Facile route to bulk ultrafine-grain steels for high strength and ductility

To fabricate bulk UFG steels with both high strength and high ductility by a simple manufacturing route, a typical Fe–22Mn–0.6C–3Cu and Fe–22Mn–0.6C–4Cu steels are referred to as 0Cu, 3Cu and 4Cu, respectively.

Mechanical performance

Figure 1a shows the true tensile stress–strain curves of the alloys annealed at 760 °C for 5 min and 20 min. The yield strength and ultimate tensile strength ($\sigma_{uts}$) were markedly higher for the Cu-doped steels. Specifically, 4Cu after 5 min annealing has a yield strength of 710 ± 26 MPa—almost double that of 0Cu (365 ± 18 MPa)—and comparable ductility to coarse-grained 0Cu (Fig. 1a, Extended Data Fig. 1). Moreover, the Cu-doped steels exhibit an ultrahigh strain-hardening rate of around 45 per cent and a tensile strength of around 2,000 megapascals. This grain-refinement approach enables the preparation of a fully recrystallized UFG structure with a grain size of 800 ± 400 nanometres without the introduction of detrimental lattice defects such as brittle particles and segregated boundaries. Compared with the steel to which no Cu was added, the yield strength of the UFG structure was doubled to around 710 megapascals, with a uniform ductility of 45 per cent and a tensile strength of around 2,000 megapascals. This grain-refinement concept should be extendable to other alloy systems, and the manufacturing processes can be readily applied to existing industrial production lines.

Steels with sub-micrometre grain sizes usually possess high toughness and strength, which makes them promising for lightweighting technologies and energy-saving strategies. So far, the industrial fabrication of ultrafine-grained (UFG) steels, which generally relies on the manipulation of diffusional phase transformation, has been limited to steels with austenite-to-ferrite transformation. Moreover, the limited work hardening and uniform elongation of these UFG steels hinder their widespread application. Here we report the facile mass production of UFG structures in a typical Fe–22Mn–0.6C twinning-induced plasticity steel by minor Cu alloying and manipulation of the recrystallization process through the intragranular nanoprecipitation (within 30 seconds) of coherent disordered Cu-rich phase. The rapid and copious nanoprecipitation not only prevents the growth of the freshly recrystallized sub-micrometre grains but also enhances the thermal stability of the obtained UFG structure through the Zener pinning mechanism. Moreover, owing to their full coherency and disordered nature, the precipitates exhibit weak interactions with dislocations under loading. This approach enables the preparation of a fully recrystallized UFG structure with a grain size of 800 ± 400 nanometres without the introduction of detrimental lattice defects such as brittle particles and segregated boundaries.
(71 GPa% for 4Cu), even when compared with the UFG TWIP steels fabricated by complicated processes such as flash annealing24 or repeated cold rolling and annealing26. This demonstrates the advantages of this grain-refinement strategy in simultaneously enhancing yield strength and toughness.

**Microstructure and thermal stability**

The synchrotron high-energy X-ray diffraction (XRD) pattern (Fig. 2a) and electron back-scattering diffraction (EBSD) map (Fig. 2b) of 4Cu annealed at 760 °C for 5 min revealed a single-phase, fully recrystallized face-centred cubic (fcc) structure with a fine grain size of 800 ± 400 nm. Further analysis by annular dark-field scanning transmission electron microscopy (ADF-STEM; Fig. 2c) revealed the presence of nanoprecipitates (bright particles) with a high number density and uniform intragranular distribution. Energy-dispersive spectroscopy spectrum imaging (EDS-Si; inset of Fig. 2c) confirms that these nanoprecipitates are enriched in Cu. The selected area electron diffraction (SAED) pattern (Extended Data Fig. 2a) taken along the [110] zone axis and the atomic-resolution ADF-STEM image (Fig. 2d) show that the precipitates (bright contrast) do not exhibit extra periodicity compared with that of the fcc matrix, confirming their disordered fcc nature. Moreover, these precipitates have a diffuse and fully coherent interface with the matrix (Fig. 2d), which is responsible for their homogeneous distribution25. Note that a UFG structure (900 ± 400 nm) was also obtained in 3Cu, while the grain size of 0Cu reached 2.2 ± 1.1 μm (Extended Data Fig. 2b, c). This suggests that the addition of Cu has a critical role in grain refinement and property enhancement.

Fig. 2e shows a reconstruction from one atom probe tomography (APT) dataset for 4Cu, revealing that the diameter of the Cu-rich nanoprecipitates is 84 ± 6 atomic per cent (at%). The one-dimensional concentration profile (Fig. 2g) of a cylindrical region across the grain boundary indicates slight C segregation26 but no Cu or Mn segregation at grain boundaries. Therefore, in contrast to conventional stabilization strategies—such as boundary segregation and precipitation—the current approach did not introduce any excess defects at grain boundaries, which is beneficial for ductility.

