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Perspective

Metastability Engineering in Titanium Alloys Enables Advanced Structural/Functional Properties

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Abstract

The concept of "metastability engineering" has been successfully used in metallic structural materials to enhance mechanical properties. In the present perspective, the authors propose that the metastability engineering strategy can be introduced to titanium (Ti) alloys by destabilizing the β phase and taking advantage of metastable phases mediated phase transformation and mechanical twinning. The utilization of metastability engineering strategy and associated structural and functional properties of Ti alloys are outlined.

Key words: Titanium alloy; Metastability engineering; Mechanical properties; Elasticity.

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Titanium (Ti) alloys have found widespread applications ranging from aerospace to biomedical fields owing to their diverse phase transformations, microstructures, and associated mechanical properties across a wide spectrum. Exploring the upper limit of mechanical properties has been a key issue for Ti society in recent decades. For regulating microstructures and mechanical properties, what matters is to manipulate α phase (hexagonal close-packed, HCP) precipitation for strengthening and tailor β phase (body-centered cubic, BCC) stability to enable desired deformation mechanisms. Fine α precipitation renders high strength that is desirable for structural applications,[1,2] and β phase stability dependent reversibly thermoelastic martensitic transformation imparts unique functional properties including shape memory effect (SME) and superelasticity (SE).[3,4] Except for equilibrium α and β phases, the metastable ω phase, O' phase, and martensite play a key role in microstructure evolution and mechanical properties of Ti alloys in either a direct or indirect way. Directly, they act as strengthening phases. The indirect effects are manifested as metastable phases mediated formation of fine and dense α precipitates and deformation mechanisms under external stress. The presence of various metastable phases expands the mechanical properties spectrum of Ti alloys.

Energetically stable carbon can transform into metastable diamond under certain conditions, which well illustrates the significance of the concept of "metastability engineering".[5] Recently, the metastability engineering strategy has been successfully employed in steels[6] and high entropy alloys[7,8] to obtain synergetic high strength and ductility. The underlying idea of applying metastability engineering is to fine-tune the chemical composition to destabilize the austenitic phase to promote stress-induced martensitic transformation (SIMT), which in return enhances the strength and ductility simultaneously through the transformation-induced plasticity (TRIP) effect. As an important category of metallic materials that possess martensitic phase transformation, we demonstrate here that the metastability engineering strategy can also be adopted to Ti alloys to not only enhance strength-ductility synergy but also render promising functional properties via destabilizing the β phase and taking usage of metastable phases, as schematically illustrated in Fig. 1.

The current near/metastable β-type high-strength Ti alloys suffer from drawbacks of limited ductility and strain hardening ability owing to dislocation-dominated plasticity. By decreasing stability of the β phase, the deformation mechanism of β-Ti alloys changes from dislocation slip to deformation twinning and finally stress-induced martensitic transformation, which inspired the development of a new generation of β-Ti alloys showing twinning-induced plasticity (TWIP) and TRIP effects.[9–12] TWIP/TRIP Ti alloys exhibit a superior combination of ultimate tensile strength and uniform ductility. Nevertheless, the metastable nature and BCC asymmetry of the β phase lead to low critical resolved shear stress (CRSS) required to initiate twinning and stress-induced martensitic transformation, thus low incipient yield strength that is usually lower than 600 MPa, limiting their practical applications.[13] Besides, easy activation of reorientation of stress-induced orthorhombic α" martensite as well as the intrinsically soft nature of α" phase and twinned β structures resulted in strain hardening rate typically not exceeding 2000 MPa.[12]

