Manufacture-friendly nanostructured metals stabilized by dual-phase honeycomb shell

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Refining grains to the nanoscale can greatly enhance the strength of metals. But the engineering applications of nanostructured metals are limited by their complex manufacturing technology and poor microstructural stability. Here we report a facile “Eutectoid element alloying→Quenching→Hot deformation” (EQD) strategy, which enables the mass production of a Ti6Al4V5Cu (wt.%) alloy with α-Ti grain size of 95 ± 32 nm. In addition, rapid co-precipitation of Ti2Cu and β phases forms a “dual-phase honeycomb shell” (DPHS) structure along the grain boundaries and effectively stabilizes the α-grains. The instability temperature of the nanostructured Ti6Al4V5Cu alloy reaches 973 K (0.55Tₘ). The room temperature tensile strength approaches 1.52 ± 0.03 GPa, which is 60% higher than the Ti6Al4V counterpart without sacrificing its ductility. Furthermore, the tensile elongation at 923 K exceeds 1000%. The aforementioned strategy paves a new pathway to develop manufacture-friendly nanostructured materials and it also has great potential for application in other alloy systems.

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nanostructured metals (with grain size below 100 nm) exhibit ultrahigh strength and hardness, making them very attractive for developing novel lightweight and energy-efficient structural components. However, the large volume fraction of grain boundaries provide a strong driving force for grain coarsening. In most nanostructured metals, prominent grain growth is observed in a temperature range of 0.25–0.4 $T_m$ ($T_m$ is the melting temperature). Under loading conditions, the stability of nanostructured materials is further degraded. For example, in nanostructured pure Al and Ni, mechanically driven grain growth was observed during plastic deformation at room temperature. The inherent thermal and mechanical instability of nanostructured metals render them difficult to be manufactured into bulky components, which severely limit their application in engineering practice. Consequently, it is a long-term endeavor for material scientists to develop nanostructured metals with higher stability.

Over the past few decades, extensive investigations have shown that nanostructures can be stabilized through either thermodynamic or kinetic strategies. Thermodynamically, lowering grain boundary energy can reduce the driving force for grain coarsening. This is often achieved by solute segregation, such as in Ni-W, Co-P, and Ni-Fe alloys. In addition, using low angle boundary or twin boundary architectures in pure Cu or Ni can stabilize nanostructures as well. Kinetically, the driving force for grain coarsening could be counteracted by precipitate particles pinning the grain boundaries. This is normally achieved by mechanical alloying, such as in Cu-WC and Cu-Ta alloys. The stability of nanostructure can be further enhanced when thermodynamic and kinetic strategies are favorably combined together. However, this requires a more ingenious nanostructured design strategy that should not only employ low-energy interfaces, but also introduce thermally stable secondary phases pinning on the low-energy interfaces.

In this work, we have developed an idea to stabilize nanosized grains by a dual-phase honeycomb shell (DPHS) nanostructure in the Ti6Al4V5Cu model alloy (Fig. 1a). Here, equiaxed nanograins are analogous to the compartments in a honeycomb, they are fully encapsulated in thin dual-phase shells. The phases which make up of the dual-phase shells have low interfacial energy with the matrix. Hence, conventional high angle grain boundaries (HAGBs) with poor thermal stability are replaced by low-energy phase boundaries to thermodynamically stabilize the nanostructure. Moreover, the growth of any phase in the dual-phase shell is constrained by the other, thus the shell itself is of high stability. Such stable shells can exert an effective pinning force on nanograins to kinetically stabilize the nanostructure when it is exposed to high temperature and/or plastic deformation. The microstructural design concept, which synchronizes the thermodynamics and kinetics strategies prominently enhances the stability of the nanostructured metallic materials.

