Hierarchical nano-martensite-engineered a low-cost ultra-strong and ductile titanium alloy

Due to the low thermal stability of crystallographic boundaries, the grain boundary engineering (GBE) manifests some limits to the fineness and types of microstructures achievable, while unique chemical boundary engineering (CBE) enables us to create a metallic material with an ultrafine hierarchically heterogeneous microstructure for enhancing the mechanical properties of materials. Here, using a low cost metastable Ti-2.8Cr-4.5Zr-5.2Al (wt.%) alloy as a model material, we create a high density of chemical boundaries (CBs) through the significant diffusion mismatch between Cr and Al alloying elements to architecture hierarchical nano-martensites with an average thickness of ~20 nm. For this metastable titanium alloy, the significantly enhanced yield strength originates from dense nano-martensitic interface strengthening, meanwhile the large ductility is attributed to the multi-stage strain hardening of hierarchical 3D $\alpha'$/$\beta$ lamellae assisted by equiaxed primary $\alpha$ ($\alpha_p$) nodules. The hierarchical nano-martensite engineering strategy confers our alloy a desired combination of strength and ductility, which can potentially be applied to many transformable alloys, and reveal a new target in microstructural design for ultrastrong-yet-ductile structural materials.

Martensitic phase transformation in metastable alloys$^{1-4}$, such as titanium (Ti) alloys$^{5-6}$, steels$^{7-9}$ and multicomponent alloys$^{10-11}$, could achieve one even both of following key benefits: interface hardening due to a dual-phase microstructure (resulting from reduced thermal stability of the high-temperature phase) and transformation-induced hardening (resulting from the reduced mechanical stability of the room-temperature phase)$^{12}$. The stress-driven martensitic transformation in alloys, often rendering low yield strength ($\sigma_y$)$^{13-17}$, enables notable enhancement of ultimate tensile strength ($\sigma_{UTS}$), work hardening rate ($\delta$) and elongation to failure ($\varepsilon_f$), known as the transformation-induced plasticity (TRIP) effect$^{14,18}$. Generally, martensite hardening is captured by the Hall-Petch (like) relationship$^{19,20}$, thus it is anticipated to engineer nano-martensites in microstructures so as to strengthen and ductilize alloys for excellent mechanical properties.

High specific strength Ti alloys that can be engineered to high $\sigma_y$ with large $\varepsilon_f$ are important structural materials for light-weighting$^{15,16}$. In principle, the extraordinary mechanical properties of duplex Ti alloys are tuned by modulating the quantity or arrangement of grain boundaries (GBs) and hetero-phase boundaries (PBs), e.g., $\alpha/\beta$ interfaces, which are planar discontinuities in alloys$^{21-23}$. The duplex microstructure composed of equiaxed primary $\alpha$ ($\alpha_p$) nodules and colonies of secondary $\alpha$ ($\alpha_s$) lamellae embedded in the $\beta$ matrix endows Ti alloys with a well-balanced property profile$^{21,22}$. In addition to the diffusion ($\beta$-to-$\alpha$) transformation, PBs can be introduced via a diffusionless displacive ($\beta$-to-$\alpha'$) transformation depending on the cooling rate and chemical composition$^{23,24,25}$. The density of PBs or the size of martensites $\alpha'$ can be tuned by the density of chemical boundaries (CBs) defined by a sharp discontinuity of at least one...
elemental concentration inside a lattice-continuous region\textsuperscript{26}, because CBs at high temperature can restrict the growth of martensites for microstructural refinement. Recent findings in Ti-4Mo and Ti-6Al-4V alloys have demonstrated that when the microstructure consists of micron- and submicron-scaled \(\alpha\) and primary \(\alpha\) phases, they exhibit notably enhanced tensile properties\textsuperscript{5,27}. However, metastable duplex Ti alloys (containing micro-martensites), e.g., Ti-6Al-4V alloys often suffer from relatively low \(\sigma_f\) on the order of 1100 MPa or even less\textsuperscript{15,26}. It is desirable, therefore, to devise a nano-martensite-strengthened Ti alloy with high yield strength \(\sigma_f\) and ductility via the CB engineering (CBE) strategy.

