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Colossal grain growth yields single-crystal metal foils by contact-free annealing

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Single-crystal metals have unique properties due to the absence of grain boundaries and strong anisotropy. Commercial single-crystal metals are usually synthesized by bulk crystal growth or by deposition of thin films onto substrates, and they are expensive and small. We prepare extremely large single-crystal metal foils by ‘contact-free annealing’ from commercial polycrystalline foils. The colossal grain growth (up to 32 cm²) is achieved by minimizing contact stresses, resulting in a preferred in-plane and out-of-plane crystal orientation, and is driven by surface energy minimization during the rotation of the crystal lattice followed by ‘consumption’ of neighboring grains. Industrial scale production of single-crystal metal foils is possible from this discovery.

Polycrystalline metals have numerous grain boundaries (GBs) that affect their electrical and mechanical properties, whereas single-crystal metals have no GBs and show different properties. For example, single-crystal Cu has a lower electrical resistivity than polycrystalline Cu due to the elimination of electron scattering at GBs (1, 2), and single-crystal superalloys have a high resistance to creep (3), which can be driven by the sliding of GBs. The growth of graphene on catalytic single-crystal metal substrates by chemical vapor deposition (CVD) has attracted great attention because certain planes have a small lattice mismatch with graphene (Cu(111): ~3–4%, Ni(111): ~1%, Co(0001): ~2%) (4, 5), and can be used as substrates for the heteroepitaxial growth of single-crystal graphene without GBs (6–10). The epitaxial growth of large scale hexagonal boron nitride, diamond, and tetrahedrally bonded BN that have a small lattice mismatch with a single-crystal metal has also increased interest in and demand for large area single-crystal metal substrates.

The traditional methods for synthesizing single-crystal metals are by bulk crystal growth (the Czochralski or Bridgman methods). Single-crystal thin metal films can also be deposited on top of single-crystal inorganic substrates (8, 11–14). These methods lead to small and expensive single-crystal metals. An alternative strategy is to eliminate GBs in polycrystalline solids by grain growth during annealing. Grain growth produces single-crystal alloy metal sheets but only for the Cu-Al-Mn alloy (15, 16). Annealing of polycrystalline Cu foils yields Cu(111) oriented foils (9, 10), but the mechanism

for this transformation remains unclear. We prepared Cu(111), Ni(111), Co(0001), Pt(111) and Pd(111) single-crystal foils with a large grain size up to 32 cm² with “contact-free annealing” (CFA). CFA has advantages as it does not require single-crystal seeds or templates that limit the maximum crystal size, and commercial polycrystalline metal foils are readily converted into single crystals. We heat the foils near their melting temperatures and typically under a hydrogen atmosphere and find an unusual conversion from the polycrystalline grains to a specific orientation in both the in-plane and normal directions. This specific orientation likely arises by crystal lattice rotation accompanied by the removal of stacking faults resulting in a lowered surface energy.

Single-crystal metal foils produced by contact-free annealing

Grooves typically develop along the GBs on the surface of metals during annealing due to equilibrium between the energy of the free surface and the GBs; such ‘thermal grooves’ can be observed with the naked eye when the size of individual grains reaches the cm-scale (17–19). We annealed commercial polycrystalline Cu foils near their melting points with CFA ((20), Fig. 1, A and B). Thermal grooves are typically not present on the surface of the annealed Cu foil after CFA (Fig. 1C), reflecting an absence of GBs in the entire foil (about 2 cm × 8 cm in size).

We studied the crystallographic orientations of the annealed Cu foils by X-ray diffraction (XRD) and electron

backscatter diffraction (EBSD). We found Bragg reflections from the (111) and (222) crystal planes (Fig. 1D). The inverse pole figure (IPF) color maps from EBSD show only the (111) plane of Cu (blue color, Fig. 1E), consistent with the XRD data. The entire region also has the same crystallographic orientation in the in-plane direction ($\langle 112 \rangle$, the rolling direction), as shown in the pole figures of the (001) poles (Fig. 1F). We found a very small misorientation (below 1°) in all kernel average misorientation (KAM) maps, which measure the local average misorientation between a measured point and its neighbors (21) (Fig. 1H). Our measurements show the Cu foil was converted to a $\{111\}\langle 112 \rangle$ single crystal over an area of 2 cm by 8 cm. In contrast, the grain sizes in thin metal films have a maximum of a few millimeters (22–29), by abnormal grain growth. CFA reproducibly yields (111) single-crystal foils up to 32 cm² (fig. S1). This colossal grain growth dramatically improves the size of single-crystal foils.

