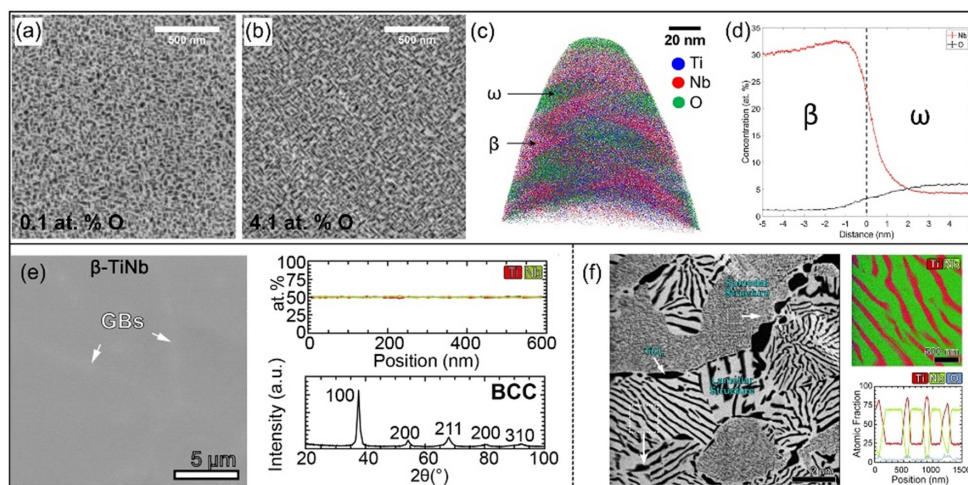


Figure 6. Oxygen-stabilized metastable phases for strengthening. (a, b) ω -phase distribution after aging at 0.1 at.% O and 4.1 at.% O, showing the ω fraction increasing with oxygen content. (c, d) Atom probe tomography and concentration profiles showing the oxygen-enriched and Nb-depleted ω phase relative to the β matrix [57]. (e) Initial β -TiNb with homogeneous composition and BCC structure. (f) Spinodal and lamellar structures with Ti-Nb composition modulation after oxygen-induced decomposition. [59].

Ti-rich regions evolved along the Burgers path from BCC through orthorhombic O' and α'' to the HCP α phase [60]. The strength increased with decreasing wavelength, reaching about 2.43 GPa at wavelengths below 100 nm [60]. Oxygen stabilizes the α phase and diffuses rapidly, and it can also be used to engineer α precipitates of multiple morphologies. Zhang et al. obtained three types of secondary α in Ti-4.1Al-2.5Zr-2.5Cr-6.8Mo-0.17O-0.10 N, namely grain boundary α , grain boundary sideplate α , and intragranular Widmanstätten α . The sideplate α linked the grain boundary α to the intragranular α and eliminated the precipitate-free zone, giving the aged alloy a yield strength of 1580 MPa and an elongation of 8.2% [61].

In summary, the strengthening effect of oxygen extends well beyond solid solution strengthening. Oxygen can pin dislocation cores, regulate the competition between twinning and slip, suppress the SIMT, stabilize the ω phase, and induce spinodal decomposition. These mechanisms often operate in parallel within the same alloy, and their combination depends on the form and spatial distribution of oxygen. This relationship between oxygen distribution and strengthening also provides the foundation for the multiscale heterostructure design.

4. Damping mechanisms of oxygen in titanium alloys

Besides strengthening, solid-solution oxygen can also improve the damping capacity of β -Ti, giving the alloy both load-bearing capacity and vibration damping. This damping comes from the anelastic relaxation of interstitial oxygen atoms, and its energy-dissipation mechanism differs from that in conventional damping alloys. Damping alloys dissipate vibrational energy as heat through the motion of

internal defects under cyclic stress. According to the dominant defect types responsible for this dissipation, damping alloys are classified into planar-defect, line-defect, and point-defect types [62]. The ferromagnetic, multiphase, and twin types dissipate energy through magnetic domain walls, phase boundaries, and twin boundaries, respectively, whereas Mg-based and Fe–Mn alloys dissipate energy through dislocation motion [62, 63]. However, both the planar-defect and line-defect types suffer from an inherent conflict. High damping requires mobile defects, whereas high strength requires defect pinning, so the two are difficult to combine. In addition, such mobile defects are unstable at high temperatures, and the damping decreases readily [62]. By contrast, point-defect damping comes from the thermally activated relaxation of interstitial atoms rather than the motion of macroscopic defects, thereby overcoming the strength-damping trade-off. Snoek-type damping is a typical example [64].