In this work, we tailor the density of CBs at high temperature by tuning the \(\beta\)-stabilizer Cr concentrations, thereby regulating the subsequent phase transformation behavior of low-cost Ti-xCr-4.5Zr-5.2Al (x = 1.8, 2.3 and 2.8 wt.\%) alloys (Refer to Supplementary Figs. 1, 2 for the detailed composition design of our nano-martensitic Ti alloys). Utilizing the CBE strategy, we create the finest size of nano-martensites reported by far to realize the highest yield strength of martensitic Ti alloys with great ductility. Compared with the forged alloys undergoing air cooling (AC, with \(\sigma_f\) ~981 MPa and \(\epsilon_f\) ~22.8%), this hierarchically structured WQ Ti-2.8Cr-4.5Zr-5.2Al alloy with -20 nm-thick nano-martensites exhibits ultra-high strength \(\sigma_f\) ~1266 MPa with great ductility \(\epsilon_f\) ~12.6%.

**Results**

**Hierarchical microstructures of Ti-Cr-Zr-Al alloys**

The formation of CBs at high temperature (e.g., above the phase transformation temperature) during either the AC or the WQ process is determined by the difference in the diffusion distance \(L\) of alloying elements at a time period \(t\) that can be simply calculated via \(L = \sqrt{Dt}\), where the diffusion coefficient \(D\) at a specific temperature \(T\) (in Kelvin) can be measured in the Arrhenius diagram of element diffusion in the BCC or HCP-Ti matrix\textsuperscript{28-30}, see Fig. 1a. The Cr element has a much larger \(D\) of \(1.56 \times 10^{-14}\) m\(^2\) s\(^{-1}\) in \(\beta\)-Ti than that of Al (with \(D\) = \(2.01 \times 10^{-14}\) m\(^2\) s\(^{-1}\) in \(\beta\)-Ti) at 1193 K (920 °C) (Fig. 1a, b). Therefore, the obvious difference in \(L\) between Cr and Al inevitably leads to the formation of a high density of nonequilibrium CBs before phase transformation in the high-temperature \(\beta\) phase. It should be pointed out that although the diffusion distance of the Cr element decreases during quenching, it is still much higher than that of the Al element, see Fig. 1b. These CBs divide the coarse \(\beta\)-grains into a large number of ultrafine even nanoscale domains alternately enriched or depleted in Al (and simultaneously depleted or enriched Cr). Once formed, CBs act as barriers restricting subsequent phase transformation within nanoscaled domains enriched in Cr or depleted in Al, while the nanoscaled Al-enriched or Cr-depleted domains serve as the fertile for the formation of dense nano-precipitates. Thus, in addition to CBs, the high density of CBs existing inside the \(\beta\)-grains can act as a new feature to realize microstructural architecture.

To utilize the CBs for creating a refined microstructure, a solution temperature of 920 °C lower than the \(\beta\)-transus temperature \((T_d)\) ~955 °C was selected for 1 h to homogenize the chemical composition of both the primary \(\alpha(\alpha_f)\) and \(\beta\)-parent phases in our duplex Ti-2.8Cr-4.5Zr-5.2Al alloys, and the thermomechanical processes see Supplementary Fig. 3. When subsequent cooling, i.e., AC and WQ, were respectively performed, and the \(\alpha_f\) phase was retained while the \(\beta\) phase suffered from different phase transformations associated with different morphologies (see Fig. 2 and 3 for AC and WQ samples, respectively), depending on the phase stability of the local regions, which was influenced by the cooling rate-related CBs\textsuperscript{12,28}.