The thermal stability of UFG alloys determines the processing window of manufacturing—that is, the range of annealing temperatures and times that are suitable for production27. We therefore evaluated the thermal stability of 0Cu and of UFG 3Cu and 4Cu over a wide range of annealing temperatures (730–910 °C) and times (5–60 min) (Fig. 3, Extended Data Fig. 3). The grain size of 0Cu increases rapidly with annealing temperature. By contrast, the UFG microstructures of the Cu-doped steels can be retained over a wide temperature range. Notably, the stability of these Cu-doped steels varies with the Cu content, which corresponds well to the Cu solubility in austenite at different temperatures (inset of Fig. 3a). The 4Cu UFG structure is stable up to 910 °C (or 0.64Tm, where Tm is the melting point, is approximately 1,430 °C), which indicates a broad temperature processing window of more than 150 °C (Fig. 3a, Extended Data Fig. 3). This is in marked contrast with previous reports on other UFG alloys28–30, in which rapid grain growth occurs when the annealing temperature approaches 0.3Tm. Furthermore, when the annealing time was increased from 5 min to 60 min at 760 °C, limited grain growth (from 0.8 μm to 1.3 μm) was observed for 4Cu, whereas grains grew considerably (from 2.1 μm to 5.7 μm) for 0Cu (Fig. 3b, Extended Data Fig. 3). This further demonstrates the high thermal stability of the prepared UFG steels.

**Grain-refinement mechanism**

To determine the grain-refinement mechanism, we studied annealing effects in 4Cu by EBSD, annular bright-field (ABF) STEM and APT techniques (Fig. 4, Extended Data Fig. 4). Figure 4a shows that recrystallization occurred extensively after 0.5 min annealing. Upon extension of the annealing time to 1 min and 2 min, the recrystallized volume fraction increased to 76% and 95% while the grain size increased to 300 ± 150 nm and 500 ± 200 nm, respectively (Fig. 4b, Extended Data Fig. 4a–d). Cu-rich clusters with an average diameter of 2.6 nm and a number density of 1.6 × 10^{23} m^{−3} formed after 0.5 min annealing (Fig. 4a). As the annealing time was extended to 1 min and 2 min, the average precipitate size increased slightly to 3.7 nm and 4.5 nm, and the number density decreased to 8.8 × 10^{22} m^{−3} and 6.1 × 10^{22} m^{−3}, respectively (Fig. 4a, b, Extended Data Fig. 4e). Accompanying the growth in size, the Cu content in these precipitates also increased from 56 ± 4 at%
after 0.5 min annealing to 76 ± 5 at% after 2 min annealing, as shown by the proximity histograms in Fig. 4a, b (for details regarding particle composition correction, see Methods and Extended Data Fig. 5). The gradual enrichment of Cu in the precipitates with growth suggests that the formation of these disordered precipitates is dominated by a simple solute-enrichment process, which contributes to the rapid nanoprecipitation; this is discussed in more detail below.

To further decipher the relationship between recrystallization, nanoprecipitation and the mechanism responsible for the high thermal stability of 4Cu, we compared the evolution of the driving pressure for recrystallization ($P_r$, the stored energy of the unrecrystallized grains), the Zener pinning pressure ($P_z$, resulting from the formation of excess incoherent interfaces owing to the interaction between the coherent nanoprecipitates and migrating grain boundaries) and the driving pressure for grain growth ($P_g$, originating from the decrease of total grain boundary energy) as a function of annealing time at 760 °C (Fig. 4c).

Although the overall dislocation density decreases greatly with annealing, the local dislocation density of unrecrystallized grains decreases only slightly, leading to a constant $P_g$ (Fig. 4c). Thus, $P_r$ (approximately 28.6 MPa, see Methods) is always higher than $P_g$ (Fig. 4c), resulting in a rapid recrystallization process (after around 2–3 min annealing). However, owing to the rapid and copious precipitation at the onset of annealing, $P_r$ increases rapidly and exceeds $P_g$ after 1 min annealing, suggesting that these freshly recrystallized sub-micro grains are stabilized immediately after recrystallization. When the annealing is extended from 1 min to 5 min, the precipitates grow slightly from 3.7 nm to 6.0 nm, and $P_g$ peaks at around 5 min (Fig. 4c) whereas $P_r$ decreases gradually. When the annealing time exceeds 5 min, nanoprecipitation progresses into the capillary-driven coarsening stage, which generally exhibits slow kinetics owing to the low driving force and to long-range diffusion. As a result, $P_r$ inevitably decrease but is still much higher than $P_g$. Consequently, the UFG structure is continuously stabilized by Zener pinning (Fig. 4d, e).
It should be noted that the pinning effect actually arises from the precipitates adjacent to grain boundaries. However, the capillary-driven growth of the precipitates inevitably increases the space between precipitates and boundaries. As the grain boundaries of the sub-micrometre grains are highly mobile, they quickly migrate towards these precipitate-free regions until they interact with new internal nanoprecipitates, where the pinning reestablishes (Fig. 4d, e). A precipitate-free space is then left behind the migrating boundary; the small width of this space (around 50 nm; Figs. 2e, 4d) indicates a substantially lower rate of grain growth. Therefore, after the boundaries are pinned by nanoprecipitates, the coarsening of the nanoprecipitates—which is a much slower process that involves long-range diffusion—then governs the grain-growth process. In conjunction with the low-misfit (0.11%, see Methods), fully coherent interfaces that considerably lower the driving force for precipitate coarsening, the intrinsically unstable UFG grains are then continuously stabilized by the stable nanoprecipitates. The high-resolution TEM image (Fig. 4f) shows that the precipitate at a grain boundary is coherent with the shrinking grain, confirming that the strong Zener pinning effect results from the intragranular nanoprecipitates instead of grain-boundary precipitation.