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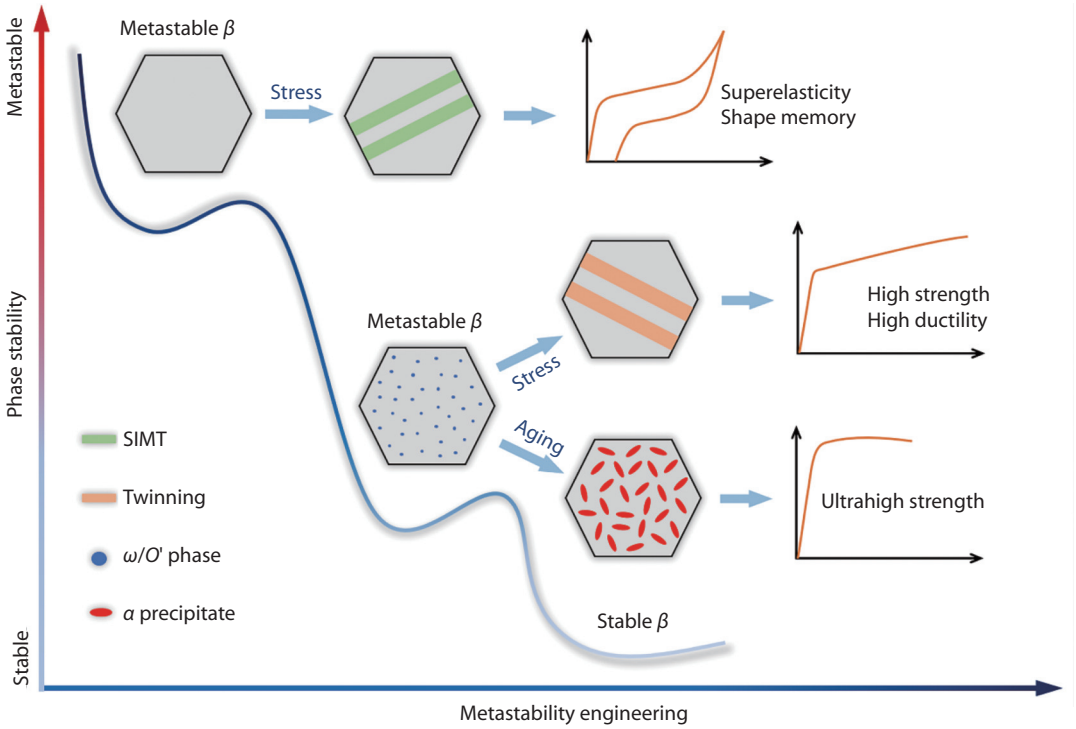

Fig. 1 Schematic illustration of structural/functional properties enabled by metastability engineering in Ti alloys.

We propose that by taking advantage of stress-induced reversible ω phase transformation coupling with multiple $\{332\}_\beta$ and $\{112\}_\beta$ twinning systems, a relatively high yield strength of 670 MPa and ultrahigh fracture elongation of 52% were achieved in near β-Ti alloy Ti-6Cr-4Mo-2Al-2Sn-1Zr (wt.%, Ti-64221).[14] Furthermore, unprecedented high yield strength of 870 MPa along with excellent fracture elongation of 41% and high strain hardening rate of 2500 MPa were acquired in a metastable β-Ti alloy Ti-4Mo-3Cr-1Fe (wt.%, Ti-431) showing stress-induced hierarchical $\{112\}_\beta$ twinning structures promoted by reversion of athermal ω phase.[11] The superb combination of mechanical properties of TWIP Ti-64221 and Ti-431 alloys are highly related to the stress-induced reversion of the athermal ω phase. The brittle ω phase typically can not bear plastic deformation. However, the detrimental effect of the ω phase on ductility of Ti alloys can be eliminated by promoting stress-induced reversion of ω to β phase, which is highly related to the lattice instability under applied external stress. Lattice instability of metastable β phase promotes the formation of energetically unfavorable {332} twinning as compared to {112} twinning in BCC metals[15], which led to low yield strength of TWIP Ti alloys. It is thus challenging to design TWIP Ti alloy with solo $\{112\}_\beta$ twinning operated with applied stress. The activation of $\{112\}_\beta$ twinning is related to the reverse transformation from ω to the parent β phase.[16,17] With the aid of stress-induced reversion of ω phase, $\{112\}_\beta$ twinning system with high CRSS is activated within a wide strain range, contributing to high yield strength and uniform elongation.[11] ω reversion assisted activation of $\{112\}_\beta$ twinning sheds light on the development of TWIP Ti alloys with an excellent combination of mechanical properties. Further destabilizing the β phase leads to the activation of stress-induced β to α' martensitic transformation. α' martensite with HCP crystallographic symmetry provides greater capability to impart strengthening to Ti alloys than orthorhombic α" martensite and $\{332\}_\beta$ twinning, hence a Ti-15Nb-5Zr-4Sn-1Fe alloy (wt.%, Ti-15541) showing stress-induced β to α' martensitic transformation was developed.[12] The Ti-15541 alloy exhibited an ultrahigh strain hardening rate of 6100 MPa tripling the conventional TRIP/TWIP Ti alloys, which guides the design of a new class of TRIP/TWIP Ti alloys with superior strain hardening ability. Stress-induced β to α' martensitic transformation is also highly related to the reversion of the athermal ω phase[12] and another metastable phase O'.[18] The reversion of the ω phase holds a new avenue for developing advanced TRIP/TWIP Ti alloys, and this needs fine-tuning of the β phase stability.