**Results and discussion**

The microstructural thermal stability of the as-fabricated Ti6Al4V5Cu alloy with equiaxed α grains of 95 ± 32 nm (Supplementary Fig. 1) was determined by exposure for one hour at various temperatures (Fig. 1b). The onset instability temperature, was identified as high as 973 K (0.55$T_m$). This is notably higher than those of the nanostructured metals fabricated through conventional “bottom up” or “top down” technologies at the same grain size level (~100 nm). The mechanical properties of as-fabricated samples were tested at room temperature. For comparison, a commercial Ti6Al4V alloy consisting of equiaxed α grain with a size of 8.9 ± 3.8 μm (Supplementary Fig. 2) was also tested at the same loading conditions. The tensile strength of as-fabricated Ti6Al4V5Cu alloy is (1.52 ± 0.3) GPa, which is 60% higher than that of the Ti6Al4V counterpart without sacrificing its ductility (Supplementary Fig. 3). The comprehensive mechanical properties were greatly improved compared with commercial α, β, or (α + β) titanium alloys in the ASTM standard (Fig. 1c). The phenomenon of strength and ductility trade-off which was often reported in other nano-grained materials did not occur in the present study. This can be attributed to the high mechanical stability inhibiting the occurrence of strain localization and early necking (Supplementary Fig. 4a). Furthermore, we performed high-temperature tensile tests at 923 K to examine the stability under a thermomechanical coupling condition (Fig. 1d and Supplementary Fig. 4b). Surprisingly, the model alloy was not fractured when the elongation exceeded 1000%, meanwhile, the fine grains still remained their initial size after the deformation. This superplasticity and high stability enable this nanostructured material to be easily manufactured into complex components through common bulk metal forming processes.

The high stability and mechanical properties originate from the alloy’s unique microstructure. Transmission electron microscopy (TEM) analysis performed using high-angle annular dark field (HAADF) imaging indicates that alloying elements segregated along the nano-grain boundaries to form a shell structure (Fig. 2a). We randomly characterized a nano-grain by X-ray energy dispersive spectroscopy (XEDS) analysis (Fig. 2b). The equiaxed, aluminum enriched α-Ti nano-grain is fully enveloped by copper enriched Ti3Cu phase and vanadium enriched β phase. For these reasons, we have called it the dual-phase honeycomb shell (DPHS) structure.

The formation of nanosized α-Ti grains and DPHS structure is promoted by our ‘Eutectoid element alloying→Quenching→Hot deformation’ (EQD) strategy (Fig. 2c). Here, the E step is to alloy metals with eutectoid-forming elements that will contribute to the formation of eutectoid intermetallics constituting the shell in the last step (D step). The Q step refers to quenching the material at above the eutectoid transformation temperature. A combination of E and Q steps strongly suppress the eutectoid reaction, which will generate severe lattice distortion in martensite as a result contributing to the formation of a nanoscale lath precursor. The role of the D step is to convert the nanoscale lath precursor into an equiaxed nano-grained structure through hot deformation. Meanwhile, the dual-phase shell formed as a result of strain-assisted phase transformations. The EQD process can be achieved by traditional hot processing technologies that are compatible with the present industrial production lines (Supplementary Fig. 5). This circumvents the dilemma of high-cost and low-efficiency in the current nanostructured metal fabrication strategies. For titanium alloys, eutectoid-forming elements include Cu, Si, Co, Ni, Mn, W, Cr, et. al. Given a high solubility of Cu in β titanium, a big atomic radius difference with respect to titanium, and the fact that Ti3Cu phase can rapidly precipitate from a titanium, Cu was selected as the additional alloying element in the most widely used Ti6Al4V alloy.

To determine the formation mechanism of the nanoscale lath precursor in E and Q steps, we performed X-ray diffraction (XRD) analysis on the as-quenched Ti6Al4V5Cu alloy (Fig. 2d). The specimen was mainly identified as α′ phase, hence the eutectoid reaction $\beta \rightarrow \alpha + Ti_3Cu$ was substantially inhibited. Given supersaturated copper in the α′ matrix (Supplementary Fig. 6), and large atomic radius difference between titanium (0.147 nm) and copper (0.128 nm), a large lattice strain should be stored in the martensite matrix. This lattice strain is reflected by the significant peak broadening in the XRD spectrum compared to the copper free Ti6Al4V specimen. Further calculation using the Williamson-Hall formula indicates that the average lattice strain increases from 0.186% to 0.228% due to copper alloying.
To accommodate the excessive lattice distortion in the copper supersaturated matrix, higher number density of thin lath variants should be formed. This is consistent with the TEM observation that copper alloying resulted in a significant decrease in the lath width from 100–500 nm to 10–70 nm (Fig. 2f).