The Snoek effect was first observed by Snoek in α -Fe and originates from the stress-directed jumping of interstitial atoms, as shown in **Figure 7a** [65]. Oxygen atoms in β -Ti occupy the octahedral interstices and create elastic dipoles oriented along the $\langle 100 \rangle$ directions. Without applied stress, the three sets of sites have the same energy. Stress makes them unequal, and oxygen atoms jump between sites to reach a new equilibrium. When the relaxation time approaches the loading period, the strain is delayed relative to the stress, producing a Debye peak in the internal friction spectrum [64]. The peak temperature is determined by the activation energy for jumping and the measurement frequency, while the peak height increases with the dissolved oxygen concentration. The Snoek relaxation in group V solid solutions such as Ta–O and Nb–O was investigated early, and the peak temperatures, activation energies, and oxygen diffusion behavior are clear [66, 67]. However, the low strength of these alloys limits their use as load-bearing components. β -Ti is single-phase BCC at room temperature and has a high oxygen solubility, which makes it the first structural material used for Snoek damping. Yin et al. [9] dissolved a high oxygen content into Ti–25 Nb–O in 2006 and increased the damping peak from about 0.01 to 0.09, achieving Snoek-type high damping in a structural alloy for the first time and establishing the concept of high-damping β -Ti alloys with high oxygen content, **Figure 7b**. Subsequent research on the Ti–Nb–O system has focused on two main aspects: the mechanism of its high damping and how to control it effectively.

The broadening mechanism of the damping peak has been clarified. The measured Snoek peak is much broader than a single Debye peak because oxygen atoms occupy sites with different nearest-neighbor configurations [24]. Yu and Yin [25] further confirmed that oxygen prefers interstitial sites with Ti nearest neighbors, where its energy is lower and the configuration is more stable. In fact, the multiple peaks of the Snoek relaxation had been observed in experiments well before these analyses. Ahmad et al. [67] identified several interaction peaks in Nb–O, and Almeida and Niemeyer [68, 69] separated binary damping peaks such as Nb–O and Ti–O in the internal friction spectra of Nb–Ti–O and measured their activation energies (**Figure 7c**). The statistical-mechanics model of Yu, Yin, and Ping [24] provided a theoretical explanation for these experimental observations, and Ren et al. [70] later extended it to the Nb–V–O system (**Figure 7d**). Beyond the type of nearest neighbors, the interaction between interstitial atoms also changes the peak shape, as Weller et al. [71] confirmed the existence of oxygen–oxygen pairs in Ta–O solid solutions through internal friction measurements. First-principles