The above results show the importance of rapid precipitation and high stability of the nanoprecipitates to the grain refinement. The reasons for the rapid precipitation are threefold. First, the fast kinetics, which result from the high annealing temperature when compared with that of other high-Mn steels (around 550 °C). Second, the low nucleation barrier that results from the fully coherent interfaces. In addition, the disordered nature renders the precipitation a continuous localized-enrichment process for Cu (Fig. 4a, b), which reduces the incubation time of nuclei when compared with that of intermetallic precipitates that require the localized enrichment of at least two elements with a strict stoichiometric ratio. Third, the positive mixing enthalpy between Cu and Fe (13 kJ mol⁻¹) suggests that atomic-scale Cu-rich clusters exist in the melt, which also facilitates fast precipitation.
Plastic-deformation mechanism

Compared with 0Cu annealed at 760 °C for 5 min (Fig. 1a), the yield strength of 4Cu is increased by 345 MPa. As expected, the calculation (see Methods) reveals that grain refinement dominates the yield-strength enhancement, with an estimated contribution of 286 MPa. Owing to the ultralow elastic misfit (the lattice misfit is 0.11%) and the disordered nature, the elastic and interfacial strengthening of the Cu-rich nanoprecipitates were estimated to be 19.9 MPa and 0.08 MPa, respectively (see Methods). Therefore, the main role of these coherent Cu-rich precipitates is to refine the grains, rather than to produce strong precipitation hardening, which often leads to a trade-off between strength and ductility.

To determine the role of Cu-rich nanoprecipitates in dislocation motion and nanotwin formation, we fabricated a UFG 0Cu alloy with a grain size of 1.1 ± 0.5 μm for comparison (see Methods and Extended Data Fig. 6a). In the early deformation stage (up to 15% strain), a high density of dislocation walls and cells are observed in both the 4Cu and UFG 0Cu alloys, along with some nanotwins with an interspacing of 300–500 nm in both alloys. Dark-field TEM images of 0Cu (c) and 4Cu (d) pre-strained to 45%. The insets in a–d show the corresponding SAED patterns. e–h, APT reconstructions (e, f) and ADF-STEM images (g, h) of 4Cu pre-strained to 15% (e, g) and 45% (f, h), showing the development of nanoprecipitates with strain and their interaction with nanotwins.

The question arises as to how the coherent disordered nanoprecipitates can hinder grain-boundary migration but not pin dislocations. When a grain boundary encounters a coherent nanoprecipitate, an incoherent interface is created between the matrix and the precipitate, with an interfacial energy that is orders of magnitude higher than the initially low-energy coherent interface (22 mJ m⁻²) would emerge as an additional obstacle to resist subsequent twinning and to constrain the growth of the twins, thus refining the twinning substructures. More importantly, numerous small dislocation cells are observed around the thinner and denser nanotwins (Extended Data Fig. 7d, e); this suggests that the refined nanotwins could still accommodate additional dislocation accumulation, which is also critical for sustaining a continuous high strain-hardening rate.

An increase of strain to 45% leads to continuous formation of nanotwins in both 0Cu and 4Cu UFG alloys (Fig. 5c, d, Extended Data Fig. 7a, b). The average width and interspacing of the nanotwins in 4Cu are 7.9 ± 5.4 nm and 15.2 ± 14.3 nm, respectively, whereas those in 0Cu are much larger, at 15.6 ± 13.7 and 69.2 ± 38.4 nm. Beyond 15% strain, the smaller width of the nanotwins and their denser distribution in 4Cu mean that twinning gradually dominates the strain hardening, whereas dislocations still govern hardening in 0Cu (Extended Data Fig. 6b).