In order to convert the nanoscale lath precursor to an equiaxed nano-grained structure during the D step, transverse boundaries that are perpendicular to the longitudinal direction of lath martensite should be introduced. Experimental results showed that all the prismatic planes of hcp α phase are parallel with the long-prismatic planes of hcp β phase. α → β martensite transformation is driven by transformation strain, which is greater by orders of magnitude faster than that in the crystal lattice. The newly formed equiaxed α laths got coarsened during the deformation. It is well known that self-accommodation of lattice distortion is achieved by different lathy variants in neighbors. To accommodate the excessive lattice distortion in the copper supersaturated matrix, higher number density of thin lath variants should be formed. This is consistent with the TEM observation that copper alloying resulted in a significant decrease in the lath width from 100–500 nm to 10–70 nm (Fig. 2f).

The present study determined as 973 K (Fig. 1b). The high thermal stability we observed supports the belief that these shells did not only inhibit grain coarsening during the high-temperature fabrication process, but also significantly enhance the stability of the nanostructure against post-fabrication annealing (Fig. 3a). When annealed below 923 K for 1 h, both the nanostructure and the texture characteristic were barely evolved. That is why the onset thermal instability is determined as 973 K (Fig. 1b).

The high thermal stability we observed supports the belief that nanostructures can be remarkably stabilized when thermodynamic and kinetic strategies were favorable combined together through constructing the DPHS structure. Thermodynamically,
the driving force for grain coarsening was noticeably reduced when conventional high-energy HAGBs were replaced with low-energy α/Ti₂Cu or α/β phase interfaces. By tilting the specimens under high-resolution TEM (Fig. 3b), we found a set of low-lattice-misfit orientation relationships between the core α phase and the shell Ti₂Cu/β phase: (0001)α//[013]Ti₂Cu//[101]β; [1120]α//[100]Ti₂Cu//[111]β. Based on the first-principles calculations (Fig. 3c, Supplementary Table 1), the phase interfacial energies of α/Ti₂Cu and α/β are only of 0.070 J/m² and 0.219 J/m² respectively, which are an order of magnitude smaller than that of conventional α/a HAGBs of 0.8–2.0 J/m².²¹ This indicates that both types of interface enclosing the nanosized α grains are thermodynamically stable. It should be noted that the low-energy phase interface in the present study is different from the low-energy LAGBs which could gradually accumulate their misorientations at high temperatures to form high-energy HAGBs.²² Our pole figure results (Fig. 3d) proved on a macro level that the initial low-lattice-misfit orientation relationship among α, Ti₂Cu and β phase was still maintained even after annealing at 973 K.

Kinetically, the Ti₂Cu/β dual-phase shells would exert a substantial pinning force on α grains and hence offsetting the driving force for grain coarsening. The role of the Ti₂Cu/β dual-phase shells to a large extent depends on two important factors: Firstly, whether they can precipitate immediately after the formation of nanosized α grains; secondly, the thermal stability of the Ti₂Cu/β shells at elevated temperatures. To elucidate these key issues, we performed in-situ scanning electron microscopy (SEM) on a focused ion beam (FIB) specimen (Fig. 3e). The material presented inferior microstructural stability because the Ti₂Cu particles readily coarsen at high temperatures. Moreover, the Ti₂Cu/β shells can also stabilize the nanostructure under thermomechanical coupling conditions, which enabled the material to present superplasticity at elevated temperatures. In order to understand the mechanism of superplasticity, we performed in-situ scanning electron microscopy (SEM) on a fiducial marked sample prepared by focused ion beam milling (Fig. 4a, b). After loading at 923 K to an average tensile strain of 40%, we neither observed any dislocation slip band nor change in grain size or aspect ratio (Fig. 4c). This precluded the occurrence of conventional deformation mechanisms such as dislocation slip or Coble diffusional creep in coarse-grained...
Fig. 3 The DPHS nanostructure is stabilized thermodynamically and kinetically. a IPF maps of the Ti6Al4V5Cu sample annealed at various temperatures, only the IPF maps of a phase is shown for brevity, compressive direction (CD) is denoted in the figure. b High-resolution TEM observation showing a low misfit orientation relationship of α/Ti2Cu/β phases. c Interfacial structural models for first principles calculations. d Pole figures of the Ti6Al4V5Cu sample annealed at 973 K, the initial low-energy orientation relationship was retained. e Atom probe tomography (APT) analysis in the as-prepared Ti6Al4V5Cu sample, the copper concentration gradient indicating that the Ti2Cu/β shell can be formed rapidly. f APT analysis of the 923 K/1 h annealed Ti6Al4V5Cu sample. Error bars in e and f indicate standard deviations of measured Al, V, Cu contents.