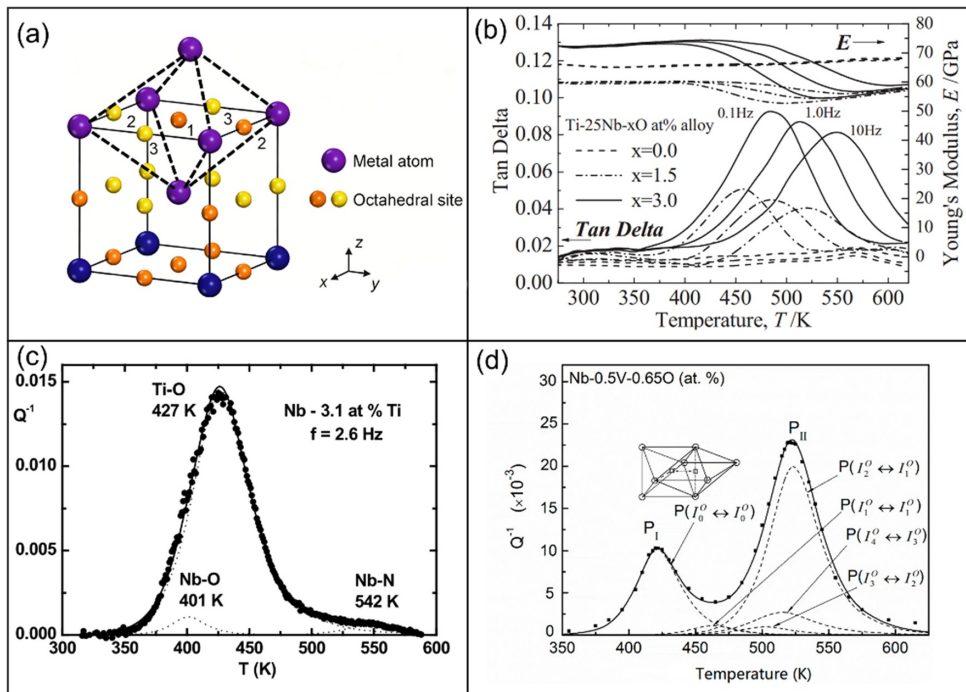


Figure 7. Snoek relaxation in BCC alloys. (a) Schematic diagram of the Snoek relaxation. (b) $\tan \delta$ and Young's modulus of Ti-25Nb-xO with temperature at different frequencies [9]. (c) Internal friction spectrum of Nb-3.1Ti, separated into Ti-O, Nb-O, and Nb-N peaks [67]. (d) Internal friction spectrum of Nb-0.5V-0.65O separated into multiple peaks [68].

calculations confirm this conclusion from energy considerations, showing that the strong repulsion between interstitial oxygen and substitutional Nb promotes oxygen clustering in Ti-rich neighboring environments [45, 72].

The damping of Ti-Nb-O is affected by oxygen content, texture, alloying elements and processing, and these effects have been gradually clarified. Yin et al. [73] found that the damping peak height of Ti-Nb-O increases with oxygen concentration. In strongly (112)-textured Ti-25.2Nb-0.6O, the Snoek relaxation along the rolling direction showed a peak temperature of 473.5 K and an activation energy of 1.51 eV. The damping varied linearly with the mean orientation parameter, giving a shape factor δ_λ of about 0.42 [26]. The effect of alloying elements is reflected mainly in the shape factor δ_λ and the self-induced ordering temperature T_c . Lu et al. [27] found that alloying elements alter Md of the system, so that T_c increases with Md while δ_λ increases as Md decreases, and that alloys containing Al or Sn show the highest damping. In Ti-36Nb-Ta-Zr-O, the interaction between Zr and O is stronger than that between Ta or Nb and O, which increases the activation energy and shifts the peak to a higher temperature [74, 75]. The damping can also be tailored through processing. Lu et al. [76] formed oxygen solid-solution zones about 120 μm and 210 μm thick on Ti-15Mo and Ti-40Mo by surface oxidation, which increased the peak height, peak temperature, and peak width. The damping of the Ti-Nb-O system can thus be controlled systematically at both the fundamental and engineering levels.

This understanding of the Ti–Nb–O system was subsequently extended to high-entropy alloys with more complex compositions to broaden the damping temperature range. The strong lattice distortion and high oxygen migration barriers in high-entropy alloys are expected to shift the damping peak to higher temperatures. Lei et al. added 2 at.% oxygen to $(\text{Ta}_{0.5}\text{Nb}_{0.5}\text{HfZrTi})_{98}\text{O}_2$ and increased the peak temperature to about 747 K. The chemical short-range order attracted some oxygen atoms to form OOCs, which enhanced both strength and ductility and produced an additional damping peak in the low-temperature region, broadening the damping temperature range [17, 18]. Wang et al. [77] distinguished two additional damping peaks in O-doped $\text{NbTiV}_{0.5}\text{Zr}$, corresponding to solid-solution oxygen and locally ordered oxygen, with a distribution much broader than in conventional BCC metals. Wu et al. [78] found that increasing the configurational entropy modulates the relaxation and produces damping peaks in different temperature regions for different compositions. Even in sintered β -type Ti–Nb, the height of the damping peak from interstitial oxygen is related to the stability of the metastable β phase [79]. The common effect of increasing compositional complexity is to further broaden the distribution of oxygen migration barriers.

Recently, research has focused on how to achieve both high damping and high strength through multiscale structural design. In Ti–36Nb–0.9O, Gao et al. [80] designed heterostructures of interleaved $(\alpha + \beta)$ and single- β bands (**Figure 8a**). Spinodal decomposition in the oxygen-rich β regions then formed Nb-depleted and Nb-rich nanodomains about 10 nm in size [80]. The nanoscale composition fluctuations reduced the oxygen diffusion barrier and enhanced the Snoek relaxation in these domains, giving the alloy a damping peak of $\tan \delta = 0.104$ at 506 K while maintaining a room-temperature yield strength of 1,090 MPa and an elongation of 23% (**Figure 8b–e**) [9, 18, 76, 81–96]. This damping peak consisted of Nb–O and Ti–O peaks together with an anomalously broadened Nb–O–O peak contributed by O–O pairs formed during spinodal decomposition [80]. **Table 1** summarizes the yield strength, ductility and damping capacity of the oxygen-containing titanium alloys discussed above. The evolution from Ti–Nb–O to multiprincipal element alloys and then to combined structure-damping designs shows that the key lies in how oxygen is distributed across different length scales. This represents a promising direction for developing strong and high-damping titanium alloys.