The close-packed $\{111\}$ crystallographic plane of Cu has the lowest surface energy of all the planes as is well known for face-centered cubic (FCC) structure (30–32). If the surface energy is the major driving force for grain growth in polycrystalline FCC metals they should spontaneously transform into grains with a $\{111\}$ surface due to surface energy minimization (22–24). However, this may not be the case if other energy terms such as strain energy caused by thermal stress are large compared to the surface energy (24). We found that suspending the metal foil eliminates or at least minimizes deformation from thermal stress that arises due to interfacial contact ((20), figs. S2 to S4). This allowed us to reproducibly obtain single grain Ni foils with a $\{111\}$ normal and Co foils with a $\{0001\}$ normal over large areas with the same strategy as for Cu ((20), figs. S5 to S7).

We used resistive heating to convert polycrystalline Pt to single crystal (Fig. 2A) due to the high melting temperature (2041 K). We first attached the Pt foil to two electrodes to pass current, and the Pt foil deforms in the middle from thermal expansion during annealing. This results in GBs near, and in, this deformed region (Fig. 2, B to D). To avoid this we attached the bottom electrode to a movable stage whose position was manually adjusted to keep the foil “flat” during expansion and contraction. We achieved a large area single-crystal Pt foil region with a $\{111\}$ surface, although the regions near the water-cooled electrode attachment did not convert (Fig. 2, E to I). As long as mechanical deformation is minimized during annealing (fig. S8), we expect this method to work for other foils (it did for Pd, (20) and fig. S9).

Colossal growth of grains with a $\{111\}\langle 112 \rangle$ orientation

We investigated the microstructural and texture evolution by varying annealing time (at 1323 K) in order to understand the colossal grain growth. We analyzed the texture of each Cu foil using the orientation distribution function (ODF) from the

EBSD data (Fig. 3A). The as-received Cu foil showed mostly elongated grains along the rolling direction, and strong $\{112\}\langle 111 \rangle$ and $\{110\}\langle 112 \rangle$ texture (Fig. 3B), as expected for a cold-rolled Cu foil (33). The elongated grains recrystallized to larger polygonal grains after 1 hour of annealing. In addition, small grains with a $\{111\}\langle 112 \rangle$ texture ($\{111\}\langle 112 \rangle$ grains) started to appear among the $\{112\}$ and $\{110\}$ grains (Fig. 3C). We found that not all $\{111\}$ grains grew to cm-scale. Only a limited number of $\{111\}$ grains located near the edge of the foils grew abnormally, likely due to the energy stored near the foil edge resulting from cutting or handling. Our observations strongly suggest that the stored energy at the edges of the foil accelerates the selective growth of the $\{111\}$ grain(s). These abnormal $\{111\}$ grain(s) grow extremely fast (10s of mm/s) by consuming the surrounding grains ((20), figs. S10 to S12). This is similar to abnormal grain growth driven by the critical strain annealing process, which promotes the growth of a limited number of grain(s) (34). After 2 hours, we observed two cm-scale grains, separated by numerous μm -scale small grains with various orientations. Both of these large grains had a $\{111\}\langle 112 \rangle$ texture (Fig. 3D). After we annealed the same Cu foil for an additional 5.5 hours, GBs (excluding the polygranular regions at the edges) were not found by the naked eye. We did however find a subgrain boundary with SEM at the marked region between the two large $\{111\}\langle 112 \rangle$ grains in Fig. 3D (Fig. 3E). This region showed a strong $\{111\}\langle 112 \rangle$ texture, and there is no clear contrast difference across the subgrain boundary in the IPF map (Fig. 3F) which showed only a small misorientation, below 1° , across the subgrain boundary (Fig. 3G). Unlike typical abnormal grain growth, the extremely fast growth of particular $\{111\}$ grain(s) allows further growth up to cm-scale. In addition, those grains (or nuclei) that can grow rapidly, which are limited in number throughout the sample, have an identical $\langle 112 \rangle$ in-plane orientation and they form single-crystal foil over large area when they grow larger and coalesce.