Under the AC condition, the chemical gradients of CBs decrease with decreasing temperature before phase transformation, and the concentrations of alloying elements in the matrix have sufficient time to homogenize. Based on the CBE viewpoint\textsuperscript{26}, sufficient time for atomic long-range diffusion in \(\beta\)-grains allows for a wide chemical discontinuity in the spatial distribution of alloying elements of Cr and Al, resulting in the formation of nonequilibrium wide CBs with a low density. Once the structural transformation occurs, these wide CBs would coexist with the crystallographic lattice discontinuity, rendering the formation \(\alpha_f/\beta\) PBs at low temperature. Figure 2a, b shows the hierarchical microstructure of AC Ti-Cr-Zr-Al alloys consisting of microscaled equiaxed \(\alpha_f\) grains and submicron-scaled \(\alpha_f\) nanoscale \(\beta\) lamellae and the distribution of alloying elements. Indeed, the displacive \(\beta\)-to-\(\alpha\) transformation takes place mainly in Al-enriched (and simultaneously Cr-depleted) domains inside each \(\beta\)-grain and thus the secondary \(\alpha\)-phase (\(\alpha_f\)) precipitates in AC Ti-Cr-Zr-Al alloys, see Fig. 2c. Subsequently, these \(\alpha_f\) precipitates grow up with decreasing temperature until the chemical gradient can stop their propagation and thickening by a local reduction in driving force\textsuperscript{31}, rendering the formation of submicron-scaled \(\alpha_f\) laths and wide \(\alpha_f/\beta\) PBs in the range of -25 to 35 nm, see Fig. 2c, d. An High-resolution transmission electron microscope (HR-TEM) image shows the semi-coherent \(\alpha_f/\beta\) phase.
interface\textsuperscript{2,3,3} decorated with misfit dislocations (Fig. 2e, f), and the α phase maintain the typical Burgers orientation relationship (BOR) with the β phase, i.e., (0001)\textsubscript{α}//(011)\textsubscript{β} and [\overline{1}100]\textsubscript{α}//[\overline{1}1\overline{2}]\textsubscript{β}. Given the experimental scatter in energy dispersive spectroscopy (EDS) data, the element distribution between the as-forged and AC samples is nearly identical, see Supplementary Fig. 6 and Supplementary Table 1. These results imply that the continuous transformation of α\textsubscript{α}, accompanied with the growth of α\textsubscript{α} (and migration of PBs), leads to each phase of AC samples is in equilibrium at ambient temperature after sufficient diffusion. Furthermore, this bimodal α structure was quantified by measuring their dimensions and fractions of both α\textsubscript{α} and α\textsubscript{β} precipitates, see Fig. 2g. It appears that the average diameter D\textsubscript{ave} and the volume fraction F\textsubscript{v} of the α\textsubscript{α} precipitate are ~2.9 μm and ~30%, respectively, while these values of the α\textsubscript{β} phase are T\textsubscript{ave} ~313 ± 14 nm and F\textsubscript{v} ~52.4%, respectively. The average thickness of β-lamellae is λ\textsubscript{β} ~75 ± 8 nm, see Fig. 2h.

By contrast, the WQ process triggers intense concentration fluctuations to form dense narrow CBs in the β-parent (above the phase transformation temperature), which will be frozen at relatively low temperature due to the insufficient diffusion time and the fast cooling rate\textsuperscript{36}. These CBs can divide each β-grain into a large number of nanodomains for martensitic transformation and strongly restrict the growth of nano-martensites in our WQ Ti alloy. However, these CBs are not preserved at room temperature as well, because diffusionless martensitic transformation with fast speed can complete instantaneously, rendering these CBs with notable concentration gradients transform into the α/β PBs with crystallographic lattice discontinuity. In this scenario, these α/β PBs in WQ Ti alloys mainly stem from the prior CBs existed above the phase transformation temperature, similar to the case of a low carbon steel\textsuperscript{27}. Thus, for the sake of simplicity, the density of CBs is considered to be almost equal to that of PBs. Figure 3a shows the hierarchical microstructure of WQ Ti-Cr-Zr-Al alloys consisting of microscaled equiaxed α\textsubscript{α}-grains and nano-scaled α\textsubscript{α} and β nanolamellae. According to their sizes and orientations, these α\textsubscript{α} martensites (with the lattice parameters of a = 0.293 nm, and c = 0.466 nm, Supplementary Figs. 4, 5) can be divided into primary, secondary and even tertiary nanomartensites (Fig. 3a). As a result, these 3D α/β-nanolamellae intersect with each other and effectively divide the β-parent into a large number of β nano-domains. These nanomartensites maintain a Burgers orientation relationship with the b-parent as (0001)\textsubscript{α}//(011)\textsubscript{β} and [\overline{1}100]\textsubscript{α}//[\overline{1}1\overline{2}]\textsubscript{β}, as verified by the selected area electron diffraction (SAED) in Fig. 3a. These fine α\textsubscript{α} plates result in the broadening of their diffraction peaks in the XRD pattern in Supplementary Fig. 5.