5. Multiscale heterostructure design and conclusions

The above three sections described the configurations of oxygen in titanium alloys and how they affect strengthening and damping. The effect of oxygen on properties depends not only on its content but also on its spatial distribution across the multiscale structure. At the atomic scale, the interstitial site that oxygen occupies and its surrounding atoms determine solid-solution strengthening and Snoek relaxation. Ordered oxygen complexes, spinodal domains, and oxygen-stabilized metastable phases then control the deformation path at the nanoscale. At the micron scale, the segregation of oxygen at phase, grain, and twin boundaries determines interfacial behavior and fracture.

This approach is consistent with the design principles of heterostructured materials. Heterostructures, which contain soft and hard regions with substantially different mechanical properties, accumulate geometrically necessary dislocations at

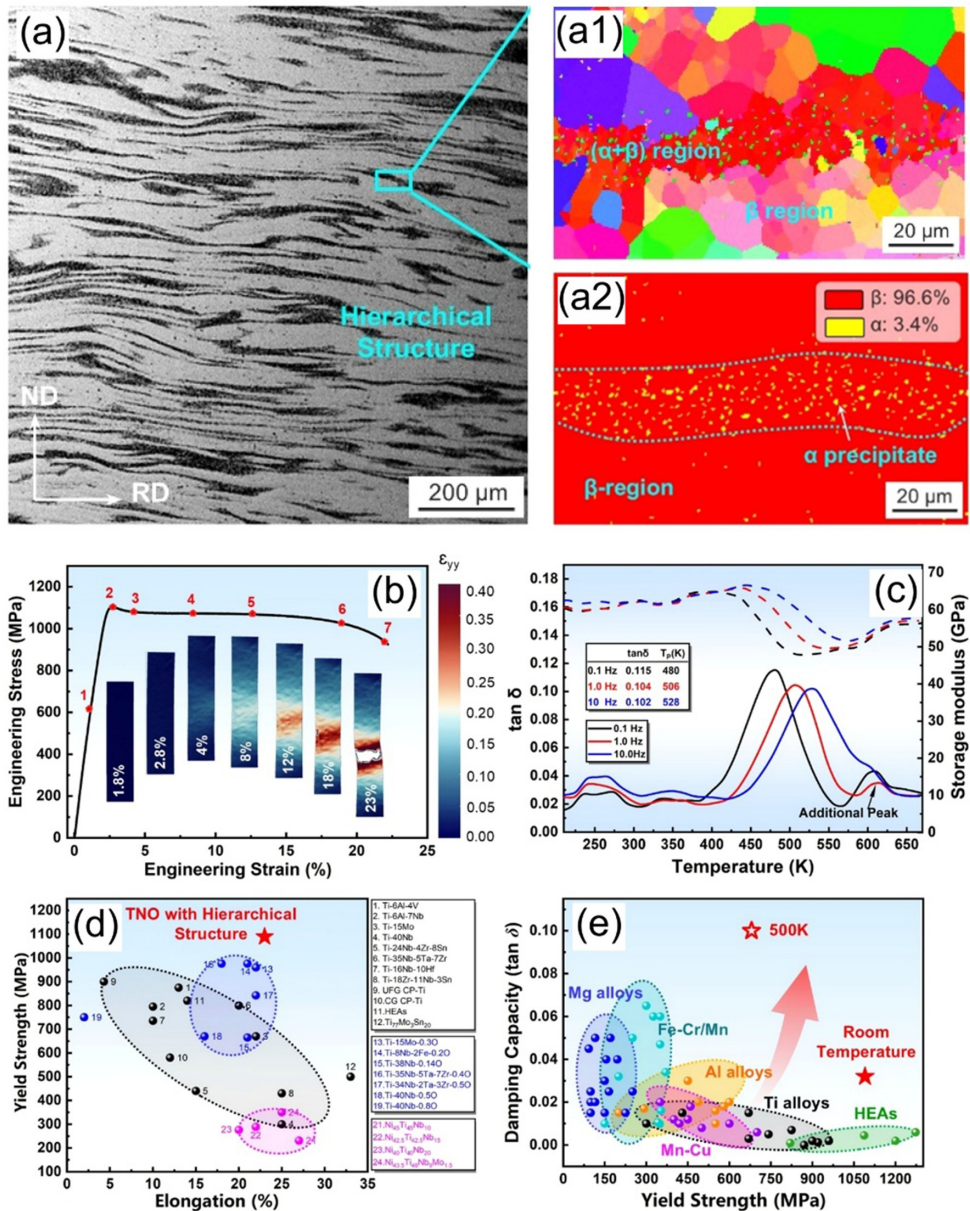


Figure 8. Strength-damping synergy in Ti-36Nb-0.90 through oxygen-induced spinodal decomposition [79]. (a-a2) Hierarchical structure containing (α + β) and single-β bands. (b) Engineering stress-strain curve. (c) tan δ with temperature at different frequencies. (d) Yield strength and elongation compared with reported titanium alloys. (e) Yield strength and damping capacity compared with conventional damping alloys [9, 18, 76, 81-96].

the interfaces during deformation and generate back stress, producing an excellent combination of strength and toughness [97, 98]. Oxygen provides an effective way to create such heterogeneity. Oxygen partitions between the α and β phases and promotes spinodal decomposition within the β matrix, forming nanodomains that differ in composition and hardness. Gradient oxygen doping can produce hardness

Alloy	Yield strength (MPa)	Elongation (%)	Damping	Ref.
Ti-0.34O-3.25Fe	1,194	~ 22	*	[22]
Ti-0.45O-4Fe	≥ 980	≥ 27	*	[23]
Ti-0.5O-5Fe	≥ 1,075	≥ 23	*	[23]
Ti-12Mo-0.3O	826	~ 24	*	[39]
Ti-4.1Al-2.5Zr-2.5Cr-6.8Mo-0.17O-0.10 N	~ 1,580	~ 8.2	*	[61]
Ti-25Nb-1.5O	~ 650	~ 17	0.05	[9]
(Ta _{0.5} Nb _{0.5} HfZrTi) ₉₈ O ₂	~ 1,200	~ 22	0.02	[18]
Ti-36Nb-0.9O	1090	23	0.104	[79]
Ti-Nb-1.7O	*	*	0.0258	[27]
Ti-Nb-1Al-1.7O	*	*	0.0409	[27]
Ti-Nb-2Al-1.7O	*	*	0.038	[27]
Ti-Nb-1Sn-1.7O	*	*	0.0371	[27]
Ti-Nb-2Sn-1.7O	*	*	0.0304	[27]
Ti-Nb-2Cr-1.7O	*	*	0.027	[27]