In this study, we have demonstrated a pathway to achieve ultra-stable nanosized grains by constructing a DPHS nanostructure through a low-cost EQD strategy in a Ti6Al4V5Cu model alloy. As a result, the key challenge to retain nanosized grains in metal bulk forming processes has been effectively overcome. Moreover, the EQD strategy is also applicable to other eutectoid alloy systems when a martensitic transformation is available. For example, we have also fabricated high stability Ti15Zr7Cu alloy with a DPHS nanostructure (Supplementary Figs. 12 and 13). We expect that the strategy reported here can be extended to other alloy systems, such as alloy steels, promoting the development and mass applications of bulky nanostructured metal products in future.
**Tensile testing.** Tensile tests were performed on a Shimadzu AG-100KN universal testing machine which was equipped with a non-contact laser extensometer. Standard cylinder samples with the diameter of 5 mm and gauge length of 25 mm (ASTM standard E8/E8M-08) were used. They were machined with the use of the as-prepared Ti6Al4V5Cu plates. Tensile loading direction was perpendicular to the thickness direction of Ti6Al4V5Cu plates. Room temperature tensile tests were conducted with an initial strain rate of 0.001 s⁻¹. High temperature tensile tests were conducted at 923 K with an initial strain rate of 0.001 s⁻¹. The strength and elongation of samples were given by the averages of five parallel measurements.

**X-ray diffraction analysis.** Samples for XRD analysis were mechanically polished, then electrolytically polished using a mix solution of 5 vol.% perchloric acid, 35 vol.% n-butyl alcohol and 60 vol.% methanol at 25 V for 20 s. XRD experiments were performed on a Bruker D8 X-ray diffractometer using a Cu anode, the diffracted energy was in a range of 30° to 180° with a step size of 0.02° and a counting time of 5 s. The reflections of [1010], [0002], [1011], [1012], [2110], [1013] and [2112] of the α′ phase were measured. The modified Williamson-Hall formula was used to calculate the lattice strain ε and crystalline domain size D:

\[
\beta \cdot \cos(\theta) = \frac{\lambda}{D} + \delta(\theta) \cdot \varepsilon
\]

where, β is the integral peak width, θ is the diffraction angle, λ = 0.15418 nm is the X-ray wavelength.

**Electron backscatter diffraction.** Samples for EBSD analysis were sectioned along the compression direction by wire-electrode cutting, then mechanically grinded and polished, finally subjected to vibration polishing using a VibroMet2 machine in a thickness of below 40 μm. Foils with a diameter of 3 mm were punched out and two-jet thinning in an electrolyte of 5 vol.% perchloric acid, 35 vol.% n-butyl alcohol and 60 vol.% methanol at −30°C with a voltage of 25 V, followed by ion-beam thinning at 2 kV using a Gatan PIPS™ facility. TEM observations were performed on a JEOL 2100 F microscope which was equipped with a X-ray energy dispersive spectrum detector and operated at 200 kV. High-angle annular dark field (HAADF) imaging was used to characterize the DPHS nanostructure. X-ray energy dispersive spectroscopy (XEDS) analysis was used to reveal the chemical composition distribution within the shell structure. High-resolution TEM imaging was used to identify α, Ti₃Cu and β phase and to determine their crystallographic orientation relationship.

**Transmission electron microscopy.** Samples for TEM observation were ground to a thickness of below 40 μm. Foils with a diameter of 3 mm were punched out and two-jet thinning in an electrolyte of 5 vol.% perchloric acid, 35 vol.% n-butyl alcohol and 60 vol.% methanol at −30°C with a voltage of 25 V, followed by ion-beam thinning at 2 kV using a Gatan PIPS™ facility. TEM observations were performed on a JEOL 2100 F microscope which was equipped with a X-ray energy dispersive spectrum detector and operated at 200 kV. High-angle annular dark field (HAADF) imaging was used to characterize the DPHS nanostructure. X-ray energy dispersive spectroscopy (XEDS) analysis was used to reveal the chemical composition distribution within the shell structure. High-resolution TEM imaging was used to identify α, Ti₃Cu and β phase and to determine their crystallographic orientation relationship.