The atom probe tomography (APT) analysis for the WQ Ti-Cr-Zr-Al sample shows that the neutral Zr element is homogeneously distributed throughout the microstructure, while notable compositional partitioning of Cr, Ti and Al takes place between α\textsubscript{α} and β phases, where the former is enriched by the α-stabilizer (Al), while the latter is enriched by the β-stabilizer (Cr), see Fig. 3b, c. The corresponding APT maps and 1D concentration lines of Cr and Al in the WQ samples confirm a narrow chemical transition region with a width of ~4 nm for the α/β PBs (Fig. 3c), much narrower than that of in their AC siblings. This is because the rapid cooling strongly limits the diffusion length of alloying elements, resulting in a high density of sharp prior CBs in these metastable β-grains that can significantly refine the size of nanomartensites. Figure 3a shows that the martensitic lamella interiors are decorated by dislocations rather than twins, implying that the produced nanomartensites actually belong to dislocation-structured martensites. An HR-TEM image shows the nanoscaled α\textsubscript{α} lamellae (~19.2 nm), see Fig. 3d. In particular, the interfacial structure between α\textsubscript{α} and β is fully coherent (Fig. 3e), which is different from the conventional steel associated with semi-incoherent or incoherent interfaces between the matrix and martensites decorated with misfit dislocations\textsuperscript{34–36}. Moreover, in WQ Ti-Cr-Zr-Al alloys, the average thickness T\textsubscript{ave} and volume fraction F\textsubscript{v} of α\textsubscript{α}-lamellae are ~20 ± 6 nm and ~83.7%, respectively, see Fig. 3f. The average thickness of β-lamellae is only λ\textsubscript{β} ~22 ± 5 nm, see Fig. 3g. Obviously, this is a record fine α\textsubscript{α}-lamellar thickness among all martensitic Ti alloys reported to date, see Fig. 3h.
In contrast, the WQ samples manifest a dramatically enhanced strength of \( \sigma_f \approx 1390 \) MPa and fracture ductility \( \varepsilon_f \approx 12.6\% \). The inset in f is the distribution of \( \alpha_p \) particles in the WQ sample. A comparison of the \( \alpha' \) thickness for the present Ti-Cr-Zr-Al alloys, including Ti-4Mo, Ti-5Al-3Mo-1.5V, As-HIPed TC4, TC4 (prior-\( \beta \) grain), Ti-V-Al, Ti-V-Sn series, and Ti-V-Sn series. Error bars represent standard deviation.

Extraordinary mechanical properties

Figure 4a shows representative tensile engineering stress-strain curves of both AC and WQ Ti-Cr-Zr-Al alloys. It appears that the AC samples initiate to yield at a stress of \( \sigma_y \approx 920 \) MPa and have an ultimate tensile strength \( \sigma_u \approx 1413 \) MPa associated with good ductility \( \varepsilon_f \approx 22.8\% \). In contrast, the WQ samples manifest a dramatically enhanced strength of \( \sigma_f \approx 1266 \) MPa and \( \sigma_u \approx 1920 \) MPa along with a large ductility \( \varepsilon_f \approx 126\% \). Figure 4b, c respectively plots the elongation to fracture \( \varepsilon_f \) that characterizes the resistance to damage against the reported high performance \( \alpha'/\beta \)-Ti alloys, including Ti-4Mo, Ti-5Al-3Mo-1.5V, As-HIPed TC4, Ti-V-Al, Ti-V-Sn series, and Ti-V-Sn series. Obviously, our Ti-Cr-Zr-Al alloy exhibits a better combination of strength and ductility, in comparison to other duplex \( \alpha'/\beta \)-Ti alloys reported to date. In particular, the unprecedented high strength \( \sigma_f \approx 1266 \) MPa and \( \sigma_u \approx 1920 \) MPa sets the present Ti-Cr-Zr-Al WQ alloy apart from all the reported \( \alpha'/\beta \)-Ti alloys, which in general have either low strength or low ductility (or both low). In other words, the WQ alloy displays the highest strength and tensile ductility, i.e., an excellent combination of strength and ductility.