At the early stage of plastic deformation, some Cu-rich particles are sheared by dislocations and become elongated along the loading direction (Fig. 5e, Extended Data Fig. 7c), which is consistent with their weak strengthening effect. At the late stage, the Cu-rich precipitates are uniformly fragmented into smaller ones (Fig. 5f), resulting in a much greater number density. The STEM-EDS-Si images (Fig. 5g, h) confirm that the nanotwins frequently cut through the Cu-rich precipitates and, in combination with dislocation shearing, cause their fragmentation; in turn, the Cu-rich clusters refine the nanotwins, leading to a twinning-dominated stage of deformation. In contrast to full dislocation movement, twinning proceeds though the co-operative motion of Shockley partial dislocations on the [111] planes. When the partial dislocations cut through the Cu-rich clusters, a stacking fault with higher energy in the Cu-rich clusters (78 mJ m⁻² for Cu) than in the matrix (22 mJ m⁻²) would emerge as an additional obstacle to resist subsequent twinning and to constrain the growth of the twins, thus refining the twinning substructures.
As discussed earlier, in this case grain-boundary migration occurs only after the dissolution or/and coarsening of the nanoparticles near the boundary, which is a slow, long-range diffusion process. By contrast, dislocation movement is not substantially hindered by the nanoparticles, because of their disordered structure and ultra-low misfit and interfacial energy terms. Therefore, the nanoparticles can provide grain-boundary pinning without substantially affecting dislocation glide. It is important to point out that the estimation of the Zener pinning force is simplified as a result of assumptions, and further discussion and investigation are required to fully understand the underlying origins of the effects of coherent nanoparticles on grain growth, dislocations and twinning.

In summary, we have introduced a simple but reliable approach to the development of bulk UFG structures without the introduction of crystal defects. Such a grain-refinement strategy leads to the development of UFG structures that are not only highly stable but are also compatible with the typical deformation mechanisms of metallic materials—such as dislocation motion and multiplication, transformation induced plasticity and TWIP—thereby taking advantage of the presence of fine grains and substantially enhancing the overall mechanical performance of UFG alloys. The alloy design principle and the criteria for selection of the strategic element (Cu in this study) are summarized in Methods.

This concept could be extended to other alloy systems (Extended Data Fig. 8) and facilitate the exploration and development of advanced metallic materials.

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Article

Methods

No statistical methods were used to predetermine sample size. The experiments were not randomized and the investigators were not blinded to allocation during experiments and outcome assessment.

Composition design

To realize rapid and copious nanoprecipitation, we chose to use Cu in Fe–22Mn–0.6C on the basis of the following considerations: first, Cu has a high tendency to precipitate out (that is, the solubility of Cu in the matrix is very limited) but it is not possible for it to form intermetallic compounds with the constituent elements (Fe, Mn and C); second, the crystalline structure and lattice parameters of the austenitic matrix are almost identical to those of Cu, thus resulting in a very low lattice misfit ($\Delta a = a_{\text{Cu}} - a_{\text{matrix}} = 0.1\%$ for Fe–22Mn–0.6C austenite, $a_{\text{matrix}} = 0.3611$ nm), which substantially decreases the nucleation barrier for precipitation and also hampers the rapid coarsening of nanoprecipitates; and third, Cu-rich precipitates are a fully coherent disordered nanophase, and thus exhibit weak resistance on dislocation motion and refine nanotwins, leading to an excellent combination of strength and ductility.

Specimen preparation

Alloy ingots with compositions of Fe–22Mn–0.6C–xCu (x = 0, 3, 4, 5 wt%) were prepared by arc-melting. The ingots were re-melted at least five times under an argon atmosphere and were then cast into a 45 $\times$ 12 $\times$ 70 mm$^3$ copper mould. The as-cast ingots were cold-rolled to a thickness of 6 mm and then homogenized at 1,040 °C for 3 h under an argon atmosphere. In the case of 5Cu, full dissolution into the matrix after solid solution treatment could not be achieved and localized melting occurred, so in this work we focused on 0Cu, 3Cu and 4Cu. The homogenized materials were cold-rolled again from 6 mm to 1.5 mm and were subsequently annealed at 760, 810, 860 and 910 °C for 5 min, followed by water quenching. The 1.5-mm sheets of 0Cu and 4Cu were also annealed at 760 °C for 20, 40 and 60 min. To achieve a ultrafine structure, the 0Cu was cold-rolled from 8 mm to 4 mm and annealed at 800 °C for 5 min to refine the coarse grains after homogenization. Then the 4-mm-thick plate was cold-rolled again to 1.5 mm and flash-annealed at 760 °C for 2 min. After annealing, the 0Cu, 3Cu and 4Cu samples were analysed for Fe, Mn and Cu content using inductively coupled plasma optical emission spectrometry (ICP-OES) and for C content using a Leco ONH836 instrument, and the results are listed in Extended Data Table 1. Sheet tensile samples with a gauge length of 15 mm and a cross-section of 1.5 $\times$ 3 mm$^2$ were cut and mechanically polished to 2,000 grit size. Tensile tests were performed on a Zwick/Roell Z050 with laser extensometer at a strain rate of $4 \times 10^{-4}$ s$^{-1}$ at room temperature. Tensile force was applied in the rolling direction. At least five samples were tested for each condition.