Another approach employing metastability engineering for developing high-strength Ti alloys is to utilize metastable phases as the precursor to promote the precipitation of dense and fine α strengthening phase. Traditional high-strength near/metastable β-type Ti alloys exhibit not only limited ductility but also unsatisfied quenching permeability partly ascribed to the formation of metastable ω phase and its assisting role in precipitating α phase during quenching process and/or heating to targeted aging temperature. Previous reports documented that the precipitation of acicular α during aging was assisted by decomposition of the ω phase.[19,20] Therefore, it is possible to fabricate strong and ductile Ti alloys on a large scale by controlling the precipitation of metastable phases and regulating their phase transformation sequence. Our recent results found that spinodal decomposition assisted phase separation[21,22] and metastable O' phase[23–25] act as homogeneous nucleation sites for the formation of spatially uniform and dense distribution of fine α phase, thus leading to high strength. Especially, metastable phase O' is more thermally stable within a wider temperature range than the ω counterpart, serving as a complementary

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way for microstructure engineering of high-strength β-Ti alloys.[24–26] In summary, by destabilizing β phase stability and taking usage of metastable phases as a medium to promote TWIP and TRIP effects or as the precursor to assist α precipitation, high-strength or ultrahigh-strength Ti alloys with an excellent combination of mechanical properties suitable for structural applications can be developed.

Reversible first-order martensitic transformation results in shape memory and superelasticity in Ti alloys. However, the first-order nature of the martensitic transformation results in stress/strain hysteresis and temperature dependence of superelasticity. By completely suppressing the stress-induced martensitic transformation while keeping the β phase in a metastable state, or changing it to continuous structure transition, i.e., from first-order long-range martensitic transformation to short-range ordering (nanodomain), superior elasticity including low Young's modulus, high elasticity, and superelasticity over a wide temperature range can be tailored.

The rapid growth of surgical bio-implant materials calls for elastic Ti alloys with low Young's modulus and high strength for addressing the "stress shielding" problem. The reduction of Young's modulus is usually accompanied by a decrease in β phase stability, which resulted in easy activation of stress-induced martensitic transformation and consequently low yield strength. We illustrate that by destabilizing the β phase stability as low as possible while impeding the stress-induced martensitic transformation by high-density dislocations and grain boundaries, simultaneous low Young's modulus and high yield strength can be obtained.[27] This is realized by severe cold deformation to introduce high-density defects into the elaborately designed β matrix with extremely low phase stability and subsequent low-temperature short-time annealing. Accordingly, Ti-33Nb-4Sn (wt.%) alloy with ultralow Young's modulus (36 GPa, versus ~30 GPa for human bone) and high ultimate tensile strength (853 MPa) was fabricated.[28] The sluggish stress-induced martensitic transformation and low β phase stability also led to nonlinear elastic deformation with a huge elastic strain of ~3.0%.[27] Similarly, an excellent combination of low Young's modulus and high yield strength can be obtained in (α+β) dual-phase Ti alloys with metastable β matrix hardened by ultrafine equiaxed α phase.[29–31] The core of this strategy is to design a metastable β matrix to provide low modulus while totally or partially suppressing the stress-induced martensitic transformation by high-density defects and ultrafine α phase. In this way, the extremely low β phase stability (below the critical level required to stabilize the β phase at room temperature) helps further reduce Young's modulus, and the high yield strength is augmented by high-density dislocations, grain boundaries, and ultrafine equiaxed α phase.