Discussion

Formation of hierarchical nano-martensite microstructure

Often, a high cooling rate can strongly restrict the diffusion of atoms, resulting in the formation of micron- and submicron-martensites in metastable Ti alloys. For the present Ti-Cr-Zr-Al alloy, the formation of dense nanomartensites originates from the CBs that represent a notable chemical discontinuity inside a continuous lattice region during WQ. In other words, the coupling effect of Cr and Al diffusion leads to a novel hierarchically heterogeneous microstructure consisting of nanomartensites and residual \( \beta \) nanolamellae in each original \( \beta \) grain. To fully understand the formation of hierarchical nanomartensites in this work, phase field modeling (Supplementary Note 5) was employed to elucidate the underlying mechanism(s). It

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should be noted that our simulations only focused on the intragranular microstructure and no consideration of GBs or other defects.

For a more precise observation of the microstructure evolution during the cooling process, we displayed in Fig. 5 the structure field and concentration field every 50°C from 750°C to 450°C (temperature below which the results can be found in Supplementary Fig. 8). Indeed, if the cooling rate is slow (V1 for AC), there is sufficient time to homogenize the distribution of solutes associated with the reduction in chemical fluctuations with decreasing temperature, see Fig. 5a1, b2. At this cooling rate, the precipitation of α phase is dominated by the classical nucleation and growth mechanism, see black arrows in Fig. 5a2. If the cooling rate is faster (take V2 as an example for WQ), intense concentration fluctuations (Cr-depleted domains were marked via white circles) existed at 920°C are still maintained at 700°C, Fig. 5d1, d2. When the temperature decreases to 600°C, the α’-phase nucleus (structural transformation) are more easily generated at these Cr-depleted domains, see black circles in Fig. 5c3, c4. These Al-enriched or Cr-depleted nanodomains serve as the fertile for the formation of nano-martensites, while the CBs act as barriers restricting subsequent phase transformation within nanodomains enriched in Cr or depleted in Al, see Fig. 5c4, d4. Similar phenomenon is observed at higher cooling rates, Fig. 5e–h. The calculated microstructure with increasing the cooling rate from 1°C s⁻¹ to 250°C s⁻¹ are displayed in Supplementary Fig. 8, which proves the sizes and types of α and β are closely related to the cooling rate. Specifically, the average size of nano-martensites from the simulation at fast cooling rate (V2: 50°C s⁻¹) corresponds well to that of the WQ Ti alloys.

Further, more obvious evidences indicate that different cooling rates correspond to different nucleation mechanisms according to the evolution of structural field and concentration field (the distribution of Cr element) along supercritical nucleus, as shown in Fig. 6. Figure 6a, b respectively shows the evolution of the structural field and concentration field along a core of α precipitates formed by the classical nucleation mechanism, in which transformation of the structure field is complete (order parameter: Eta > 0.8) and the concentration field reaches the equilibrium states simultaneously. In contrast, the structure field and concentration evolution of the α’-phase nucleus generated by V2 shown in Fig. 6c, d, respectively, prove the existence of the martensitic mechanism, where concentration diffusion and structural transformation are not synchronized. This is similar to the main characteristic of the pseudospinodal mechanism, that is, the structure transformation is complete and rapidly while the concentration keeps evolving towards equilibrium. However, due to the continuous increase in cooling rates, the concentration field will maintain the initial distribution. Therefore, the microstructure formed by rapid cooling, most of its composition change originates from the CBs with notable concentration gradients at high temperature, can be called the martensitic phase.