Microstructure characterization

Samples for EBSD were mechanically polished down to a 3 μm diamond suspension. Before EBSD analysis, the samples were polished using a Gatan PECs II at 5 kV, 5° for 0.5 h. EBSD was performed using a field emission gun scanning electron microscope (FEIInspect F30) operating at 20 kV with a step size in the range of 0.05 to 0.2 μm, depending on the sample grain size. EBSD data were analysed using CHANNELS software (HKL) to determine the average grain size and at least 1,000 grains were used. The X-ray diffraction measurements were conducted on as-rolled 4Cu and on 4Cu and UFG 0Cu with 15% and 45% strain to calculate the dislocation density using a Bruker D2 Phaser instrument with a scan increment size of 0.02°. To obtain the melting point of 4Cu, differential thermal analysis was conducted on homogenized 4Cu using a simultaneous thermal analyser (Netzsch TG 449 F3 Jupiter). A 0.25 g portion of material was heated from 20 °C to 1,450 °C under a flowing argon atmosphere at a heating rate of 10 °C per min. Thin foil samples for TEM and STEM analysis were prepared by twin-jet electropolishing with a solution of 5% perchloric acid, 35% 2-butoryethanol and 60% methanol at −35 °C. AFEITitan 80–300 STEM/TEM instrument equipped with a monochromator and a probe spherical-aberration corrector, and a JEOL-F200 instrument were used to perform electron diffraction, diffraction–contrast imaging, STEM imaging and STEM-EDS imaging. Atomic-resolution ADF-STEM images were acquired with an operating voltage of 300 kV, a probe semi-convergence angle of 24 mrad and a high-angle annular dark-field detector collection angle of 57–325 mrad. The APT characterizations were performed in a CAMECA Instruments LEAP 5000XR. Specimens for APT were prepared in a scanning electron microscope/focused-ion beam. The data was acquired in voltage mode, with a specimen temperature of 50 K, a pulse repetition rate of 200 kHz, a pulse fraction of 15% and an ion collection rate of 0.5% per field evaporation pulse. The APT data was reconstructed using Cameca IVAS software. The reconstruction was calibrated on the basis of elements of crystallography retained within the data characterized by spatial distribution maps. To obtain a misorientation map with high resolution, a NanoMEGAS DigiSTAR system was used to analyse 4Cu with 45% strain using a 1.5 nm step size, and the results were analysed using CHANNELS software (HKL). Phase analysis of the recrystallized 4Cu was investigated by a synchrotron-based high-energy X-ray diffraction technique at the 11-ID-C beamline of the Advanced Photon Source, Argonne National Laboratory, USA. A monochromatic X-ray beam with wavelength 0.01173 nm was used. The equilibrium solubility of Cu in the austenite with a composition of Fe–22Mn–0.6C (wt%) was calculated using JMatPro over a temperature range of 650 °C to 950 °C.

Correction of particle compositions

Owing to the effect of trajectory aberrations on the composition of small particles, we corrected the compositions using the methods proposed in ref. 14. We selected three sets of particles with diameters in the range of 2.5–3, 4.5–5 and 6–7 nm to reveal the effect of trajectory aberrations. The composition profiles of these Cu-rich precipitates are shown in Extended Data Fig. 5a. As expected, the relative density ($\rho_r$) across the particles is higher than that of the matrix, and the smaller particles have higher $\rho_r$. Nevertheless, the value of $\rho_r$ is consistently lower than 1.6 (Extended Data Fig. 5a). As proposed previously14, the corrected composition is given by $C_B' = C_B + (C_B - C_A) \times \eta$, in which the correction factor $\eta$ is dependent on the change of the relative local atomic density (Extended Data Fig. 5b). As can be seen in Extended Data Fig. 5b, when the value of $\rho_r$ is lower than 1.6, the particle composition is only slightly affected by trajectory aberrations because $\eta$ is close to zero. After the correction, the Cu contents of these three sets of particles are 59 ± 2 at%, 73 ± 3 at% and 80 ± 2 at% (Extended Data Fig. 5c), respectively, confirming that Cu content increases with particle size.

Calculation of dislocation density

Modified Williamson–Hall plots were used to calculate the dislocation density from the XRD profiles of as-rolled 4Cu, and 4Cu and UFG 0Cu pre-tensioned to 15% and 45% strain for the calculation of driving pressure for recrystallization and the individual strengthening effect of different strengthening mechanisms. The diffraction profiles used for this analysis were the (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) reflections of the austenite phase.