The transition of first-order martensitic transformation to nanodomain brings about novel functional properties, such as nearly hysteresis-free superelasticity[32] and superelasticity, invariant elastic modulus (Elinvar), and zero thermal expansion coefficient (Invar) over a wide temperature range.[3,33–35] These unique properties originate from the occurrence of continuous and gradual structure transition from body-centered cubic β phase to confined growth of orthorhombic nanodomain (O') without macroscopic phase transition, i.e., strain glass transition, over a wide temperature range. Based on the framework of strain glass theory, doping point defects like Zr, Sn, and interstitial oxygen and severe plastic deformation are beneficial for the successive formation of nanodomain in Ti alloys. Nevertheless, the underlying thermal-dynamic and micromechanical mechanisms associated with the formation of nanodomain await further study.

Metastability of β phase opens new opportunities for engineering microstructures and mechanical properties of Ti alloys. Destabilizing β phase and metastable phases ω and O' involved metastability engineering strategy helps the design and fabrication of novel Ti alloys with promising structural and functional properties. Despite the impressive achievements made by metastability engineering, future effort is still required to in-depth understand the basic mechanisms responsible for the metastable phases driven/mediated mechanical response, hence guiding the application of metastability engineering strategy and improvement of mechanical performance.

(1) ω reversion mediated TWIP/TRIP Ti alloys. An in-depth understanding of chemical composition (β phase stability) dependent and atomic-level mechanism of the ω mediated activation of $\{112\}_\beta$ twinning, as well as *in-situ* characterization of microstructure evolution during static/dynamic loading need further investigation. The clarification of these issues helps the development of such kind of TWIP/TRIP Ti alloys with the aid of classic alloy design and computational methods. Accordingly, the yield strength and dynamic mechanical properties can be further enhanced by solid-solution strengthening and rational regulation of the activation sequence of ω reversion and $\{112\}_\beta$ twinning.

(2) Stress-induced α' martensitic transformation. Stress-induced β to α' martensitic transformation is rarely concerned due to the easy activation of stress-induced α" martensitic transformation and its resultant shape memory and superelasticity in metastable β-Ti alloys. The underlying chemical composition design criteria, crystallographic mechanism, microstructure evolution, and associated mechanical behaviors of stress-induced α' martensitic transformation remain unclear. Further investigation concerning these issues constitutes an original result for developing a new class of TRIP/TWIP Ti alloys or even shape memory Ti alloys based on β to α' martensitic transformation.

(3) Nanodomain (O' phase). Nanodomain has earned increasing interest since the came out of gum metal. It demonstrates notable benefits to Ti alloys, not only in retarding long-range α" martensitic transformation and assisting fine α precipitation but also in inducing martensitic α' and α", as well as assisting $\{332\}_\beta$ twinning with applied external stress. It is of great significance to systematically investigate the formation mechanism of nanodomain and correlated mechanical properties in order to obtain gum metal-like multifunctional Ti alloys.

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Conflict of interest

The authors declare no conflict of interest.

Author contributions

The manuscript was written by Yu Fu under the conception of Wenlong Xiao. The final version of the present paper was reviewed by Wenlong Xiao, Xinqing Zhao, and Chaoli Ma and proved by all the authors.

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