**Atom probe tomography.** Samples for APT analysis were fabricated using a dual-beam focused ion beam (FIB) on Helios Nanolab 600i from FEI. Rectangular cubes with dimensions of 2 × 2 × 10 μm were extracted from samples’ surface then mounted on silicon micropip. They were subsequently trimmed by annular ion milling to sharp needles with a tip diameter of 30–60 nm and length of 6 μm. APT experiments were performed on a LEAP 4000X instrument, at a sample chamber temperature of 50 K, under a pulse frequency of 200 kHz and a target evaporation rate of 0.8% per pulse. APT Data reconstruction was analyzed by Cameca IVAS 3.6 software.

**In-situ tensile scanning electron microscopy.** The specimen for the in-situ tensile test was a plate with gauge portion dimensions of 2 mm length × 3 mm width × 1 mm thickness, it was sectioned from the central part of the as-prepared Ti6Al4V5Cu plate. The surface was electropolished by a mix solution of 10 vol.% perchloric acid and 90 vol.% alcohol at −30°C with a voltage of 25 V. In order to measure the strain distribution in the specimen, fiducial markers were milled on the surface using the FIB instrument. Markers were carved to the minimum possible depth to avoid cutting the sample. The dimensions of the fiducial markers were 5 × 5 μm with pitches of 500 nm. The in-situ tensile experiment was performed on a micro-tensile testing stage placed inside the chamber of a TESCAN MIRA high-resolution scanning electron microscope. The module is equipped with a resistance heater, which is capable of heating up to 1123 K. The temperature of the specimen was precisely controlled by a thermocouple wire spot welded on the
sample surface. The tensile test was conducted at 923 K at a strain rate of 0.01 s⁻¹. Every 10% of strain increment the tensile test was paused to acquire a SEM image.

First-principles calculations of phase interface energies. In order to calculate α and β-Ti/Cu phase interface energies, we have constructed interfacial structural models based on the experimental orientation relationship of [0002]//[013]Cu//[011]Ti and [1120]//[001]Cu//(111)Ti (Fig. 3c). 24 atoms were used for building (1100)++){(211)} interface model and 90 atoms were used for building (0002)–(013)Cu interface model. For an interface model consisting of two phases M and N, the interface energy can be expressed as:

$$\gamma = \frac{E_{\text{sys}} - mE_{\text{bulk}} - nE_{\text{bulk}}}{A} / N$$  (2)

where $E_{\text{sys}}$ is the total energy of the interfacial modeling system, $E_{\text{bulk}}$ and $E_{\text{bulk}}$ are the energies in bulk M or N system in the unit of eV/atom, A is the surface area of the interfacial structure, m and n are the number of atoms in the slabs of M and N. Here, $\sigma_M$ and $\sigma_N$ are the surface energy of the slab of M and N, which can be derived through the following equation as:

$$\sigma = \frac{(E_{\text{bulk}} - mE_{\text{bulk}})}{2A}$$  (3)

where $E_{\text{bulk}}$ is the total energy of the relaxed slab, $E_{\text{bulk}}$ is the total energy of the bulk per atom, A is the area of the surface slab. A 15 Å vacuum is used for the models to minimize the interaction in periodic images.

Using Density Functional Theory first principles calculations25, we have calculated all the above energies by employing the Vienna ab initio simulation package (VASP)26. We have adopted the projected augmented wave (PAW)27 method in describing the plane-wave basis and the generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof (PBE) in describing the exchange-correlation functional28. The valence electrons of Ti, Cu, Al and V atoms are treated as 3p63d24s2, 3d104s1, 3s23p1, and 3p63d34s2. The cut-off energy of the plane waves is set at 400 eV. All the Brillouin zone integrations are performed on the Gamma centered k-mesh and sampled with a resolution of 2π × 0.025 Å⁻¹.

Data availability
The data generated in this study are provided in the Source Data file. Source data are provided with this paper.

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Author contributions
H.W. performed the experimental studies. W.S. and S.Z. carried out the analysis. M.L. performed modeling and simulation. D.Q. and X.C. gave guidance on experimental design. L.R. and K.Y. supervised the study.

Competing interests
The authors declare no competing interests.

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