According to the modified Williamson–Hall methods, the average crystalline size, dislocation density and planar defects (stacking fault and twinning) all contribute to the broadening of diffraction peaks, as illustrated in the following modified Williamson–Hall equation44:

$$\Delta K = \beta W_{\text{std}} = \frac{0.9}{D} + \left(\frac{\pi a^2 b^3}{2}\right)^{1/2} \rho \tau K c^2 + O(K^2 c^2),$$
where the diffraction vector is \( \mathbf{K} = 2\sin \theta /\lambda \) and \( \Delta \mathbf{K} = 2\cos \theta (\Delta \theta) /\lambda \). Here, \( \Delta \theta \) represents the full-width at half-maximum (FWHM) of diffraction peaks at \( \theta_{\text{p}} \); \( \theta \) is the diffraction angle and \( \lambda \) is the wavelength of the X-rays. In the current study, Cu radiation with \( \lambda = 0.15405 \text{ nm} \) was applied. \( D, \rho \) and \( \beta \) represent average grain size, dislocation density, and the magnitude of the Burgers vector, respectively. \( \alpha \) is a constant that depends on both the effective outer cut-off radius of dislocations and the dislocation density. \( \beta \) is a constant related to the effect of twinning and the stacking fault, and can be calculated by trial- and-error through curve fitting of the plot of \( \Delta \mathbf{K} - \mathbf{K}_{\text{slip}} \) against \( KC^{1/2} \). \( h, k \) and \( l \) are the Miller indices and \( W_{\text{slip}} \) is a coefficient related to the \( hkl \) lattice plane. \( O \) is the higher-order term of \( KC^{1/2} \). The dislocation contrast factor \( C \) can be expressed as\(^{44} \):

\[
C = C_{\text{000}} \left[ 1 - q \left( \frac{h^2 k^2 + k^2 l^2 + l^2 h^2}{(h^2 + k^2 + l^2)^2} \right) \right],
\]

where \( C_{\text{000}} \) and \( q \) are constants and can be obtained from anisotropic elastic constants of materials\(^{44}\). The austenite peaks, including (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) reflections, are listed in the plot of \( \Delta \mathbf{K} - \mathbf{K}_{\text{slip}} \) against \( KC^{1/2} \) (Extended Data Fig. 9). The values of dislocation density \( \rho \) and average dislocation size \( D \) can be further determined from the best linear fitting between \( \Delta \mathbf{K} - \mathbf{K}_{\text{slip}} \) and \( KC^{1/2} \) (Extended Data Fig. 9).

Calculations of \( P_s, P_t \), and \( P_g \)

\( P_s, P_t \), and \( P_g \) are calculated as follows\(^{39}\):

\[
P_s = \frac{3F_s}{2\alpha}, \quad P_t = \alpha pGb^2, \quad P_g = \frac{2y}{R},
\]

where \( r \) and \( R \) are the effective outer cut-off radius of dislocations and recrystallized grains, \( \gamma \) is the high grain boundary energy of \(-0.6 \text{ J m}^{-2}\) for austenite steel\(^{43}\), \( F_s \) is the local volume fraction of nanoprecipitates and can be expressed as: \( F_s = \frac{4\pi v_{N}}{3} \), \( N_v \) is the number density of nanoprecipitates in one unit volume, \( a \) is a constant with a value of around 0.5, the typical average dislocation density \( \rho \) was calculated from XRD profiles, \( G \) and \( b \) are the shear modulus and the Burgers vector, and for Fe–22Mn–0.6C steel are 65 GPa and 0.25 nm, respectively\(^{44}\). The averaged grain size, precipitate size and volume fraction of precipitates are obtained from STEM images, EBSD results and APT results, respectively.

**Precipitation hardening**

For coherency strengthening, the stress increment can be described by\(^{44}\):

\[
\Delta \sigma_{\text{coherency}} = 4.1MG\varepsilon^{3/2} \left( \frac{br}{b} \right)^{1/2},
\]

where \( M \) is the Taylor factor of 3, \( G \) is the shear modulus of 65 GPa, \( \varepsilon \) is the lattice misfit of 0.11%, \( r \) is the nanoprecipitate volume fraction of 4.2%, \( r \) is the radius of Cu-rich nanoprecipitates (2.8 nm) and \( b \) is the Burgers vector of 0.25 nm. \( \Delta \sigma_{\text{coherency}} \) was then calculated to be 19.9 MPa.