Origin of the $\{111\}\langle 112 \rangle$ orientation in single-crystal FCC metal foils

Most of our FCC (111) foils (which had initial $\{112\}\langle 111 \rangle$ texture) showed identical orientations of both their in-plane and normal directions ($\{111\}\langle 112 \rangle$) (Fig. 4A). While the preferential growth of grains with a $\langle 111 \rangle$ normal direction in FCC metals by surface energy minimization has been reported (22–24), growth of preferred in-plane orientation in FCC metals has been harder to achieve. We studied various factors that we thought could affect the colossal grain growth of $\{111\}\langle 112 \rangle$: initial textures, misorientation angles, thickness, and purity of the metal foil. We found that the initial textures of foils are critical to obtain single-crystal $\{111\}\langle 112 \rangle$ foils. If the strongest texture in the initial foil is not $\{112\}\langle 111 \rangle$, it results in the different final orientation such as $\{111\}$ fiber and

$\{100\}<001\}$ ($\{20\}$, tables S1 and S2 and figs. S13 to S18).

We also considered the possibility that the dominant $\{112\}<111\}$ orientation of our cold-rolled metal foils was responsible for the final $\{111\}<112\}$ orientation after CFA. To test whether $\{111\}<112\}$ arises from $\{112\}<111\}$, we performed CFA on sub-mm scale $\{112\}<111\}$ grains. We found these sub-mm scale $\{112\}<111\}$ grains in the polygranular region of the annealed Cu foil that was in contact with the ceramic holder during CFA. We cut this region to have only $\{112\}<111\}$ grains at the edge of the Cu foil sample, and further annealed in the suspended sample configuration at 1323 K for 12 hours. We found that $\{112\}<111\}$ grains converted to $\{111\}<112\}$ grains after CFA without substantial change of microstructure (Fig. 4B). Thus, $\{111\}<112\}$ grains originate from $\{112\}<111\}$ grains.

A contact-free foil is very likely a stress-free foil, thus the driving force for the continuous rotation required for the transformation from a $\{112\}<111\}$ grain to a $\{111\}<112\}$ grain was not immediately obvious. We know that annealing near the melting point activates many vacancies in the bulk, and the concentration of these vacancies is further increased by the introduction of hydrogen into the metal. Our density functional theory (DFT) calculations show the formation energy of a single vacancy in bulk Cu is 1.64 eV, but it is 1.20 eV and 0.72 eV when the vacancy is passivated by either one or two H atoms, respectively ($\{20\}$, fig. S22). This large reduction of the vacancy formation energy must result in a substantial increase in the bulk vacancy concentration. Our experiments and simulations show the importance of hydrogen for grain growth, because vacancies in the bulk are critical for grain rotation and when H atoms diffuse in these metals they strongly stabilize vacancies. As an exceptional case, Pt foil samples showed cm-scale grain growth during CFA both with, but also without, hydrogen. Because Pt has a much higher vacancy concentration than other metals at the annealing temperature used, we found the Pt foil has a large-scale grain without hydrogen ($\{20\}$, table S3 and figs. S19 to S21). We did molecular dynamics (MD) simulations on a model grain possessing a $\{112\}$ surface with $\sim 4.5\%$ vacancies in the bulk to further understand the relationship between the vacancies and the grain rotation. We found that, after the simulation, the entire grain rotated 2.02° toward the $\{111\}$ direction which resulted in the removal of one step on the surface and a $\{7\ 7\ 13\}$ surface. We introduced additional vacancies ($\sim 5.0\%$) to this rotated structure, and after relaxation, a further 7.42° rotation toward the $\{111\}$ direction was observed resulting in the removal of two additional surface steps and a $\{7\ 7\ 10\}$ surface (Fig. 4C). A larger scale model also showed a similar result ($\{20\}$, fig. S23).