Mechanisms for ultra-high strength

A combination of high strength and good ductility has been demonstrated in our designed Ti-2.8Cr-4.5Zr-5.2Al alloy. In particularly, the ultra-high strength (σₚ ≥ 1266 MPa and σ_{UTS} ≥ 1413 MPa) sets the present WQ nano-martensitic Ti alloy apart from all the previously reported α'/β-Ti alloys. The deformation mechanism and microstructural morphologies are two key factors in determining alloy deformability. In the deformed microstructure, there is only a large number of dislocations and dislocation entanglements, and no deformation twins are observed. It has been verified that prismatic slip is preferentially activated, especially for slip systems with high Schmid factors. With respect to the microstructure morphology, these α' grains with larger sizes have relatively longer effective slip lengths,
thereby a lower deformation resistance for \( \alpha_p \) with respect to \( \alpha_s \) or \( \alpha' \) lamellae\(^6\). Upon loading, the soft \( \alpha_p \) precipitates plastically deform first (Supplementary Fig. 9), and they cannot deform freely and are constrained by the surrounding hard \( \alpha'/\beta \) nanolamellae structure in our WQ samples, see Fig. 7b1. While for the \( \beta \)-transus microstructure, the ultrafine 3D martensitic network isolates each \( \beta \)-grains in sub-micron domains, which strongly restricts dislocation pile-up at \( \alpha'/\beta \) PBs. This hinders slip propagation from \( \beta \) to \( \alpha' \) lamellae, thus a higher stress is required to initiate macroscopic yielding of the \( \beta \)-transus microstructure. Therefore, the yielding of CBE-processed martensitic Ti alloys is governed more by the hard nanomartensite frame rather than by the soft \( \alpha_p \) phase. As a result, the strength discrepancy between \( \alpha_p \) and the \( \beta \)-transus microstructure would cause severe strain incompatibility and thus strain gradients, which is accommodated by geometrically necessary dislocations (GNDs) piled up against the PBs\(^6\)\(^{,62}\), see white arrows in Fig. 7b2. Similarly, there is a notable strain gradient between soft residual \( \beta \) and hard \( \alpha' \) nanolamellae in the WQ sample. It is the root of the large heterogeneous deformation-induced stress that contributes to the measured ultra-high strength, even the good strain hardening capability and thus the uniform elongation of our nanomartensitic Ti alloy\(^46\)\(^{-48}\).

In general, the strengthening mechanisms of nanomartensitic Ti alloys usually include solid solution strengthening, dislocation strengthening (Supplementary Figs. 10, 11), precipitation strengthening and boundary/interface strengthening. In the present \( \alpha' \)-martensitic Ti alloys, the characteristics of laths, blocks and packets are obvious, and the packet size or block size is often regarded as the effective grain size for GB strengthening\(^5\). The high strength is predominantly produced by the high-density fine-dispersed \( \alpha' \)-martensite platelets. A simple strengthening model is employed to estimate the various contributions to the yield strength \( \sigma_y \) of AC and WQ Ti alloys, which is in good agreement with the experimental results of AC and WQ samples, as marked in Supplementary Fig. 12. The contribution of \( \alpha'/\beta \) interface strengthening is ~421 MPa, verifying that the high yield strength of WQ alloys indeed comes from hierarchical nano-martensite interfaces. For the detailed calculation,
Origin of high ductility

High strain hardening capability is the premise of large uniform elongation for ductile alloys. Figure 7a, b show the strain hardening rate ($\dot{\theta}$) as a function of the true strain for AC and WQ Ti-Cr-Zr-Al alloys, respectively, both of which have three distinguishable stages. The AC sample shows $\dot{\theta}$ first drops quickly in stage I, and then almost maintains a $\dot{\theta}$-plateau in stage II. With increasing strain, $\dot{\theta}$ slowly decreases in stage III. By contrast, $\dot{\theta}$ initially descends to 2.2 GPa in the WQ sample, followed by a slight increase to 2.75 GPa at a strain of ~3.2%, whereas $\dot{\theta}$ again decreases after a strain of ~4.6%. Moreover, the WQ Ti alloy always exhibits a higher $\dot{\theta}$ than that of the AC sample before necking.