For chemical strengthening, the stress increment can be described by\(^{44}\):

\[
\Delta \sigma_{\text{chemical}} = \left( \frac{6\gamma \mu b^2}{\pi Tr^2} \right)^{1/2},
\]

where \( \gamma \) is the specific interface energy of 0.017 J m\(^{-2}\) (ref. 44), \( T \) is the line tension of the dislocations, approximately equal to \( Gb^2 / 2 \) (ref. 44). \( \Delta \sigma_{\text{chemical}} \) was calculated to be 0.08 MPa.

**Grain-refinement hardening**

The effect of grain size on yield stress \( (\sigma_y) \) can be expressed as:

\[
\sigma_y = \sigma_0 + \frac{K}{\sqrt{\delta}},
\]

where \( \sigma_0 \) is the lattice friction stress, \( K \) is the strengthening coefficient and \( \delta \) is the grain size. To calculate the yield strength of Cu with a grain size of 800 nm, the values of \( \sigma_0 \) and \( K \) were adopted from that of the matrix—that is, the 22Mn–0.6C steel—for which \( \sigma_0 \) is around 170 MPa and \( K \) is 428 MPa \( \mu \text{m}^{-1/2} \); therefore, for the Cu alloy with a grain size of 800 nm, \( \sigma_0 \) is determined to be 651 MPa. For Cu annealed at 760 °C for 5 min, the yield stress is 365 MPa, and the stress increment due to grain refinement is 286 MPa.

The total stress increment due to grain-refinement and precipitation hardening therefore amounts to 306 MPa; this agrees with the experimental result of 345 MPa, which also includes the contributions of Cu solid solution strengthening.

**Twining and dislocation hardening**

We further calculated the individual strengthening contribution of dislocation and twinning in 4Cu and UFG 0Cu pre-tensioned to 15% and 45% strain. Using the modified Williamson–Hall plots of the XRD patterns (Extended Data Fig. 9), the dislocation densities \( \rho \) of 4Cu and UFG 0Cu for the 15% strain are 3.5 \( \times \) 10\(^{15} \) and 3.9 \( \times \) 10\(^{15} \) m\(^{-2}\), respectively, but increase to 6.4 \( \times \) 10\(^{15} \) and 1.6 \( \times \) 10\(^{16} \) m\(^{-2}\), respectively, for the 45% strain. The flow strength after yielding can be expressed as:

\[
\sigma_{\text{flow}} = \sigma_0 + \frac{K}{\sqrt{\delta}} + \sigma_4 + \sigma_c,
\]

where \( \sigma_c \) is the contribution of dislocation hardening and \( \sigma_4 \) is the contribution of twinning hardening. \( \sigma_c \) can be calculated using the Taylor hardening law: \( \sigma_c = MaGb\gamma /\sqrt{\delta} \), where \( M \) is the Taylor factor, which is 3.06 for austenitic steel\(^{46}\), \( a \) is a geometrical factor with a value of 0.136 for TWIP steels\(^{46}\), \( G \) is the shear modulus and is taken to be 65 GPa for the current base alloy\(^{46}\), and \( b \) is the magnitude of the Burgers vector, which is 0.25 nm\(^{46}\). For 4Cu and UFG 0Cu alloys at 15% strain, \( \sigma_4 \) was thus calculated to be 396 MPa and 418 MPa, respectively, which increased to 536 MPa and 867 MPa, respectively, at 45% strain. \( \sigma_4 \) was estimated to be 34 MPa and 714 MPa for 4Cu at strains of 15% and 45%, respectively, and 46 MPa and 368 MPa for UFG 0Cu. These results are summarized in Extended Data Fig. 6b.

**Data availability**

The data that support the findings of this study are available from the corresponding author upon reasonable request. Source data are provided with this paper.

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Author contributions J.G., S.J., W.M.R. and Z.L. designed the experimental programme. J.G. carried out the main experiments. S.J. and Z.P.L. conducted the 3D-APT, synchrotron experiment and analysed the data. H. Zhang conducted the HR-STEM characterization and analysed the data. J.G. and H. Zhang conducted STEM-EDS mapping and analysed the data. Y.H. analysed XRD patterns for calculation of dislocation density. J.G., S.J., H. Zhang, Z.L. and W.M.R. wrote the manuscript and discussed the results. All authors reviewed and contributed to the final manuscript.