Our MD simulations indicate that, with vacancies, the rotation of the $\{112\}$ grain may occur in a stress-free environment. The mechanism we observed has several steps (Fig. 4D): (i) Vacancies first aggregate to form an intrinsic $\{111\}$

stacking fault (SF) accompanied by Frank partial dislocations (FPDs). (ii) The climbing of the FPD occurs by absorbing more vacancies resulting in SF growth (fig. S24), which eventually spans the entire thickness of the grain, and leads to the disappearance of the FPDs on the surface. (iii) The interaction between the SF and the surface causes a Shockley partial dislocation (SPD) at one side of the SF. This SPD then glides from the surface into the bulk, resulting in continuous shrinkage of the SF area accompanied with rotation of the crystal lattice toward the $\{111\}$ direction. The gliding of the SPD is key in forming the $\{111\}$ surface. Because the gliding of the SPD along the SF results in both the removal of SFs and the forming of a perfect crystal lattice (lower energy state), motion of the SPD is irreversible once SPD initiates from the surface. The gliding of the SPD can initiate in two directions from the surface (Fig. 4E). Initiation in one direction causes the surface step height to increase, while initiation in the other direction results in the removal of the surface step and a flat surface. DFT energy calculations of these states demonstrate that the gliding of the SPD that results in the flat surface is more energetically favorable, and this causes rotation toward the $\{111\}$ orientation. Accordingly, during annealing, the grain surface both flattens and rotates eventually resulting in a $\{111\}$ surface.

These observations show that the grain rotation happens along the ‘surface energy minimization pathway’ of Cu from $\{112\}$ to $\{111\}$ (fig. S25) during the migration and elimination of SFs in the $\{112\}$ grain(s), which are the major component ($\{112\}<111\}$) in cold-rolled FCC metal foils. But our experimental results show that the $\{110\}$ grain(s), which are the second major component ($\{110\}<112\}$) in cold-rolled FCC foils, do not rotate during the annealing (fig. S26). The $\{110\}$ orientation is located at a saddle point in the calculated surface energy map (fig. S25), therefore, the driving force for initiating the rotation is zero. The observed rotation from $\{112\}$ to $\{111\}$ is the rotation along the $\langle 110 \rangle$ axis, which corresponds to the rotation from the $\{112\}<111\}$ orientation to the $\{111\}<112\}$ orientation. Once the new $\{111\}<112\}$ grain(s) are nucleated by grain rotation, they grow rapidly in the highly textured matrix to minimize the surface energy. This is accelerated by the locally stored energy at the edges. Eventually this transformation forms the large $\{111\}<112\}$ grain(s) over the entire foil.

Potential applications of single-crystal metal foils

These single-crystal metal foils will find many uses in surface science, fundamental catalysis research, and a variety of other applications. As an example of using a single-crystal metal foil as a high quality catalyst, we demonstrated the heteroepitaxial growth of single-crystal monolayer and multilayer graphene islands on a pure Cu(111) foil and a Cu/Ni(111) foil, respectively ($\{20\}$, figs. S27 to S29). In addition, we

measured a 7% reduction in the room temperature resistivity of Cu(111) foils compared to the as-received Cu foils (table S4 and figs. S30 and S31). In another example, we obtained different single orientation surfaces (than (111)) by ‘simply’ cutting polycrystalline foils and then annealing them (fig. S32).

Contact-free annealing enables preparation of single-crystal metal foils with specific in-plane and out-of-plane crystallographic orientations. The orientation originates from the rotation of the dominant texture component of the as-received foils, likely through dislocation gliding as a result of removal of the stacking faults in the presence of large amounts of vacancies. Our results suggest the possibility of achieving very large single-crystal metal foils from polycrystalline foils for many other metals, in addition to the scaled manufacture of at least Cu, Ni, Co, Pt, and Pd foils, by a process such as CFA.