Next, the dynamic evolution of the deformation substructure was uncovered to elucidate the different mechanisms for the work hardening capability of the WQ and AC samples. In stage-I, the sharply reduced $\dot{\theta}$ is caused by dislocation slip in the soft $\alpha_p$ phase for both stretched AC and WQ Ti-Cr-Zr-Al alloys, see Fig. 7a1, b1. In stage-II, the nearly $\dot{\theta}$-plateau mainly originates from the activation of confined dislocation slip in the $\beta$-transus microstructure with lamellar structure in AC samples (Fig. 7a2), similar to that of multilayered materials. For the WQ sample, the hetero-deformation triggers abundant GNDs pile-up against PBs with high hetero-deformation induced stresses, leading to increased strain hardening rate (see white arrows in Fig. 7b2). At the same time, the increased stress not only promotes dislocation-interface interactions such as dislocation transmission across the interface (as marked by
Dislocation accumulation, thereby enhancing the fracture resistance of such alloys for their structural applications. Figure 8 shows the fractography images of the AC and WQ samples. Generally speaking, the phase interfaces in materials serve as preferential sites for the initiation and propagation of micro-voids due to the strain incompatibility between hard and soft phases. For the AC sample, many micro-voids were observed in the fracture sub-surface, see Fig. 8a. These voids are uniformly distributed in the α'/β (yellow arrows) and α/β (red arrows) interfaces due to relatively homogeneous plastic deformation between α and β phases (Fig. 8a). The corresponding fracture
surface images show many deeper and larger dimples and a few voids, indicating that the AC Ti alloys are ductile fracture via the growth and coalescence of micro-voids, see Fig. 8b, b1. Moreover, note that in the center of the fracture surface there are some voids and small dimples, but no long cracks, see Fig. 8b.2 This phenomenon is attributed to the fact that thick α+ β plates could deform homogeneously, which in turn suppresses crack initiation and propagation for enhanced fracture resistance.

For our designed hierarchical nano-martensite Ti alloy, there are two pathways to hinder crack propagation for the observed great ductility. First, micro-voids are initially formed at sites with remarkable strain incompatibility, e.g., α/β (yellow arrows) and α_p/β (red arrows) PBs in WQ Ti alloys, see Fig. 8c. Furthermore, the fracture surface image indicates many smaller and shallower dimples in the WQ samples, while it contains numerous voids, see Fig. 8d, d1. These micro-voids will gradually expand to form cracks, see Fig. 8d2. Subsequently, the soft β lamellae could trap cracks or inhibit their propagation by blunting the crack tip in WQ samples.6 Obviously, when a crack propagates at a PB, owing to the 3D α/β network, it may either run into the soft β phase or be deflected to a different path, as marked by the yellow dash line in Fig. 8c. Therefore, compared to α+β lamellae in AC samples, it appears that the α/β nanolamellae make a greater contribution to hinder crack propagation for enhanced fracture resistance since the β-transus microstructure has higher mechanical strength and a higher density of PBs. Simultaneously, the soft α_p phase could not resist cracking at PBs (as marked by red arrows in Fig. 8c), but also could alleviate local stress concentrations via storing dislocations during plastic deformation. Therefore, the heterogeneous microstructure confers the present WQ Ti alloys, in addition to ultra-high strength and great ductility, excellent fracture resistance for promising engineering applications.

In this work, we propose an alloy design strategy that hierarchical nano-martensites with an average thickness of ~20 nm is introduced into a cost-effective duplex Ti alloy, utilizing the diffusion mismatch between fast diffusive Cr and slow diffusive Al to architecture a high density of CBs. We can tailor the fast-diffusive element content to control the density of CBs, which in turn restricts the martensitic phase transformation during quenching. The hierarchical nano-martensite engineering strategy can potentially be applied to many other alloys without complex thermomechanical processing and expensive doping elements, including advanced steels and multicomponent alloys, especially the ability to form quenched martensites in a metastable matrix.

Methods

Alloy fabrication

The designed Ti-2.8Cr-4.5Zr-5.2Al alloy in weight percentage (wt.%) was casted by vacuum arc melting. A 20 kg ingot was melted from industrial purity Ti sponges, Cr granules, a high purity Zr plate and Al shots. The actual chemical compositions of the ingot was measured to be 2.82% Cr, 4.48% Zr, 5.26%Al and the balance Ti (wt.%) with unavoidable elements such as O (0.12%), N (0.014%), C (0.01%) and H (0.001%) by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The β-transus temperature (T_β) of the alloy was determined to be ~955 °C by the metallographic method. The as-cast ingot was homogenized at 1050 °C for 12 h under vacuum, followed by β-forging at 1050 °C to obtain 100 mm thick slab. Subsequently, the slab was forged by a through-transus-processed forging starting at ~980 °C and ending at ~700 °C to produce 30 mm thick plates with ~70% thickness reduction. The forged plates were solution treated in the (α + β) phase region at 920 °C for 1 h with two types of cooling conditions, i.e., air cooling and water quenching (referred to as AC samples and WQ samples, respectively).