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Additional information

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Extended Data Fig. 1 | Mechanical properties. Engineering stress–strain curves of 0Cu and 4Cu annealed at 760 °C for 5 min and 20 min, and 3Cu annealed at 760 °C for 5 min. Upon the addition of Cu both the yield strength and ultimate tensile strength increase markedly, with ductility comparable to that of 0Cu.
Extended Data Fig. 2 | ADF-STEM analysis of 4Cu, 0Cu and 3Cu annealed at 760 °C for 5 min. a, ADF image (left) of 4Cu showing a high density of nanoprecipitates, and the corresponding SAED pattern (right) showing only the matrix reflection of the [110]$_{fcc}$ zone axis without any extra reflection of the precipitates. b, ADF image of 0Cu showing an average grain size of 2.2 μm. c, ADF image of 3Cu presenting a UFG structure with a high density of nanoprecipitates. No elemental segregation at grain boundaries was detected.
Extended Data Fig. 3 | Thermal stability evaluation of UFG structures. a–d, EBSD analysis of 0Cu (a1–d1), 3Cu (a2–d2) and 4Cu (a3–d3) annealed at 760 °C (a), 810 °C (b), 860 °C (c) and 910 °C (d) for 5 min. a4, b4, EBSD maps of 0Cu annealed at 760 °C for 20 min (a4) and 60 min (b4). c4, d4, EBSD maps of 4Cu annealed at 760 °C for 20 min (c4) and 60 min (d4). Owing to their enhanced thermal stability, UFG structures of the Cu-doped alloys can be obtained over a wide range of annealing temperatures and times.
Extended Data Fig. 4 | Microstructural analysis of 4Cu annealed at 760 °C for 0.5 min, 1 min and 2 min. a–c, EBSD analysis of 4Cu annealed at 760 °C for 0.5 min (a), 1 min (b) and 2 min (c), revealing that nucleation for recrystallization occurred extensively after 0.5 min of annealing. As the annealing time extends from 1 min to 2 min, the volume fraction of the recrystallized matrix increases from 76% to 95%. d, e, ABF-STEM image (d) and the reconstruction of the APT dataset (e) of 4Cu annealed for 1 min, showing the formation of equiaxed grains of size 300 ± 150 nm and Cu-rich precipitates with an average size of 3.7 nm and a number density of $8.8 \times 10^{23} \text{m}^{-3}$. The isoconcentration surfaces are 20 at% Cu.
Extended Data Fig. 5 | Effect of the trajectory aberrations of APT on the composition analysis of particles. The error bars are standard deviations of the mean. The isoconcentration surfaces are 30 at% Cu.
Extended Data Fig. 6 | EBSD map of UFG 0Cu and calculation of individual strengthening contribution of dislocations and nanotwins of UFG 0Cu and 4Cu. **a**, The EBSD map of UFG 0Cu processed by a two-step cold-rolling and flash-annealing process shows a grain size of 1.1 ± 0.5 μm. **b**, Twinning gradually dominates the strengthening beyond 15% strain in 4Cu, whereas dislocation multiplication governs the strengthening in the entire deformation stage of the UFG 0Cu.
Extended Data Fig. 7 | Deformed microstructure analysis of 4Cu pre-strained to 15% and 45%. **a, b.** The corresponding bright-field images of Fig. 5c, d, respectively, showing a high density of dislocations and nanotwins with interspacing of between 300 nm and 500 nm. **c.** Reconstructed APT data of 4Cu pre-strained to 15% showing some of the nanoprecipitates flattened along the loading direction. **d, e.** Bright-field TEM image (d) and its corresponding high-resolution misorientation map superimposed with nanotwin boundaries (e) (solid red lines, indexed nanotwin boundaries; thin dashed red lines, nonindexed nanotwin boundaries) obtained using a NanoMEGAS DigiSTAR system with a step size of 1.5 nm. Numerous small dislocation cells (blue arrows) were observed in nanotwins and their interspaces. The isoconcentration surfaces are 20 at% Cu.
Extended Data Fig. 8 | Microstructure and mechanical property analyses of TRIP steels and medium entropy alloys with small amounts of Cu. a, b, EBSD maps of the TRIP steels with composition Fe–15Mn–0.4C (a) and Fe–15Mn–0.4C–3Cu (wt%) (b) after annealing at 730 °C for 5 min. c, Tensile stress–strain curves of the TRIP steels in a, b, d, e. EBSD maps and of 33Co–33Cr–34Ni (d) and (33Co–33Cr–34Ni)0.97Cu0.03 (at%) (e) after annealing at 810 °C for 10 min. f, Tensile stress–strain curves of the alloys in d, e. The alloys with minor Cu content exhibit finer microstructures and enhanced mechanical properties.
Extended Data Fig. 9 | Modified Williamson–Hall plots of FWHM as a function of $K^{1/2}$. 

a, Analysis of peak broadening for cold-rolled 4Cu alloys. 
b, Analysis of peak broadening for the pre-strained UFG 0Cu and 4Cu alloys.
## Extended Data Table 1 | Composition (wt%) of 0Cu, 3Cu and 4Cu alloys

| Alloy/Elements | Mn (wt %) | C (wt %) | Cu (wt %) | Fe (wt %) |
|---------------|-----------|----------|-----------|-----------|
| 0Cu           | 21.74     | 0.58     | --        | Bal.      |
| 3Cu           | 21.93     | 0.55     | 2.67      | Bal.      |
| 4Cu           | 21.61     | 0.59     | 3.84      | Bal.      |