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SUPPLEMENTARY MATERIALS

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Materials and Methods

Supplementary Text

Figs. S1 to S32

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Fig. 1. A single-crystal Cu(111) foil produced by CFA. (A) Schematic of the quartz holder that the Cu foil is suspended from, (B) photograph of the configuration shown schematically in (A). (C) Photograph of the annealed single-crystal Cu foil (the larger numbered lines on the ruler in the photographs are centimeters), (D) The XRD 2θ scans of the three regions in the annealed single-crystal Cu foil indicated by P1-P3 in (C) by using Cu-K α radiation (45 kV and 200 mA). The peaks at 43.3 and 95.1 are assigned to Bragg reflections from the (111) and (222) crystallographic planes. (E) EBSD IPF maps in the normal direction. (F) (001) pole figures. (G) KAM maps (1st nearest-neighbor kernel) of the single-crystal Cu foil at various points along the section from P1 to P3 (the distance between adjacent EBSD measurement points was more than 5 mm). (ND = normal direction, RD = rolling direction, TD = transverse direction).

Fig. 2. A single-crystal Pt(111) foil region produced by CFA. (A) Photograph of water-cooled electrodes with a Pt foil for resistive heating (left: front view, right: side view). Different from CFA with a ceramic holder, we fixed the foil to two water-cooled electrodes. (B) Photograph of a Pt foil before heating (left), and then during heating (right) but without stage movement; white arrows indicate bending of the foil. (C) Photograph of the same annealed Pt foil (yellow dashed lines correspond to GBs between large single-grain and polygranular regions or between large grains that have orientations close to (111)). (D) EBSD IPF map of the white square region in (C). (E) Photograph of a single-crystal Pt foil (about 3 cm² in the single-crystal region; yellow dashed lines indicate GBs between the single-grain and polygranular regions) after annealing with appropriate movement of one electrode (stage) to minimize the thermal stress during annealing and cooling. (F) Temperature distribution in a Pt foil during annealing (left), and EBSD IPF map of the region marked "GB" in (E). (G) EBSD IPF maps, (H) (001) pole figures, (I) KAM maps (1st nearest-neighbor kernel) of the single-crystal Pt foil at various points along its length in the large single grain region (the distance between each EBSD measurement point was more than 5 mm). All these foils were annealed at 1883 K for 12 hours (ND = normal direction, RD = rolling direction, TD = transverse direction).

Fig. 3. Texture evolution and grain growth for the large area single-crystal Cu. (A) ODF section with $\phi_2 = 45^\circ$ indicating the position of the major components of the texture in FCC metals. IPF (left) and ODF (right) maps (ϕ , $\phi_1 = 0 \sim 90^\circ$, $\phi_2 = 45^\circ$) of (B) an as-received Cu foil, (C) a Cu foil annealed at 1,323 K for 1 hour. (D) A Cu foil annealed at 1,323 K for 2 hours: photograph (left, yellow dashed lines correspond to GBs between large single-grain and polygranular regions), and IPF (middle), ODF (right) maps of the region marked with a white rectangle in the photograph. (E) The same Cu foil in (D) after it was annealed for an additional 5.5 hours at 1323 K: photograph (left), and SEM (middle) and its higher magnification SEM (right) images of the region marked with a white cross in the photograph. (F) IPF (left) and ODF (right) maps at the same region as the lower magnification SEM in (E). (G) IPF (left) maps at the same region as the higher magnification SEM in (E) and the misorientation profile along the white arrow in this higher magnification SEM image and the corresponding IPF map. Note that all SEM images are tilted 70° because it is necessary to use a sample tilt of 70° for EBSD observation.

Fig. 4. Transformation from the {112}<111> to the {111}<112> orientation for the single-crystal FCC foils. (A) ODF section with $\phi_2 = 45^\circ$ of as-received Ni and Pt foils, and Ni(111) and Pt(111) foils ($\phi, \phi_1 = 0 \sim 90^\circ$), (B) SEM image of the isolated {112}<111> grain region (left), IPF maps of this region before (middle) and after (right) CFA, (C) Cu grain model viewed in the surface normal (top) and <110> direction (bottom) surface: initial {112} grain (left), annealing at 1000 K for 10 ns with 4.5% vacancies (middle), further annealing at the same condition with 5.0% vacancies (right). The color profile on the right represents the relative height of surface. The slab contains $3,604$ atoms with $5.01 \times 2.04 \times 4.40$ nm³. (D) Schematics of grain rotation during the removal of SF by dislocation glide (top) and its corresponding MD model (bottom), (E) relative energy of Cu unit cell with 198 atoms.