Mechanical properties test

Flat dog-bone-shaped tensile specimens with a thickness of 2 mm and a gauge section of 15 × 3.5 mm² were machined from the center region of heat-treated plates along the forging direction (RD) to avoid the surface effect on the microstructure. Uniaxial tensile tests were performed on an Instron 5969 universal testing machine at room temperature, with an initial strain rate of 1 × 10^-3 s^-1. Five specimens were tested to ensure the repeatability of mechanical testing. Tensile properties, e.g., yield strength (σ_y), ultimate tensile strength (σ_UTS) and elongation to fracture (ε) were recorded. The hardness of the α, β grains and α/β regions was measured using a TI950 TribolIndenter (Hysitron, Minneapolis, MN) with a standard Berkovich tip at room temperature. The hardness test was performed at a load-controlled mode with the prescribed loading of ~3000 μN under the loading time of 5 s, correspondingly the loading strain rate of ~0.1 s^-1. The holding time is 2 s, and the unloading time is 5 s. In the present study, the allowable-drift-rate was set at 0.02 nm s^-1, which is 5-fold smaller than the typical value (0.1 nm s^-1) generally used in typical nanoindentation compression tests for improve the reliability and accuracy of the measurements.

Microstructural characterization

Microstructural observations were performed using Olympus PMG3 optical microscopy (OM), JEOL JSM-6700F scanning electron microscopy (SEM) and electron backscatter diffraction (EBSD) embedded in the SEM microscope, respectively. The specimens were mechanically polished, followed by electro-polishing for 10–20 s, and etching was performed in a solution mixture of 2:8:90 of HF, HNO₃, and H₂O in volume fractions. The phase constitution of the specimens was examined with a Bruker D8 Discover powder X-ray diffractometer (XRD) using a Cu Kα radiation (λ=1.5406 Å) source at an acceleration voltage of 40 kV and a current of 100 mA. A transmission electron microscope (TEM, JEM-2100) operated at 200 kV was employed to reveal the microstructural features. The chemical distributions of microstructural constituents were analyzed by energy dispersive X-ray spectrometer (EDS). Needle-shaped specimens required for APT were fabricated by lift-outs and annular milled in an FEI Scios focused ion beam/scanning electron microscope (FIB/SEM). The APT experiments were performed on a CAMECA local electrode atom probe (LEAP 4000XS) under a high vacuum (Pa) at 20 K. Then, using the Integrated Visualization & Analysis Software (IVAS) version 3.6.8 for the three-dimensional reconstructions and compositional analyses of the APT data of the specimens.

Phase field modeling

Since the obvious inhomogeneity of the β-stabilizer Cr can be observed experimentally in Ti-Cr-Zr-Al alloys, a binary system Ti-2.8Cr is selected to describe Ti-2.8Cr-4.5Zr-5.2Al in our simulations for the sake of simplicity. The chemical free energy curves of the α phase and β phase can be obtained through the Pandat thermodynamic database, see Supplementary Table 3. Accordingly, the free energy expressions can be fitted by a polynomial, and the coefficients are linear with temperature. More details can be found in the Supplementary Note 5.

Data availability

The data that support the findings of this study are available from the corresponding author upon request.

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Author contributions
J.S. initiated and guided the project; J.Z. conceived the hierarchical nano-martensite strategy and supervised the experimental work. X.B., W.C., and D.Z. prepared the alloys. C.Z., and X.B. performed the property measurements and carried out the microscopy. D.W. and M.H. performed the phase field simulations. J.Z., C.Z., D.W. wrote the corresponding text with input from W.C., and G.L. All authors contribute to the discussion of results.

Competing interests
The authors declare no competing interests.

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