Ti-Nb-2Mn-1.7O	*	*	0.0244	[27]
Ti-15Mo-0.105O	*	*	0.0024	[76]
Ti-15Mo-0.19O	*	*	0.0023	[76]
Ti-40Mo-0.04O	*	*	0.0021	[76]
Ti-40Mo-0.33O	*	*	0.0020	[76]

Table 1.

Yield strength, ductility, and damping capacity of the oxygen-containing titanium alloys discussed in this chapter.

gradients through the thickness, whereas directional solidification and AM can create layered microstructures with controllable orientation [22, 23, 31]. Gao et al. [80] demonstrated that oxygen-induced spinodal decomposition can provide both strengthening and damping within the same microstructure, a typical example of chemical heterostructure design.

Combining oxygen distribution with heterostructure design still faces several challenges. The multiscale distribution of oxygen still cannot be predicted quantitatively from composition and thermal history. Oxygen atoms are mobile in the temperature range where the Snoek peak appears, which raises the question of whether these oxygen heterostructures remain stable during long-term service at elevated temperatures. Their thermal stability has not been examined, and it is not yet clear how the damping behavior evolves after prolonged exposure. The long-term stability of these oxygen distributions under cyclic loading also remains unknown. Fatigue studies are needed to find out whether the damping drops over time. And the effects of oxygen on strengthening, damping, fatigue, and corrosion are hard to optimize at the same time. Overcoming these challenges will require better integration of oxygen-behavior modeling, atomic-scale characterization, and AM.

In summary, oxygen has evolved from a harmful impurity under strict control into an alloying element that can be actively used across multiple length scales.

Multiscale heterostructure design based on oxygen distribution is therefore a promising way to develop titanium alloys that combine high strength, high damping, and low cost. Such alloys are attractive for applications that require both load-bearing capacity and vibration damping, ranging from aerospace structures to precision instruments.

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Author details

X. G. Wang, L. Y. Sun and F. X. Yin*
Shandong Key Laboratory of Advanced Structural Materials Genome Engineering,
Yantai University, Yantai, PR China

*Address all correspondence to: yinfuxing@ytu.edu.cn

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